

Supporting information

Revealing the Charge Transport Mechanism in Polymerized Ionic Liquids: Insight from High Pressure Conductivity Studies

Zaneta Wojnarowska^{1,2,3*}, Hongbo Feng⁴, Mariana Diaz⁵, Alfredo Ortiz⁵, Inmaculada Ortiz⁵, Justyna Knapik-Kowalczyk^{2,3}, Miguel Vilas⁶, Pedro Verdía⁶, Emilia Tojo⁶, Tomonori Saito¹, Eric W. Stacy⁹, Nam-Goo. Kang⁴, Jimmy W. Mays^{1,4}, Danuta Kruk⁷, Patryk Włodarczyk⁸, Alexei P. Sokolov^{4,9}, Vera Bocharova¹, Marian Paluch^{2,3}

¹Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

²Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland

³Silesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1A, 41-500 Chorzow, Poland

⁴Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA

⁵Chemical and Biomolecular Engineering Department. University of Cantabria. Avenida de los Castros s/n 39005 Santander, Spain

⁶Organic Chemistry Department, University of Vigo, Marcosende 36210 Vigo, Spain

⁷Faculty of Mathematics and Computer Science, University of Warmia and Mazury in Olsztyn, Słoneczna 54, Olsztyn PL-10710, Poland

⁸Institute of Non-Ferrous Metals, Sowinskiego 5, 44-100, Gliwice, Poland

⁹Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA

I NMR relaxometry studies

Theory

¹H relaxation is caused by magnetic dipole-dipole interactions that can be of intra-molecular (intra-ionic) or inter-molecular(inter-ionic) origin. In consequence, the overall spin-lattice relaxation rate, $R_1(\omega)$ (ω denotes the ¹H resonance frequency in angular frequency units), is given as a sum of intra-ionic and inter-ionic contributions ($R_{1,\text{intra}}(\omega)$ and $R_{1,\text{inter}}(\omega)$, respectively) [1,2]:

$$R_1(\omega) = R_{1,\text{intra}}(\omega) + R_{1,\text{inter}}(\omega) \quad (1)$$

The structure of the compound implies two ^1H relaxation channels provided by ^1H - ^1H and ^1H - ^{31}P dipole-dipole interactions. However, taking into account that gyromagnetic factor of ^{31}P is much smaller than of ^1H and the compound contains 19 ^1H nuclei and only one ^{31}P nucleus, the ^1H - ^{31}P contribution can be neglected [3]. As far as ^1H - ^1H inter-ionic interactions are concerned, one should consider cation-cation, cation –anion and anion-anion couplings modulated by the corresponding relative translational diffusion processes (cation-cation, cation –anion and anion-anion, respectively). However, anticipating the results, the ^1H spin-lattice relaxation data indicate that the diffusion coefficients for both kinds of ions are similar. Therefore one can describe the inter-ionic relaxation in terms of a single translational diffusion coefficients. According to spin relaxation theory the $R_{1,\text{inter}}(\omega)$ term can be expressed as [1-8]:

$$R_{1,\text{inter}}(\omega) = \frac{108}{5} \left(\frac{\mu_0}{4\pi} \gamma_H^2 \hbar \right)^2 \frac{N_H}{d^3} \int_0^\infty \frac{u^2}{81 + 9u^2 - 2u^4 + u^6} \left(\frac{u^2}{u^4 + (\omega\tau_{\text{trans}})^2} + 4 \frac{u^2}{u^4 + (2\omega\tau_{\text{trans}})^2} \right) du \quad (2)$$

where N_H is the number of protons per unit volume (not distinguishing between the cation and anion protons), d denotes the distance of closest approach of ions (again, we do not distinguish between cations and anions), γ_H is the proton gyromagnetic factor, μ_0 and \hbar denotes vacuum permeability and Planck constant, respectively, while the translational correlation time, τ_{trans} , is defined as: $\tau_{\text{trans}} = d^2 / 2D_{\text{trans}}$, where D_{trans} denotes a relative translation diffusion coefficient [7,8]. It has been shown that D_{trans} can be determined from a low frequency slope of the relaxation rate plotted versus square root of the frequency. At low frequencies, when $\omega\tau_{\text{trans}} < 1$, the relaxation rate $R_1(\omega)$ can be approximated by a linear function: $R_1(\omega) \cong R_1(0) - B\sqrt{\omega}$, where:

