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# Probing ion coordination in polymer electrolytes with multinuclear NMR correlation spectroscopy

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ABSTRACT

Solid polymer electrolytes (SPEs) are generally obtained by mixing an appropriate solvating polymer with alkali salt. Block copolymers based on poly(ethyleneoxide) (PEO) are suitable choices for SPEs because their polar ether moiety dissolves salts and their apolar component permits fine tuning of thermal and mechanical properties. However, the ionic properties of these materials depend greatly on the solvation state of the cation and the anion as well as the ion-pairing. In this paper, we present Heteronuclear Overhauser NMR Spectroscopy (HOESY) experiments for probing through-space proximity of the different components (cation–polymer, cation–anion, anion–polymer) within these melt electrolytes. The effect of the salt and the matrix is discussed as well as potential applications and limitations of this advanced structural tool.

## 1. Introduction

The development of new technology is often related to the availability of energy sources. When larger density energies, higher voltage and longer operating life are expected, one of the most appropriate choices for portable power would certainly be lithium-metal polymer batteries [1]. Academic research began in the 1980s, but it took more than twenty (20) years of research and development for the first batteries to become available on the market. In these complex electrochemical devices, the electrolyte component still remains one of the greatest challenges with regard to their stability, lifespan, cost, etc. Even if ionic conductivity levels are too low when the battery is below room temperature [2], the main advantages of solvent-free solid polymer electrolytes (SPEs) are the absence of liquid leakage and the simplicity of the battery design.

From the pioneering research work of M. Armand [3] and P. Wright [4], the best SPE candidates are still considered to be solid solutions of lithium salt in poly(ethylene oxide) (–[$CH_2CH_2O$]$_n$–, PEO) or PEO derivatives (poly(propylene oxide), copolymers, nanocomposites) [5]. Combining a low glass transition temperature and a high density of ether-type oxygen, PEO enables the dissolution of a large amount of alkali salts, which in turn creates materials with a reasonable level of ionic conductivity. The main drawback is the low cationic transport number which may induce some local over-voltage and parasitic reactions near the electrode [6]. This is obviously related to two major shortcomings of the PEO: its tendency to crystallize even when salts are dissolved within it, and its high donor number and low dielectric constant. Both effects are detrimental to the conductivity because i) cation mobility occurs mostly in the amorphous phase with the assistance of the polymer segmental reorientation and ii) dissolved species within the polymer are in a rather complex equilibrium with single ions, solvent separated ions, ion pairs and even bigger ionic aggregates all together. Obviously, only the smaller charged species (isolated ions) will have a high mobility in an electrical field [7].

Chemical modifications and/or cross linking of PEO chains may override some of these issues and help to improve electrical properties inside a 3D-network with better mechanical properties [8]. For the past ten (10) years, hybrid organic–inorganic nanocomposites have also been investigated as another alternative for better SPE [9]. These materials, also called Ormocer®, offer a synergy between the properties of both components: the polymer (generally a polyether) for dissolving salts, and the inorganic components (generally silica clusters) for cross linking, reinforcing mechanical properties, and reducing the tendency for crystallization [10,11]. In these materials the chemical bridge linking the two moieties is frequently a polar group (urea, urethane, or carboxyl). We recently evidenced the strong influence of these functional groups on salt solubility, dissociation processes and finally on ionic conductivity properties [12].

In order to adjust the solvation shell of ions and to optimize ionic conductivity of SPE, it is necessary to characterize the structure and dynamics at the molecular level [13]. It requires not only investigating all of the components (cation, anion, polymer, additives ...) but also measuring the pair correlations (i.e. the proximity) between all of

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them [12,14]. Many techniques and spectroscopies provide only **indirect** information on the coordination sphere. The **direct** determination of the solvation sites (i.e. the measurement of pair correlation and/or inter-species distances) is obviously more challenging. Nuclear magnetic resonance spectroscopy (NMR) by itself provides many different methods for selectively measuring local structures, mobilities and interactions between components in both solid and liquid state. NMR investigations were recently reviewed in the field of SPE [15], as were the dynamics of $Li^+$ charge carriers by specific advanced techniques [16].

Many NMR methods selectively decipher the behavior of each individual component and then **indirectly** probe coordination and solvation shells, e.g. chemical shifts probe the nucleus charge density, relaxation times reflect local dynamics and pulsed-field gradient NMR (PFG-NMR) measures self-diffusion coefficients of the nuclei. However, NMR can also provide some specific techniques which **directly** measure pair correlations between two individual nuclei via through-space dipolar interactions [17]. Such interactions are very strong in the "rigid" domain and are used to measure interatomic distances in solid materials. Recently, REDOR experiments have been used in crystalline and semi-crystalline SPE to measure the distance between the $Li^+$ cation and the PEO carbons involved in the coordination site [18,19]. Such structural determination is very helpful for describing the local geometry around the cation.

Ionic conductivity, however, occurs in the amorphous melt phase where higher mobility also reduces dipolar coupling and generally inhibits the ability to measure them. It is already well accepted that dipolar couplings vanish in liquids and may be only observed through their contribution to cross-relaxation mechanisms. This is the well-known Nuclear Overhauser Effect (NOE) which corresponds to the dynamic polarization of a nucleus when a neighboring nucleus is irradiated by a radiofrequency [20].

