

NMR Multi-Scale Description of Ionic Conductivity Mechanisms Inside Polymer Electrolytes[†]

Patrick Judeinstein,^{a,*} Detlef Reichert,^b Eduardo R. deAzevedo,^c
and Tito J. Bonagamba^c

^a R.M.N. en Milieu Orienté, CNRS UMR 8074, Bâtiment 410, Université Paris-Sud, 91405 Orsay – France.
E-mail: pjudeins@icmo.u-psud.fr

^b Department of Physics, University of Halle, Friedemann-Bach-Platz 6, 06108 Halle - Germany

^c Instituto de Física de São Carlos, Universidade de São Paulo, Caixa Postal 369, CEP 13560-970 São Carlos-SP - Brazil

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Abstract

Solid Polymer Electrolytes are obtained by dissolving an alkali metal salt inside poly(ethylene oxide) based materials. The properties of these materials are strongly related to the behavior of the different active species : solvent (polymer), cation, and anion. In this paper, we compare various NMR techniques capable of deciphering different aspects of these new materials : the structure and dynamics of the polymer, the cations and anions as well as the supramolecular interactions between these different species. These data are very useful for understanding the conductivity mechanisms inside various families of PEO-based materials (nanocomposites, block oligomers and copolymers, and liquid crystals) developed by our group.

Key words: Solid Polymer Electrolytes, NMR, lithium battery, hybrid materials, nanocomposites, liquid crystals, polymer structure, polymer dynamic

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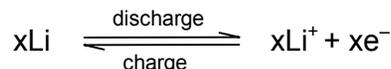
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Batteries

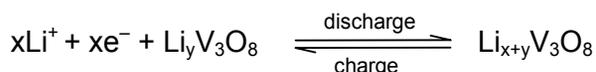
The development of hi-tech devices is often related to the availability of power energy sources. This includes a wide variety of applications from sustainable memory in credit cards or for medical purposes to electric vehicle projects or stationary applications. For this reason, rechargeable (secondary) batteries of varying geometries ranging from 100 μm laminated, flexible, thin flat cells up to large volume cylindrical or prismatic cells of high energy have to be developed.¹ Furthermore, technological choices include many factors, such as availability, price, specifications, and so on. If the main expected characteristics are outstanding density and specific energies, high voltage and a long operating life in a large temperature range or rapid recharge capability, one of the most appropriate choices for consideration would be a lithium-metal polymer battery.² The first academic research on this topic was performed in the late 1970's, however it took more than 20 years of academic and industrial research and development to have such devices available in the market.³ Lithium-metal polymer batteries are electrochemical devices capable of reversibly transforming chemical reactions

within electrical energy. They are obtained by the superposition of different active layers as depicted in Figure 1 and described below:

- a lithium foil as the **anode**. This is the lightest and the more electropositive metal (3.04 V versus Normal Hydrogen Electrode):



- an intercalation material as a **cathode**, which is based primarily on vanadium oxide :



The combination of these two electrode reactions ensures the circulation of electrons in the external circuit and the production of an electrical current.

- an **electrolyte** which should specifically ensure the transport of Li^+ charge carriers within the electrical generator. The design and conception of such electrochemical devices could be improved by using solid polymer electrolytes (SPE) instead of classic liquid, low molecular weight electrolytes.

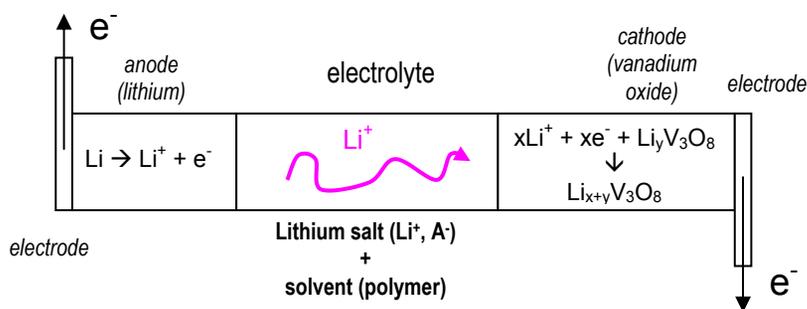


Figure 1. Scheme of a lithium ion polymer battery (discharge reaction).

Biographical Sketches



Dr. Detlef Reichert received his PhD in Physics in 1990 from the Technical University of Merseburg (East Germany). After a post-doctoral position in the group of Zeev Luz (Weizmann Institute, Israel) in 1992, he obtained a permanent staff member position in the Physics Department of Halle University (Germany) in 1993. He is Senior Researcher and teaches Physics. His research interests include the NMR investigation of structure and dynamics in organic solids and the development of new NMR methods. Among these materials are synthetic polymers, bio-polymers, molecular and liquid crystals and solid polymer electrolytes. He is the author of 56 publications in peer-reviewed journals.

Dr. Tito José Bonagamba received his Ph.D. degree in Physics in 1991 from the Institute of Physics of São Carlos (IFSC) - University of São Paulo (USP) (Brazil). Since 1988 he is Professor of Physics at the IFSC-USP. He spent two and a half years (03/1998-09/2000) in the USA in the Department of Polymer Science and Engineering at the University of Massachusetts and Ames Laboratory at Iowa State University as visiting scientist. He has since been visiting professor several times in Germany (University of Halle) and France (Paris Sud University). His research interests include the development and utilization of multidimensional solid-state NMR methods and their applications to study materials, NMR instrumentation, and quantum computation. He is the author of over 60 publications in peer-reviewed journals. He has supervised 12 M.Sc.'s, 6 Ph.D.'s, and 5 Post-Doc's.



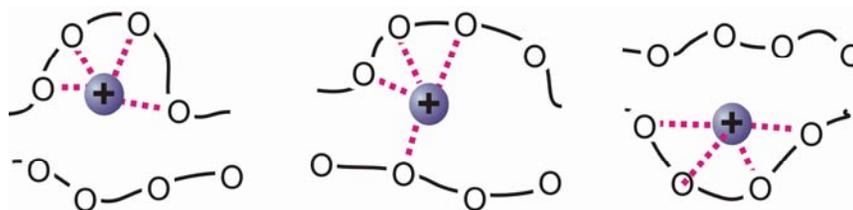


Figure 2. In SPE, cation migration is associated with the segmental mobility of the polymer chains.

