

## Poly(styrene)s with oligo(ethylene oxide) side chains as ionic conducting matrices

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Received: 10 June 1996/Accepted: 15 August 1996

### Summary

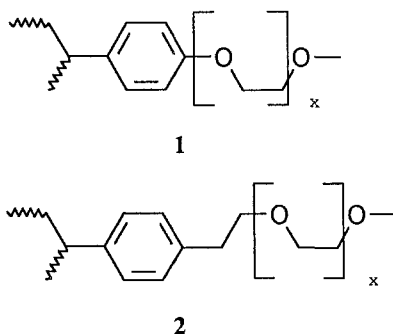
Solid phase ion conductors have been the object of studies during the last years for their potential use as conducting polymer matrices in electrochromic devices, sensors, photovoltaic and dry batteries. Comb polymers of poly(styrene) with oligo(ethylene oxide) side chains were investigated. They show reasonable conductivity of about  $10^{-7}$ - $10^{-5}$  siemens/cm at ambient temperature and lithiumperchlorate as salt electrolyte. A dependence of the conductivity from the side chain length and the amount of added salt was found.

### Introduction

A great advantage of the polymer/salt mixtures is their solid state. Although there are many advantages of nonfluid systems, the conductivity of solid ion conductors depends on various factors (1):

- High crystalline polymer matrices show poor conductivity but have good mechanical properties.
- Matrices with low viscosity show good conductivity with poor mechanical properties.
- The dielectric constant of the matrix polymer should be high to improve the salt dissociation.
- The salt should have a low dissociation energy.

Most of the work has been done on ionic conductivity of polymers containing poly(ethylene oxide) structures in the main or side chain because of their ability to dissolve inorganic salts and their availability, even so their dielectric constants are low compared to other systems. Oligo(ethylene oxide) substituted poly(styrene) comblike polymers are known systems in phase transfer catalytic reactions (2-3). The compounds investigated in this work were poly(p-1,4,7-trioxooctane-styrene ether) **1a**, poly(p-1,4,7,10-tetraoxoundecane-styrene ether) **1b** and poly(p-1,4,7,10,13-pentaoxotetradecane-styrene ether) **1c** in which the oxygen atom of the oligo(ethylene oxide) side chain is directly connected with the phenyl ring of the main chain poly(styrene), and a second series with ethylene spaced oligo(ethylene oxide) side chain comprising compounds **2a-2c**. As ionic compound lithiumperchlorate was chosen because of its low dissociation energy (4). A great advantage of these systems is their low toxicity.



	x
<b>a</b>	2
<b>b</b>	3
<b>c</b>	4

## Experimental part

### Monomer preparation

0.2 mol of the hydroxy component (p-bromophenol for type 1 monomers or 2-p-bromophenylethanol for type 2 monomers) and 3 mmol NaH were placed in an autoclave and dissolved in 50 mL diethylether. After addition of 1 mol of ethylene oxide the mixture was kept at 70°C for 24 h. The fluid thus obtained was dissolved in 100 mL THF, deprotonized with 0.2 mol of NaH and after addition of 0.2 mol of methyl iodide the solution was refluxed for 2 h. After the solution was allowed to cool to room temperature it was treated with 20 mL of water and the organic phase was dried for 24 h at 10<sup>-2</sup> bar. The product mixture containing bromides with different side chain length between 0 to 7 ethylene oxide units was used in the following reaction without further purification.

The vinyl group was established in a Heck reaction. To 20 g of the bromide mixture dissolved in 60 mL of DMF 0.7 g of palladium(tri-ortho-tolyl-phosphine acetat) and 15 mL of triethylamine were added. The mixture was transferred into an autoclave and 30 bar of ethylene were added. After heating the autoclave at 170°C for 24 h and allowing to cool to room temperature the solution was filtered and treated with 20 mL of water. From the organic phase the solvent was removed on a rotary evaporator and the products were purified by chromatography on silica with diethylether as eluent.

Monomer yield: **1a** 5%, **1b** 15%, **1c** 10%, **2a** 6%, **2b** 15% and **2c** 9%

### Polymerization

The corresponding monomers **1a**, **1b**, **1c**, **2a**, **2b** and **2c** were polymerized for 12 h in dioxan (c = 0.5 mol/L) with 3 mol% AIBN as initiator. Polymer yield: **1a** 25%, **1b** 23%, **1c** 28%, **2a** 19%, **2b** 23% and **2c** 24%. The low yields are a consequence of the retarding effect of the monomers.

### Preparation of the polymer/salt complexes

0.2 g of the polymer was mixed in an argon atmosphere with the defined amount of lithiumperchlorate. The mixture was heated to 70°C and tempered at 10<sup>-2</sup> bar until the salt was dissolved.