Efficiency of Overhauser transfer mechanisms depends on molecular correlation time, gyromagnetic ratio and the distance between the two nuclei. Therefore, this technique is a powerful structural tool for analyzing all kinds of molecules and molecular assemblies. Homo- and hetero-NOE spectroscopies (NOESY and HOESY) were developed to provide valuable information about intermolecular interactions [21], insight into the geometry of organolithium compounds [22] and complexes in coordination chemistry [23,24]. They also show solvation and non-covalent interactions [25], hydration of molecules [26], local structure of surfactant systems [27] or ion-pairing in solution [28].

Within this context, this paper will present results from HOESY experiments that obtained data about the local structure and the organization within melt SPE. We focus this study on model oligomers which mimic organic components of hybrid organic–inorganic SPE examined in our previous studies [29]. We also point out that such NMR approaches provide direct qualitative (or even semi-quantitative) data on the interactions between the various SPE components: cation–polymer, cation–anion and anion–polymer.

## 2. HOESY background

Theoretical treatment and experimental development of homo-/heteronuclear Overhauser spectroscopy are discussed in existing literature and are out of the scope of this paper [20,30]. As a reminder of the basics of Nuclear Overhauser Effect (NOE), if a weak radiofrequency field is applied at the Larmor frequency of one of the spins, *S*, during a sufficiently long time, there is a strong effect on the longitudinal magnetization of the neighboring non-irradiated spins, *I*, and in some cases it could enhance the magnetization of these spins. The efficiency through which the NOE is transferred from spin *I* to spin *S* strongly depends on the distance *r* between the two nuclei and on the tumbling properties of the molecule (expressed as a correlation time, $\tau_c$):

$$\eta = K.\tau_c.r^{-6}$$

where *K* is a factor representing the efficiency of the NOE effect. The dependence of the NOE effect on the distance shows therefore that these measurements can be an important tool for elucidating the molecular structure and architecture in solution. However, the factor *K* depends on the nuclei (gyromagnetic ratios, relaxation times, ratio of spin diffusion mechanisms ...) and this is certainly a severe restriction to quantitative measurements. Furthermore, chemical exchange between sites can also occur, which is also a major restriction for qualitative measurements. Spin diffusion mechanisms have also been observed in viscous liquids, leading to erroneous inter nuclear distances and other artifacts [31].

Perturbation from spin equilibrium and measurement of NOE effects can be produced by steady state or transient methods [20]. HOESY experiments are generally examined with bi-dimensional transient methods that allow simultaneous measurement of the NOE between all the different sites [30]. Depending on the nature and properties of the two nuclei (gyromagnetic ratio, sensitivity, relaxation time, chemical shift range …), two different approaches have been developed in literature and are now used efficiently: i) the basic direct pulse sequence [28,31] which may lack sensitivity and spectral resolution in the $f_1$ dimension (generally $^1H$) and ii) an "inverse" pulsed-field gradient-enhanced HOESY pulse sequence, which is generally more sensitive and more convenient for low abundancy nuclei [32].

In agreement with existing literature, we used the direct sequence to measure $^1H$–$^{19}F$ HOESY and to investigate the proximity of fluorinated anions to the polymer chains. We also used the "inverse" PFG sequence to measure $^1H$–$^7Li$ and $^{19}F$–$^7Li$ HOESY in order to study the solvation shell of lithium cations by polymer segments and the tendencies of ion-pair formation.

## 3. Experimental

### 3.1. Sample preparation

Triblock symmetric oligomers bis(pentylurea) poly(ethyleneoxide) and bis(pentylurea) poly(propyleneoxide) of formula $C_5H_{11}$-NHCONH-$(X)_n$–NHCONH-$C_5H_{11}$ {X = –$CH_2CH_2O$–, $n = 45$ or X = –$CH_2CH(CH_3)O$–, $n = 30$ respectively} (abbreviated C5uPEOuC5 and C5uPPOuC5 respectively) were used to mimic the organic moiety of hybrid organic/inorganic materials and solid electrolytes developed in our group [33]. The choice of linking urea groups was first proposed as a simple and quantitative reaction between the different moieties, but it may also create competition between different solvating sites for cations and anions. This was already recently depicted in a multi-spectroscopic investigation of such hybrid organic–inorganic SPEs [12]. Alkali salts ($A^+X^-$, where $A^+ = Li^+$, $Na^+$, $Cs^+$ and $X^- = CF_3SO_3^-$ [TF], $BF_4^-$, $PF_6^-$, $(SO_2CF_3)_2N^-$ [TFSI]) were dissolved inside these materials. Such small oligomers are viscous liquids around RT even when salts are dissolved, and high resolution liquid NMR spectra can be measured. Some of these salts were also dissolved in α-ω dimethyl poly(ethylene glycol) of molecular mass 2000 (abbr. PEO) to decipher specific interactions of ions with ethylene oxide fragments.

C5uPEOuC5 was prepared by reacting pentyl isocyanate with diamino-end terminated PEO following procedures already described in our previous papers [11,12,33]. Stoichiometric amounts of these two reactants were dissolved in THF, and the mixture was heated under reflux for 24 h. The urea formation is quantitative, as checked by $^1H$ and $^{13}C$ NMR, and the pure C5uPEOuC5 material was obtained after evaporation of the solvent under vacuum. Chemical and alkali salts were used as received from the different companies (Aldrich, Fluka).