Most of these materials are based on lithium salts dissolved within poly(ethylene oxide) (PEO)-based media. PEO is considered to be the first solid solvent investigated as SPE,^{4,5} but it is still considered as the best candidate for solid electrolytes, despite its too low ionic conductivity at room temperature, meanwhile some power batteries need an additional heating system.^{6,7}

PEO : a model Solid Polymer Electrolyte

The chemical structure of PEO [$-(\text{CH}_2\text{CH}_2\text{O})_n-$] explains most of the properties of this polymer: a strong solvating character due to the high donating character of the numerous ether oxygens, a low dielectric constant arising from the high ratio of alkyl segments and a strong tendency for crystallization correlated with the high organization and rigidity of the segmental units. As stated by most experimental work, cation mobility occurs in the amorphous phase and its diffusion occurs through a complex mechanism

involving the PEO segmental mobility (Fig. 2). For that, crystallization has to be avoided by modifying the polymer structure or by adding salts or fillers to inhibit regular packing. Moderate conductivity in amorphous materials is then a direct consequence of PEO features where high solvation is counterbalanced by the energetic complexation of cations. Equilibrium between different solvated species (“free ions”, solvent separated ion pairs, ion pairs, or higher aggregates) also has a detrimental effect on cation mobility.²

For the past 30 years, a significant amount of academic and industrial research involving both the optimization of these materials and the description of mobility mechanisms within SPE has been done. These studies allowed the optimization of SPE up to the recent production of lithium-ion polymer batteries available in the market,³ but the mechanisms are still not completely understood (and then these systems are not optimized). This could be due to their complexity, which requires the use of many different techniques in order to explore structure and dynamics on large space and time scales.

Biographical Sketches



Dr. Eduardo Ribeiro de Azevedo was born in 1974 and obtained his PhD in Physics at the Instituto de Física de São Carlos (São Paulo state, Brazil) in 2001. During his doctoral work he worked for one year at the Department of Polymer Science and Engineering in Amherst (Univ. of Massachusetts, USA) as a visiting scholar and worked under the supervision of Prof. Klaus Schmidt-Rohr and Prof. Mei Hong. In 2003, he obtained the position of Assistant Professor of Physics at the University of São Paulo (Brazil) and joined the group of Prof. Bonagamba at the Institute of Physics in São Carlos. His research activities are also centered on the development of new multidimensional NMR methods to characterize the structure and dynamics of materials, as well as quantum computation. He is the author of over 25 papers in peer-reviewed journals. He has been a visiting researcher in the University of Halle (Germany).

Dr. Patrick Judeinstein received his PhD in 1989 from Paris 6 University (France) under the supervision of Prof. J. Livage. He then received a permanent position as a research scientist at CNRS (Centre National de la Recherche Scientifique) in Orsay (Paris Sud University, France). He spent 16 months in the Institute Für Neue Materialien (Saarbrücken, Germany) as a visiting scientist in 1992/1993. His main scientific interests include the design of new, “soft nanostructured and oriented materials” with specific properties such as mechanical, optical, electrical. He is particularly interested in the description of the molecular structure and dynamic inside these heterogeneous materials by multispectroscopic approaches, especially NMR techniques, X-Ray and Raman spectroscopies. He has effective and fruitful collaborations with French laboratories (Dunkerque, Grenoble, Ecole Polytechnique...) and with different groups in Algeria, Brazil, Germany and Slovenia. He has co-authored 89 papers and has 3 patents.



In this paper, we will present several approaches for more complete research in both aspects of these materials by using various nuclear magnetic resonance (NMR) methodologies. We aim to point out some experiments that can be used for exploring segmental dynamics of the solvent polymer, self-diffusion of the different species and also for investigating the proximity of two different species, cations *vs.* polymer, and cation *vs.* anion. These experiments will be presented to highlight the properties of original SPE and advanced materials such as organic-inorganic nanocomposites, liquid crystals, block oligomers, etc.

I. Structural determinations

I.1 Chemical shifts

Chemical shifts are induced by the indirect magnetic interaction between an external magnetic field and the nuclear spins through the involvement of neighboring electron clouds. For this reason, the interaction is related to the electronic density around the nuclei. These terms are of major importance in the analysis of organic molecules, because such interaction is mainly intramolecular, although intermolecular interactions are also effective, even in ^1H NMR as well-known “solvent effects”. In the case of lithium salts dissolved in SPE, the scale of ^7Li NMR chemical shifts for cations is very small (less than 1 ppm) compared to the typical linewidths of these signals, making the analysis of Li^+ environments rather difficult.⁸ Bigger cations with more external electrons are more sensitive to such influences, as depicted by the study of hybrid organic-inorganic SiO_2 -poly(propylene oxide) in which NaClO_4 salts were dissolved.⁹

In order to reduce the chemical shift and quadrupolar anisotropies, and consequently the linewidths, ^{23}Na NMR spectra are recorded under Magic-Angle Spinning (MAS). Under this condition, three different regions are observed in the ^{23}Na MAS NMR spectrum corresponding to NaCl -like aggregates ($\delta = 7$ ppm), ion-pairs with NaClO_4 -like environment ($\delta = -5$ ppm) and Na^+ ions wrapped inside the polyether chains (solvent separated single ions, broad band centered around $\delta = -20$ ppm).¹⁰ In this example, the presence of NaCl aggregates results from the synthetic process, which was used for obtaining these hybrid materials. Because these clusters are too small or amorphous, they cannot be detected easily by other analytical methods. The presence of other aggregated structures also has a deleterious effect on the ionic conductivity because the number of charge carriers is much lower than that expected from the initial composition. Numerical integrations of the different signals could lead to the relative concentration of the

different species, and an external reference could also be used in order to quantify the absolute concentration of the different species.