### Instrumentation

Conductivity measurements were performed with a WTW-Conductometer Type LBR with platin electrodes.

<sup>1</sup>H NMR spectra were registered on a FT-NMR-Spektrometer BRUKER WP 80 SY .

A Rheometric Science DSC-Gold differential scanning calorimeter was used to measure the glass transition temperature.  $T_g$  was taken at the midpoint of the baseline shift.

## Results and discussion

All polymer/salt complexes especially **1b-2c** show lithium ion conductivity of AgBr type with an exponential temperature dependence. Polymer **1a** does not show a significant dependence, even so a slight increase of the conductivity with rising temperature is observed. The highest conductivities (Figure 1) were obtained with polymers **1c** and **2c**, respectively, with the longest side chains. These systems have a viscosity which is considerably lower than for the polymers with the shorter side chains because of the entropic effect of the weakening influence on the main chain poly(styrene). If the side chain is longer than seven ethylene oxide monomer units the effect inverses caused by crystallisation of the oligo-(ethylene oxide) chains (5).

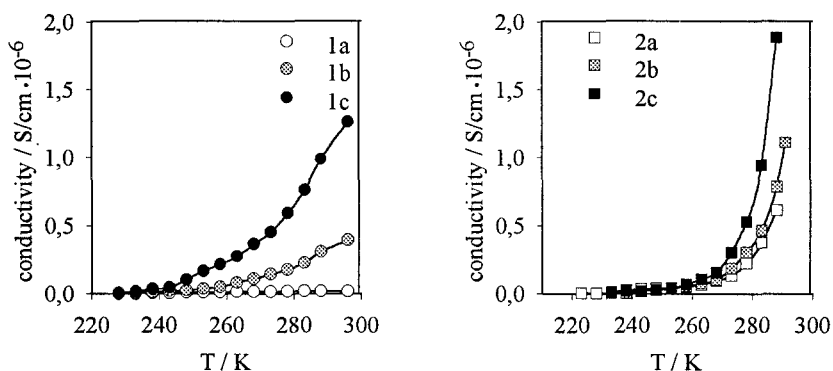


Figure 1: Temperature dependence of the conductivity for the polymers with 5 mol% LiClO<sub>4</sub>

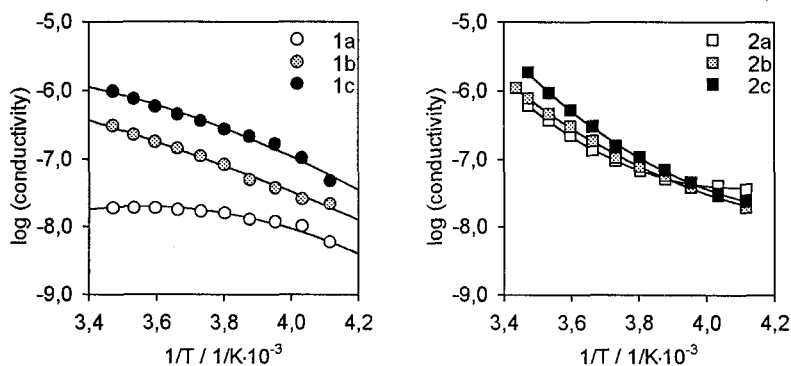


Figure 2: Logarithmic plot of the temperature dependence of the conductivity for the polymers with 5 mol% LiClO<sub>4</sub>

Figure 2 indicates that there is an Arrhenius dependence of the ion conductivity, at least for high temperatures. The discontinuities in the graph can be related to a phase change (glass transition) of the polymer/salt complexes.

Table 1: Glas transition temperature T<sub>g</sub> for pure polymer and complex

Polymer	T <sub>g</sub> / K	
	pure polymer	complex
<b>1a</b>	264,3	-----
<b>1b</b>	240,3	247,6
<b>1c</b>	228,2	245,7
<b>2a</b>	222,9	234,5
<b>2b</b>	217,4	228,5
<b>2c</b>	215,7	218,5

As assumed, the polymer/salt complexes **1c** and **2c** with the longest side chains have the lowest T<sub>g</sub> for their salt complexes (Table 1). The glass transition temperatures are higher than those for the pure polymers (Table 1). Above and below of the discontinuity there is a linear behaviour observable. This indicates a high crystallinity of the complexes (6). The relatively short side chains should prevent crystallization. Crystallization can be induced by the formation of the polymer/salt complexes as is shown later.

