Experimental report

05/11/2019

Proposal:	**CRG-2633**	**Council:**	4/2019
Title:	Understanding Ion Conductivity in a New and Promising Polymer Electrolyte		
Research area:			

This proposal is a new proposal

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Experimental team:	Michael OHL Yuya DOI
Local contacts:	Orsolya CZAKKEL

Samples: Poly(ethylene ether carbonate) with Lithium

Instrument	Requested days	Allocated days	From	To
IN15	5	5	23/09/2019	28/09/2019

Abstract:

The experiment took place Oct. 21st to Oct 30th 2019. Poly (ethylene carbonate) (PEC) samples had been synthesized as deuterated counterpart of commercially available PEC in the ratio 90/10 – deuterated/ protonated to exhibit proper visibility properly in Aluminum flat plates and brought to the beamline. With the chosen deuteration we intended to make the main chain dynamics visible.

Beside background and resolution, 3 samples of PEC with 0%, 14% and 33% Li-salt have been measured at temperatures 50, 80, 100, 120 centigrade. Proper thermalization took place and we collected highly interested data whereas we wish to mention, just with the worldwide unique time/ energy resolution such results had been possible to observe.

All samples showed a clear decay in the chosen Fourier time range up to 200ns. We measured in the momentum transfer regime from 0.5nm^{-1} to 2nm^{-1}. However, due to space limitations, we won't show the data in this short report but moreover will show the preliminary results.

From the data itself it is obvious, when adding Li – salt the blend softens and the main chain becomes faster. The higher the Li – salt content the faster the dynamics become. This isn't unexpected and already visible in several other polymeric systems. Usually when the viscosity drops, the dynamics become faster. Consequently, this wasn't unexpected. Also the Q dependence showed slower dynamics when going to lower momentum transfers (higher length scales).

Now, in a first attempt and to sighted the results, we fitted the data with a simple Kohlrausch-Williams Watts equation. Exemplary we plotted in Fig. 1 the relaxation time over Q for the 0% Li – salt blend or homopolymer. Obviously it followed a Q^{-4} behavior which – among others – is one criterion to observe the Rouse dynamics (*E. Rouse, J. Chem. Phys. 21, 1272 (1953) and M. Doi, S.F. Edwards, The Theory of Polymer Dynamics (Oxford University Press, New York, 1986*). Needless to say, that with the chosen deuteration/ protonation of the polymer with or without Li – salt we see the main chain and the Li – salt isn't visible in the intermediate scattering function $S(Q, \tau)$. This is what we intended. We directly see the influence of the Li-salt concentration on the polymer or in other words the polymer electrolyte used in Li-batteries. Also in our next steps we intend to perform MD simulations with PEC and Li-salt to calculate $S(Q, \tau)$. When achieving agreement with the experimental data, we would know how the Li-ions move through the polymer matrix and the dynamics of the polymer as well.

Furthermore, the stretching parameter β_{KWW} remained irrespective of temperature or Li – salt concentration in the range between 0.4 – 0.7 which is typical for main chain dynamics.

In an attempt to put all temperature relaxations in one plot we added data from our previous dielectric spectroscopy measurements (see Fig. 2). We clearly see the relaxation which delivers a glass transition of about 220K. However, for PEC a much higher glass transition temperature at about 290K is expected. Now we know our PEC involves 2 ethylene oxide monomer (poly (ethylene oxide) has a reported glass temperature of 207K - *http://polymerdatabase.com/polymer%20physics/Polymer%20Tg.html*) units per ethylene carbonate which makes the system much softer and is the cause for the very low glass transition temperature. In addition, the glass transition temperature depends on the molecular weight which is relatively high too.

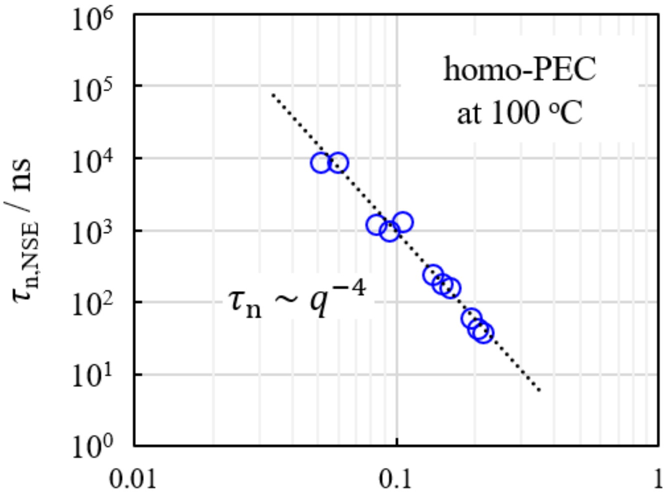

Figure 1. Relaxation time τ versus momentum transfer Q for the homopolymer – PEC.

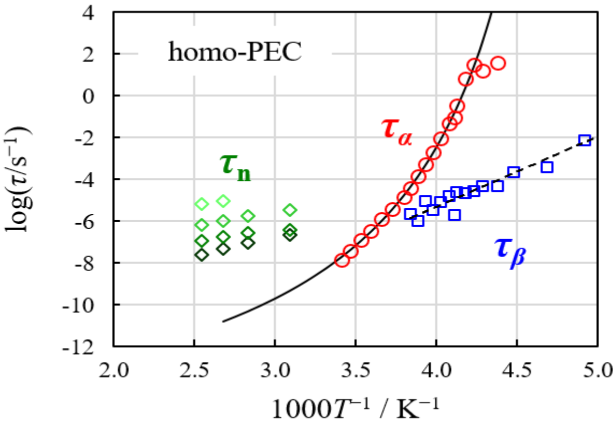

Figure 2. Arrhenius diagram of the homopolymer PEC – 0% LiTFSI.

An additional β local relaxation is visible which is indicative for molecules moving within a monomer unit. It follows the Arrhenius equation. The NS data describes the main chain/ backbone motion and is clearly slower.

However, further evaluation will be done within the next few weeks to come.

We wish to thank the instrument team – especially our local contact for their outstanding support.