Among the other NMR active alkali metal cations,¹¹ ^{39}K isotope has a large quadrupolar moment and a low sensitivity; ^{85}Rb and ^{87}Rb isotopes have incredibly large quadrupolar moments and only ^{133}Cs meets high sensitivity and small quadrupole moments required to show high sensitivity and narrow NMR signals. Furthermore, the ^{133}Cs nucleus has a large electronic cloud and Sternheimer antishielding factors, leading to a wide chemical shift range (more than 700 ppm) and the possibility of obtaining informative and accurate data even in the solid state by MAS NMR spectroscopy.¹²

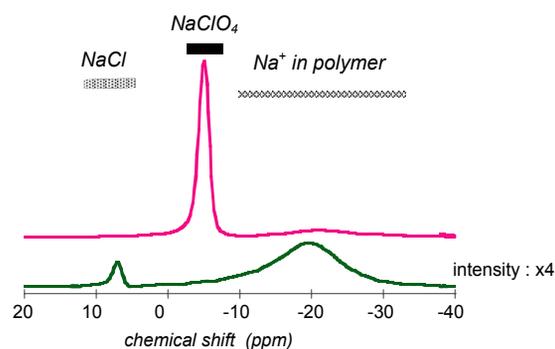


Figure 3. ^{23}Na MAS NMR in hybrid SiO_2 -PPO nanocomposites doped with NaClO_4 (chemical shifts are reported relative to a $\text{NaCl}/\text{H}_2\text{O}$ (1M) reference) $[\text{O}]/[\text{Na}]$ is equal to 4 and 15, for top and bottom curves respectively. Reprinted from⁹ with permission from Elsevier.

I.2 Internuclear distances

The next structural information step is to characterize the coordination sphere of the cation by the number, the chemical nature, and the distance from its neighbors. Two regimes have to be considered, depending on the dynamic properties of the different components of SPE. If the different species experienced high and non-correlated mobilities, an ergodic coordination sphere has to be considered (averaging the coordination sphere on time or space is identical), and NMR experiments could mainly provide an estimate of ion pairing or contact between some specific moieties of the solvent by homo- or hetero-Nuclear Overhauser Effect measurements (respectively abbreviated as NOESY or HOESY). Results obtained from such experiments are detailed in the item III.2 of this paper. If the different species can be considered to be static in the NMR timescale, then REDOR (Rotational-Echo Double Resonance) provides a structural tool for determining intermolecular distances in solids by measuring the value of the dipolar couplings between the NMR active nuclei.¹³ Despite the fact that these methods are routinely used to characterize solid-

state polymers and proteins, applications of REDOR to quadrupolar nuclei require modifications in the method. In the case of $^{133}\text{Cs}^+$ ions with low quadrupole moment, ^{13}C - ^{133}Cs and ^2H - ^{133}Cs REDOR experiments have already been performed to characterize guest-host interactions in Cs-salt calixarene complexes and proper agreement between calculated dipolar couplings and X-Ray distances were obtained.¹⁴

In the case of stronger quadrupolar moments, such as ^7Li nuclei, we were recently able to measure ^7Li - ^{13}C REDOR signals on different materials.¹⁵ Although neutron powder diffraction and REDOR distances are very similar for a reference compound (lithium acetate dihydrate), a slight discrepancy was observed for the crystalline SPE ($\text{PEO}_6:\text{LiPF}_6$). While the REDOR experiment indicated a distance for Li-C of $\sim 3.14\text{\AA}$, diffraction experiments indicated 13 nearest Li-C distances in the range 2.23\AA – 4.27\AA for the same structure.¹⁶ Even if these results are fairly good, they show some aspects of the limitation of this method, because even in the crystalline SPE the distribution of distances is really very broad, and we can suppose that it could be even worse (broader) in amorphous materials. Nonetheless, this method requires generally defined large dipolar couplings between the observed nuclei, which restricts this method to rigid structures, crystalline or glassy solids. These materials could be considered as a good model for the SPEs which present good ionic conductivity only above the glass transition. New developments of this technique, such as REREDOR could overcome these limitations and would allow study of highly mobile systems with smaller dipolar couplings.¹⁷ Thus, the interest for these methodologies would be to provide reference data on amorphous materials that can be associated with information obtained from other spectroscopy methods and which can be used for solid or soft matter and liquid state: IR, Raman¹⁸ and EXAFS.¹⁹

II. Dynamical determinations

II.1 Study of the polymer dynamics inside nanocomposites by solid-state NMR spectroscopy

Hybrid organic-inorganic materials are obtained by grafting PEO oligomers to silica clusters. These nanocomposites materials were widely studied because the intimate mixing of these two phases at the nanometer scales increases the mechanical properties and inhibits the crystallization of the polymer. When doped with lithium salts, these materials present good ionic conductivity.²⁰ The mobility mechanisms of the polymer chains and the cations were initially investigated by measuring the spin-lattice relaxation times T_1 and the linewidths ($\Delta\nu$) vs. temperature for ^1H , ^{13}C , and ^7Li nuclei.^{21,22} The temperature dependence

of these parameters is plotted in Figure 4. The trends for the cation and the polymer are similar, evidencing the strong correlation between the motion of the Li^+ charge carriers and the polymer segmental dynamics, as in pure PEO/salt mixtures.⁶

Linewidths strongly decrease between $-20\text{ }^\circ\text{C}$ and $30\text{ }^\circ\text{C}$, indicating that they are related with the increase of the polymer dynamics close to the glass transition. However, such a large span would indicate a large distribution of motion modes related to the heterogeneity of the materials. At lower temperatures, it was shown that the ^7Li linewidth is considerably reduced if a strong ^1H decoupling is applied during the experiment, evidencing the large dipolar coupling between ^7Li and ^1H and the strong complexation of the cation by the polymer chains.