The energetic terms within the complexes are obtained using the Vogel-Tammann-Fulcher equation (7).

$$\sigma = \sigma_0 \cdot \exp\left[-B / (T - T_0)\right]$$

B and T<sub>0</sub> can be achieved by computer fitting. T<sub>0</sub> represents the temperature at which the configurational entropy of the system is theoretically zero, while B represents the entropic changes within the complexes. The lower T<sub>0</sub> the higher is the flexibility of the polymer side chains and correspondingly the lower is the viscosity. The fitted data show the assumed correlation (Table 2). Polymers with the longest side chains **1c** and **2c** show the lowest T<sub>0</sub>. Their side chains are more flexible compared to the others **1a**, **1b**, **2a**, and **2c**. A longer side chain raises the probability for ions passing from one coordination sphere to another.

Table 2: Fit parameters from non-linear analysis of conductivity data between 263-293 K

Polymer	T <sub>0</sub> / K
1a	226
1b	156
1c	122
2a	165
2b	135
2c	99

The coordination spheres are formed by the fluid side chain oxygen atoms because of their ability to build up coordinative bonds with the salt cations. Thus for the polymer pairs **1a/1c**, **1b/2b** and **1c/2c**, who have the same number of oxygen atoms in the side chain, the value of T<sub>0</sub> should be comparable. The fitted data show a better accordance for the poly-

mer pairs **1b/2a** (11/10 atoms in the side chain) and **1c/2b** (14/13 atoms), respectively, with comparable side chain length. This indicates that in the ether polymers **1a**, **1b** and **1c** the oxygen atom nearest to the main chain is, by steric hindrance, not capable to interfere in an ionic complex. As the polymer side chains work as a solvent for the salts, addition of salt in the polymer/salt mixture should raise the conductivity.

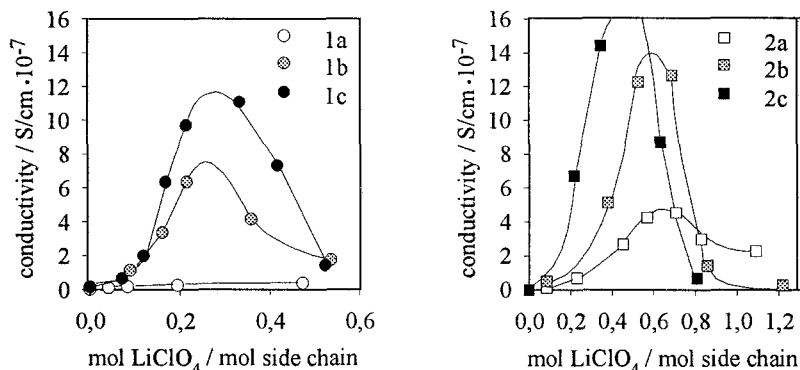


Figure 3: Dependence of the conductivity from the added amount of  $\text{LiClO}_4$

As Figure 3 shows there is a maximum in conductivity for all polymers except for polymer **1a**. The maxima are between 0.2 and 0.6 mol  $\text{LiClO}_4$ /mol side chain. An increase in conductivity is observable only for small amounts of  $\text{LiClO}_4$ . This behaviour indicates the build up of a polymer network (4) between individual polymers **1b-2c** with two or more side chains from different polymer molecules forming one complex. With only low salt concentration the cation will be complexed by side chains of one polymer molecule. The energy for a migration to another coordination sphere within an individual polymer molecule is lower than for a transfer to another polymer molecule. On the other hand, there is a loss of entropy combining two individual polymer molecules in one complex. With increasing concentration of the salt all possible coordination places on one individual polymer are filled up leaving free side chains for entropic reasons. On increasing the salt concentration more intermolecular complexes are formed incorporating these side chains, even of their disadvantageous higher energetic state. This leads to an intermolecular network which raises the viscosity of the overall matrix. The involvement of more than one side chain in the formation of a complex is indicated by the values of the maxima (see Table 3) which would be expected to be 1 for a 1:1 complex.

Table 3: Values of the maximal conductivity of the complexes

Polymer	Relation $\text{LiClO}_4$ /side chain	Polymer	Relation $\text{LiClO}_4$ /side chain
<b>1a</b>	-----	<b>2a</b>	0,63
<b>1b</b>	0,22	<b>2b</b>	0,62
<b>1c</b>	0,28	<b>2c</b>	0,43

For obtaining maximum conductivity a precise amount of salt can be added to the polymers.

**Conclusions**

The determining factor for the conductivity of the polymer/salt complexes is the flexibility of the side chains. A loss of mobility by formation of a network or shortening of the side chains causes a drop in conductivity. The glass transition temperatures could be taken as an indicator for the quality of a polymer electrolyte system.

**Acknowledgement**

The authors thank Fonds der Chemischen Industrie for financial support.

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