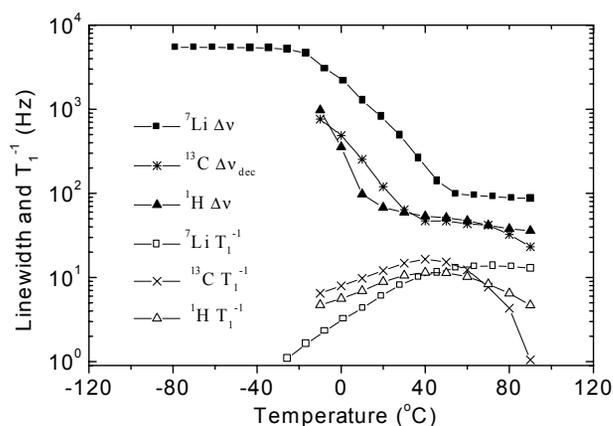


Figure 4. ^1H , ^{13}C , and ^7Li T_1 and $\Delta\nu$ temperature dependences for the organic-inorganic hybrid materials doped with LiClO_4 .²¹ Reproduced by permission of The American Chemical Society.

The $1/T_1$ curves present the usual "∩" shape and evidence that the extreme narrowing regime is nearly observed for the different components of the system above $40\text{ }^\circ\text{C}$. Further interpretation of these data could lead to the dynamic function distribution and the correlation time distribution, which are related to the motion of the species. However, it would require building a model that would describe *a priori* the motion characteristics, which is a significant limitation.²³ Furthermore, the relaxation parameters are mostly related to the rotational motion modes, which come far away from the segmental and translational motions that are implied in the conductivity properties.

Another class of experiments that can be used to study molecular motions with the advantage of being much more model independent is the Exchange NMR method.²⁴ The principles of these experiments rely on the orientation dependence of the NMR interactions for solid materials. Particularly for spin $1/2$ nuclei, such ^{13}C , it is possible to produce conditions where the NMR frequencies are only defined by the chemical

shifts. Thus, because chemical shifts are tensorial properties, the NMR frequency of a carbon located in specific molecular site depends on the orientation of the molecule. This is known as chemical shift anisotropy (CSA) and, for amorphous or polycrystalline samples, the NMR spectrum defined by such interaction has a characteristic shape known as NMR powder patterns (Figure 5a) when all orientations are present in the sample.²⁵

The basic idea of an Exchange NMR experiment is to take advantage of this orientation dependence for obtaining information about the molecular rotations. This is achieved by correlating the chemical shift frequencies of a nuclear spin observed in two different periods of time (t_1 and t_2) separated by a long mixing time t_m (generally in the range 50 ms – 500 ms), where motion inducing changes in the NMR frequency can occur. The usual way of doing such correlation is by acquiring a 2D spectrum that contains the NMR frequencies before and after t_m along the dimensions (ω_1) and (ω_2), respectively. Then, if no change in the molecular orientation occurs during t_m (no molecular motions), the 2D spectrum is fully diagonal ($\omega_1 = \omega_2$). Changes in the molecular orientations will produce off-diagonal spectral intensities, and the final shape of the 2D spectrum will depend directly on the geometry of the molecular motion, Figure 5b (left).

In more complicated cases, the analysis of these 2D spectra can be performed using simple numerical simulations, allowing the extraction of the motion geometry, Figure 5b (right). Particularly, ^{13}C exchange NMR spectroscopy experiments have been performed

for the siloxane/PEO hybrid materials mentioned above to get more accurate information about the polymer segmental dynamics.²⁶ The 2D exchange spectrum shown in Figure 5b (left) has two clearly distinct regions. In region A (see also Figure 5c), attributed to the carbons located in segments near the silica clusters, the 2D spectrum is purely diagonal, indicating that these segments are immobile or execute very small angle motion, within the ms to s time scale. In contrast, off-diagonal intensities are observed in region B, which accounts for carbons in the PEO units, showing that a significant fraction of these segments execute large angle motions. Further experiments, named 1D Pure Exchange (PUREX),²⁷ were also performed, allowing measurement of the amplitude of these motions and the fraction of carbons involved. In these experiments, instead of correlating the NMR frequencies before and after t_m in a 2D spectrum, the pulse sequence produces a modulation in the spectral intensity in such a way that it depends on the difference between the frequencies before and after t_m , ($\omega_1 - \omega_2$). Because the increase of signal intensity as a function of the total evolution time under CSA, τ_{CSA} , depends on the magnitude of ($\omega_1 - \omega_2$), which is proportional to the reorientation angle, information about the reorientation angles can be obtained in this 1D method. This technique is more sensitive to small angle motions than the 2D exchange experiment. Figure 5d shows this dependence for the ^{13}C belonging to PEO groups in siloxane/PEO hybrid at $-75\text{ }^\circ\text{C}$ and $-55\text{ }^\circ\text{C}$. The curves present a bimodal behavior, being the fast increase associated with the large angle motion (isotropic motion) and the slow

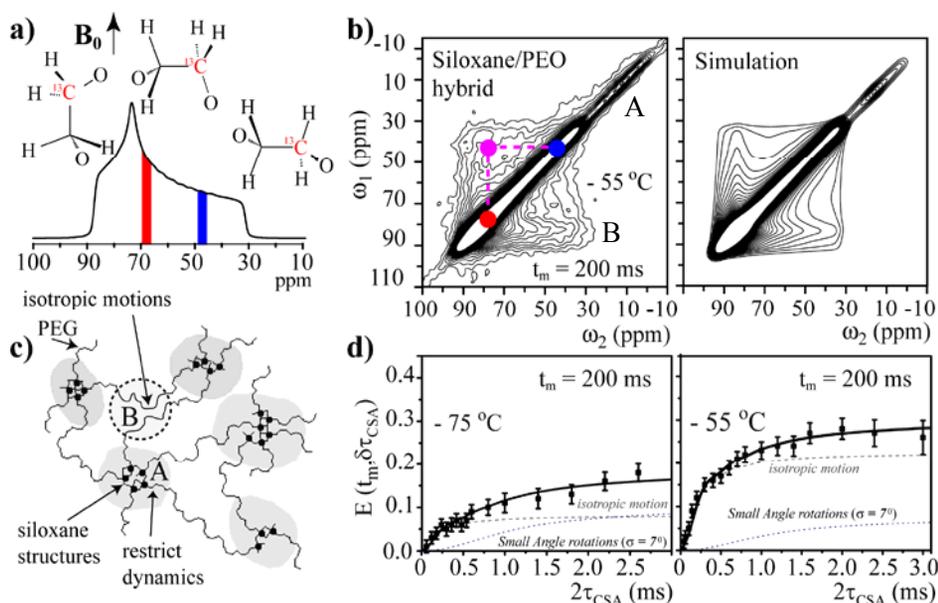


Figure 5. ^{13}C NMR of SiO_2 -PEO hybrid materials near the glass transition temperature. a) Powder pattern solid-state spectrum b) ^{13}C 2D-Exchange: off-diagonal signals correspond to carbon atoms experiencing changes of their orientation during the mixing time t_m . c) 1D-PUREX: bimodal curves evidence the simultaneous presence of small and high angle motions; d) multiphasic dynamical character of PEO. Reproduced from²⁶ by permission of The American Chemical Society.

increase with small angle motion. This shows that, besides the large angle motions observed in the 2D exchange, some of the PEO units also execute small angle motions at temperatures around the PEO glass transition temperature. Therefore, Exchange NMR clearly evidences the short reorientational behavior of the alkyl spacer and the larger motion amplitude of the PEO segments.

II.2 Measuring the mobility of the different species inside an electrolyte by determination of self-diffusion coefficient (pulsed field gradient NMR).

Ionic conductivity values are generally obtained from impedance spectroscopy. This technique provides good information for selecting the best ionic conductors (electrolytes) but does not give any significant information on the charge carriers that are involved. Generally, the Li^+ cation is more complexed by the PEO segments than the anion, reducing its mobility, which could be detrimental for applications such as lithium batteries or electrochromic devices that require the cationic transference to be favored.²⁸ Pulsed Field Gradient NMR (PFG-NMR)^{29,30} allows selective measurement of the self-diffusion coefficients for all species inside the electrolyte (if the nuclei are NMR sensitive), such as the solvent (^1H and ^{13}C), the cation (^7Li), or the anion, especially when they are fluorinated (^{19}F).^{31,32} Figure 6 presents the results obtained for lithium triflate salt (LiCF_3SO_3) dissolved inside two block oligomers recently synthesized in our laboratory. These two electrolytes present aromatic cores, aliphatic parts, and polar PEO moieties to dissolve ions. They present a

nematic phase on a large temperature range and good ionic conductivity when Li salts are dissolved. However, the PFG-NMR measurements could only be performed accurately in the higher temperature isotropic phase. For one of these electrolytes, two short PEO chains (3 monomers, $(\text{EO})_3$) are grafted at terminal positions, while a longer central PEO segment (9 units, $(\text{EO})_9$) is used in the second structure.

When Li salts are dissolved inside these electrolytes, ionic conductivity is always higher for the structure with the shorter PEO moieties. The ionic mobility mechanism has been further investigated.³³ As expected, the diffusion coefficients of all species are larger in the $(\text{EO})_3$ based electrolytes reflecting the lowest viscosity of these media. However, the most important consequence of these structural variations is sketched out by the relative translational mobilities of the different species. For materials with the longer chain, the solvent and the cation have the same diffusion coefficients and the anion translates quicker. In contrast, in the shorter chain $(\text{EO})_3$ based electrolytes, cations and anions have identical diffusion coefficients, which are larger than the solvent itself. This indicates that mobile species are different in these two materials, due to different aggregation/solvation of ionic species.

When PEO chains are long enough, the Li^+ cation can be wrapped by a unique PEO chain, and the anion stands away, as depicted in crystalline structure of PEO_3 ; LiCF_3SO_3 materials.³⁴ Otherwise, the shorter PEO chain offers only three ether oxygens, which is not enough to fulfill the coordination sphere of the cations (5 oxygen plus one anion), and then ion-pairing is probably

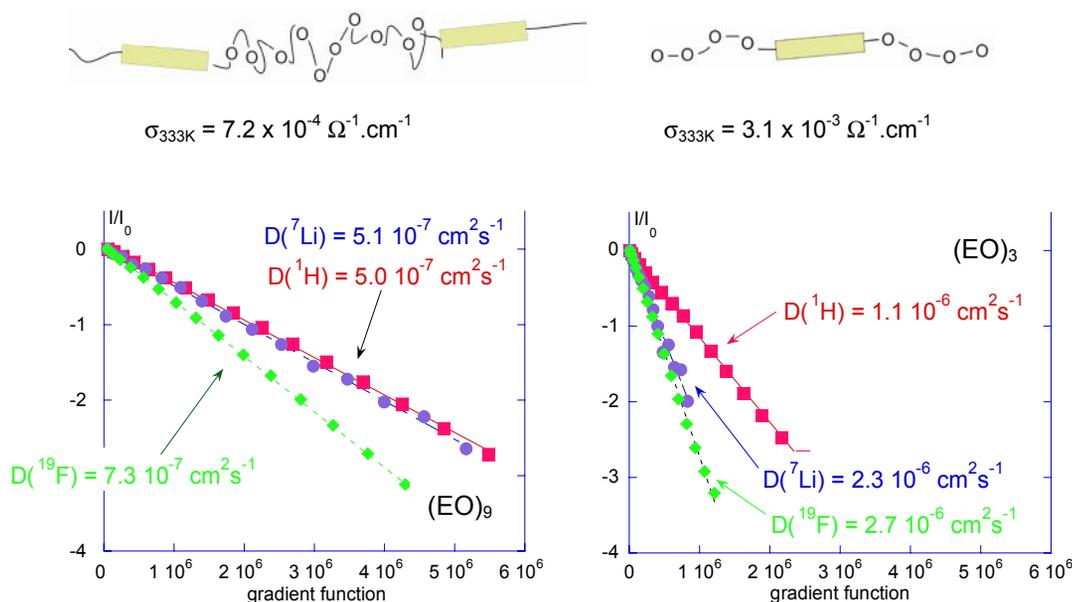


Figure 6. Diffusion coefficients D measured at 415K (isotropic phase) for the solvent (^1H), the cation (^7Li), and the anion (^{19}F) in two block-oligomer structures based on $(\text{EO})_9$ and $(\text{EO})_3$ (left and right) and doped with LiCF_3SO_3 ($[\text{O}]/[\text{Li}] = 30$).³³ Values of ionic conductivity ($\sigma_{333\text{K}}$ measured at 333K) are reported.

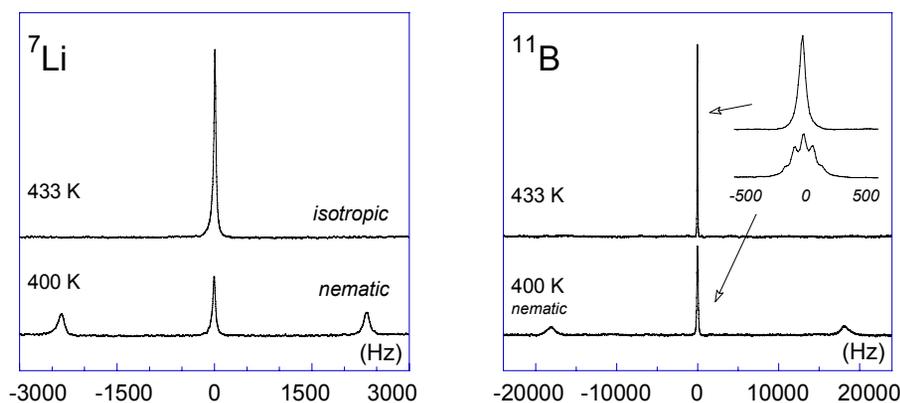


Figure 7. ^7Li and ^{11}B NMR spectra for LiBF_4 dissolved inside crown-ether based-mesogen (reproduced by permission of The Royal Society of Chemistry).³⁹ Quadrupolar splitting are observed for both nuclei, evidencing the “apparent ionic ordering”.

avored with the temporary formation of mobile aggregates such as “ $\text{Li}^+ \dots \text{O}_3\text{SCF}_3^-$ ”. Electrochemical measurements, impedance, Raman and infrared spectroscopies could give a complementary set of data to decipher the cationic transference and the ratio of the different species inside the electrolytes (isolated ions, ion pairs, aggregates). However, timescales of these various techniques are different and this could make a simple model more or less obsolete.

III. Measuring the supramolecular interactions

III.1 Quadrupolar interactions

NMR interactions are very sensitive to the local electronic environment of the nuclei and the geometry of molecules which can be depicted from chemical shifts and coupling interactions. Some of them have only the anisotropic component (such as dipolar and quadrupolar couplings) and then can be observed only when the motion is severely reduced (viscous or solid-state) and/or the molecules are oriented by external anisotropic force fields such as in liquid crystals or oriented polymers.³⁵ Extensive background discussions and applications have been presented elsewhere,³⁵ showing the sensitivity of quadrupolar interactions for probing the local anisotropy inside oriented media.

Some investigations were performed using polymers that can be permanently oriented such as PEBA copolymer (poly(amide)-PEO) doped with cesium salts³⁶ or stretched PEO doped with lithium salts.³⁷ We recently synthesized several series of liquid crystalline materials possessing PEO moieties of different lengths, positions, or shapes on the rigid aromatic core.³⁸ The NMR spectra of the quadrupolar nuclei ^7Li and ^{11}B ($I=3/2$) for LiBF_4 dissolved inside a liquid crystal, where the complexing PEO is a 15-crown-5 ether, were recorded as a function of the temperature,

see Figure 7. In the isotropic state, a single line is observed showing the isotropy of the medium. Narrow linewidths were measured for both ions ($< 20\text{Hz}$), which indicate their high mobility inside the fluid system.

In the nematic phase, triplets (3:4:3) are observed for both nuclei, indicating that both cations and anions experience the anisotropy of the media. In isotropic solvents, the average electric field gradient (*efg*) is zero and each non-equivalent nucleus contributes with a single spectral line in the fast reorientation regime. In contrast, when ions are dissolved inside anisotropic media, host-guest interactions may lead to the partial orientation of the dissolved entities and to a polarization of the electronic cloud, leading to a partially ordered *efg* around the cation and to an NMR spectrum with $2I$ equally spaced spectral lines. The existence of a quadrupolar splitting indicates that ions are effectively “distorted and oriented” inside the anisotropic media. The measured quadrupolar splitting $\Delta\nu_{\text{Q}}^{(\text{ion})}$, represents the so-called “apparent ionic order”.^{36,39}

Other lithium salts were dissolved inside the same thermotropic solvent at the same concentration and the evolution of the ^7Li quadrupolar splittings with the reduced temperature is presented on Figure 8. These different curves present the same shape and can be fitted by the classical Haller equation as a function of the reduced temperature as⁴⁰

$$\Delta\nu_{\text{Q}}^{(\text{ion})} = \Delta\nu_{\text{Q}}^* (1 - T/T^\ddagger)^F$$

where $\Delta\nu_{\text{Q}}^*$ is the limit of the observed quadrupolar splitting, T^\ddagger is a temperature slightly higher than the clarification temperature (T_{NI} , nematic \rightarrow isotropic) and the exponent F indicates the way the splitting reaches its limit. In the case of studying the orientational behavior of the different moieties of a thermotropic molecule, it was shown that for the different C-H groups within the molecule, Haller exponent F is higher for the more rigid segments (central core).⁴¹

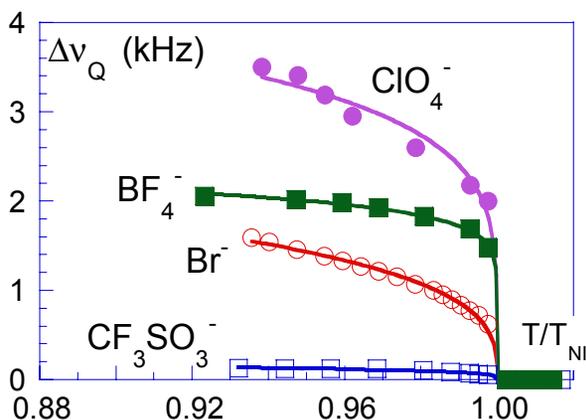


Figure 8. Evolution of ${}^7\text{Li}$ quadrupolar splittings for different salts dissolved inside the crown-ether moiety of a mesogen.³⁹

In the case of the different lithium salts dissolved inside the nematogen-crown structure, the parameters of the Haller's fits for the ${}^7\text{Li}$ quadrupolar splitting are presented in the following table. The parameters obtained do not show any clear correlation with the ion size, which suggest that the Δv_0^* parameter is related to the average distortion of the *efg*, and the variations should then express an indirect measurement for both the local geometry and/or the polarizability of the Li^+ ion.

anion	Br^-	BF_4^-	ClO_4^-	CF_3SO_3^-
size _{anion} (nm) (from ⁴²)	0.19	0.23	0.24	0.27
Δv_0^*	3270	4035	6200	270

The main factor affecting the limit of the quadrupolar coupling Δv_0^* is probably related to the

polarizability of the anion (soft/hard character,⁴³ electronegativity, ...) and its effect on the averaged deformation of the electronic orbitals of the cation. These variations can then be considered as a first step to visualizing the relative strength of the cation-anion ion pairing forces. Similar effects were measured in other nematic systems with different solvating units (linear PEO chains of different lengths)^{33,38} as well in some block copolymers (PEG distearate) presenting thermotropic phases when lithium salts are added.⁴⁴ Intramolecular dipole-dipole interactions could also provide similar information, and the behavior of the fluorinated anions such as triflate (CF_3SO_3^-) or trifluoromethanesulfonylimide, ($-\text{N}(\text{SO}_2\text{CF}_3)_2$, abbr. TFSi) have been characterized via ${}^{19}\text{F}$ NMR spectroscopy.³³

III.2 Supramolecular heteronuclear-intermolecular interaction

The direct measurement of through-space NMR interactions should appear as the ultimate evidence for spatial proximity of different species. Dipole-dipole interactions can be measured in principle between any NMR active nuclei with heteronuclear correlation experiments in the liquid or solid state.²⁵

The dipole-dipole interactions decay quickly with the internuclear distances (r^{-3}), and are difficult to evaluate for long range distances and even more difficult when exchange, conformation, or motion phenomena are present. However, the measurement of the Nuclear Overhauser method⁴⁵ (based on the dipole-dipole induced cross-relaxation) was proposed to successfully measure intermolecular interactions⁴⁶ and

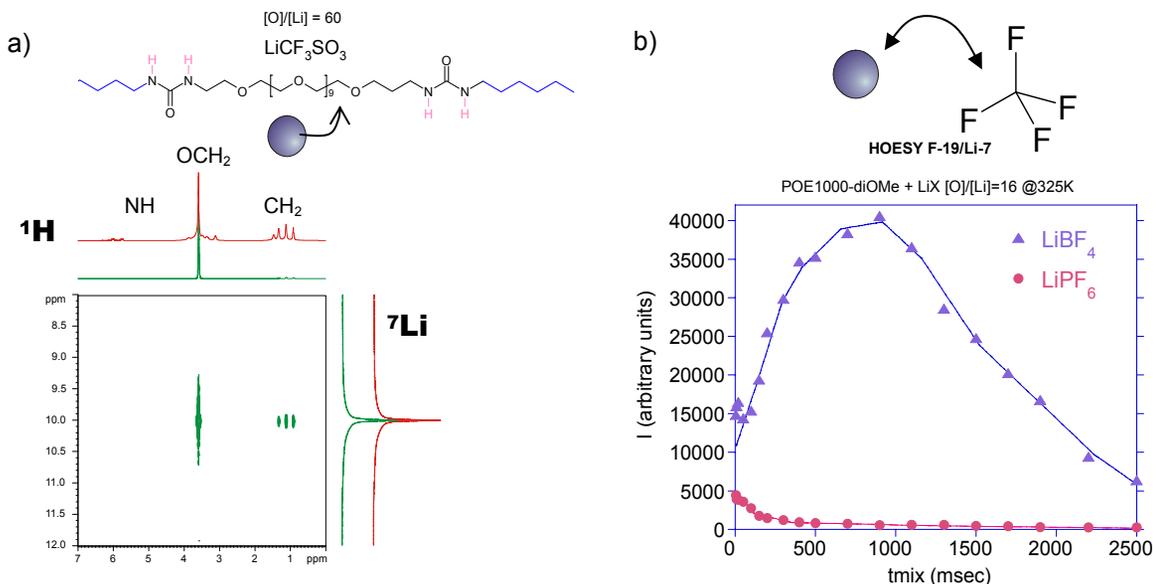


Figure 9. Heteronuclear Overhauser Spectroscopy. a) 2D ${}^1\text{H}$ - ${}^7\text{Li}$ correlation between the Li^+ cation and the copolymer evidencing the preferential solvation by ethylene oxide segments; b) Evolution of the ${}^{19}\text{F}$ - ${}^7\text{Li}$ NOE signal with the mixing time for two lithium salts. LiBF_4 forms strong ion pairs while LiPF_6 is dissociated.

the formation of ion-pairs.^{47,48} In agreement with recent studies, the pulsed field gradient enhanced inverse HOESY sequence was preferred because it is more sensitive for isotope pairs ^1H - ^7Li and also improves the digital resolution in the ^1H crowded spectrum.⁴⁹

Figure 9a presents the ^1H - ^7Li HOESY 2D spectra for lithium triflate salt dissolved inside a block oligomer $\text{C}_5\text{H}_{11}\text{NHCONH}(\text{CH}_2\text{CH}_2)_{11}\text{NHCONHC}_5\text{H}_{11}$ which can be considered as a liquid model compound of the PEO/ SiO_2 nanocomposites described in previous studies (see above and references 9, 21, 22). The major correlation peak corresponds to the proximity of Li^+ cations with the ethylene oxide segments of the heterogeneous solvent, which is obviously the most solvating moiety of these molecules. However, the small size of these segments allows some spatial proximity of the alkyl chains. Similar studies could also be used in heterogeneous and gelled SPE to observe the preferential solvating of the different constituents.⁵⁰ However, so far, only qualitative data are obtained because the theoretical background of such systems with correlated or non-correlated mobilities of the different component is under development. This HOESY methodology was also used to study the ion-pairing between Li^+ cation and fluorinated anions, tetrafluoroborate or hexafluoroborate (respectively, BF_4^- and PF_6^-) in melt PEO.

Figure 9b presents the build-up curves of the NOE effect for these two salts; they present different behaviors, the classic bell-shaped curves of the LiBF_4 salt corresponds to the formation of strong ion-pairs on the timescale of 100 – 500 ms, while the quasi null NOE effect measured for LiPF_6 ions should evidence the stronger dissociation of this salt inside the PEO. Such measurements are in agreement with the solid-state

crystalline structures,⁵¹ evidencing similar coordination shells of the cations in the solid and the melt polymers. Further investigation, such as the calibration of these curves, should also provide the ratio of ion pairs and their lifetime.

IV. Conclusion

SPE are new functional materials and their complexity is the key point of their properties. Therefore, the development of these amazing structures requires a synergetic approach in which new chemical structures are designed in parallel to the intimate knowledge of the conductivity mechanisms. All these studies converge to state that flexible and amorphous polymer structures are the best candidates as SPE. However, in the PEO based structures, cations are strongly complexed by the polymer, and enhanced cationic transference would need to balance apolar, solvating and complexing behaviors of the solvent, keeping in mind the nature of the dissolved salt. Until now, heterogeneous amorphous systems have to be considered as the best SPE candidates for tomorrow's batteries. Obviously, it also makes the description of the charge carriers transport a real challenge for which analytical tools with broad time and space scales have to be considered. NMR spectroscopy is certainly one of these techniques. Many methodologies are being developed for it to study the structural and dynamical properties of these materials, for both liquid and solid states, and with the privilege of observing selectively each of the components of the system (moieties of the solvent, cation, anion, ...). Furthermore, these techniques allow probing large spatial and temporal domains (Figure 10), even if the

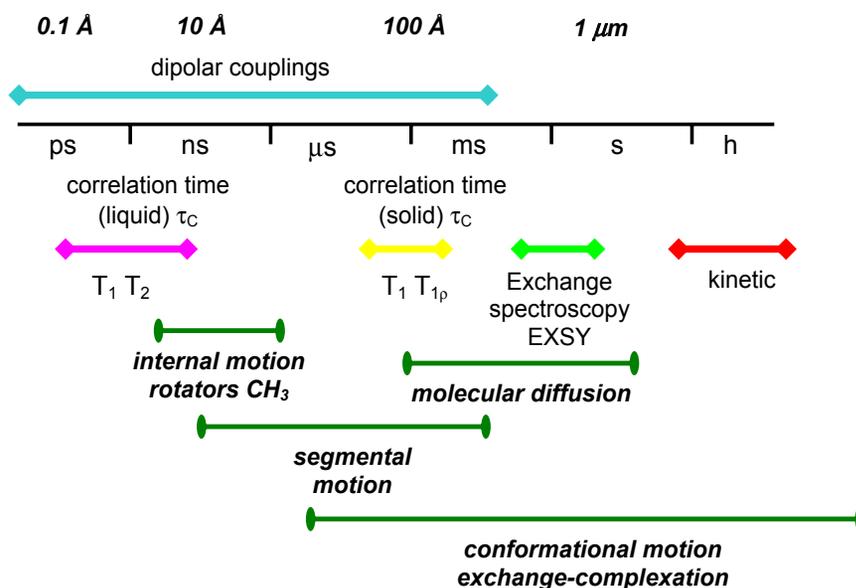


Figure 10. Space and time domains of different NMR methodologies.

information they provide has to be complemented by other techniques (thermo mechanical and rheological analyses, electrochemistry, ...) and spectroscopies (such as electrical complex impedance spectroscopy, electrochemistry, Raman and infrared, X-Ray ...).

The development of these methodologies is also essential for the characterization of other complex systems and materials, such as the solute/substrate interaction in chromatography,⁵² the hydrophobic/hydrophilic balance in porous systems,⁵³ food preservation,⁵⁴ elementary mechanisms in synthetic chemistry,⁵⁵ supramolecular chemistry,⁵⁶ rubber properties,⁵⁷ geophysical studies,⁵⁸ cement and concrete chemistry,⁵⁹ oil logging for petroleum prospecting.⁶⁰ Finally, these methodologies should answer many questions arising from the physical chemistry of Life to the raw chemistry of industry, and so many other domains where the knowledge of basic properties is essential for increasing macroscopic efficiency.

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Povzetek

Trdne polimerne elektrolite pridobivamo z raztapljanjem soli alkalijskih kovin v materialih na osnovi polioksietilena. Lastnosti teh snovi so tesno povezane z lastnostmi topila (polimer), kationa in aniona. V tem članku primerjamo več tehnik NMR, ki nam lahko razkrijejo različne lastnosti trdnih polimernih elektrolitov: strukturo in dinamiko polimera, kationov in anionov, kot tudi supramolekularne interakcije med njimi. Taki podatki so pomembni za razumevanje mehanizmov prevodnosti v različnih snoveh na osnovi polioksietilena (nanokompoziti, blok oligomeri in kopolimeri ter tekoči kristali), ki smo jih razvili.