$$B = \pi N_H \left(\frac{\mu_0}{4\pi} \gamma_H^2 \hbar \right)^2 \left(\frac{1 + 4\sqrt{2}}{30} \right) D_{\text{trans}}^{-3/2} \quad (3)$$

The N_H value can be obtained knowing molecular mass (326 g/mol) and density (1.2 g/cm³) of the compound; one obtains: $N_H = 4.56 \times 10^{-2} \text{ \AA}^{-3}$. One should note that the slope is independent of the distance of closest approach, d .

The intra-ionic dipolar couplings are modulated by rotational dynamics of the corresponding ions. Taking into account that the number of ^1H nuclei in the anion is much smaller than in the cation and, moreover, rotational dynamics of the anion is very likely faster than of the cation

(the anion is smaller) one can neglect the intra-anionic relaxation contribution. This implies that [1-6]:

$$R_{l, intra}(\omega) = C_{DD}^C \left(\frac{\tau_{rot}^C}{1 + (\omega\tau_{rot}^C)^2} + \frac{4\tau_{rot}^C}{1 + 4(\omega\tau_{rot}^C)^2} \right) \quad (4)$$

where C_{DD}^C is a dipolar relaxation constant for the cation, while τ_{rot}^C denotes its rotational correlation time (rank 2).

Data analysis

The ^1H spin-lattice relaxation data were collected by a STELAR Fast Field Cycling (FFC) relaxometer in the frequency range of 10kHz – 25MHz, at 283K, 288K, 294K and 303K. The data are shown in Fig.1.

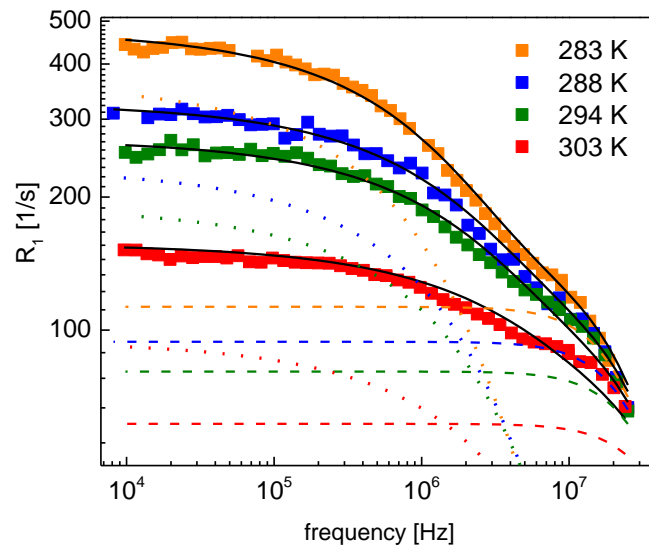


Fig.1. ^1H spin-lattice relaxation rates versus frequency. Solid lines – theoretical fits decomposed into intra-ionic (dotted lines) and intra-cationic (dashed lines) contributions.

The results have been analyzed (fitted) in terms of four parameters: D_{trans} , d , C_{DD}^C and τ_{rot}^C . The dipolar relaxation constant has been kept temperature independent – it has been obtained $C_{DD}^C = 8.17 \cdot 10^9 \text{ Hz}^2$. The other obtained parameters are collected in Table I.

Table I: Parameters obtained from the analysis of ^1H spin-lattice relaxation data for $\text{C}_{10}\text{H}_{19}\text{N}_2\text{O}_6\text{PS}$

T [K]	τ_{rot}^c [s]	d [Å]	D_{trans} [m^2/s] full analysis	D_{trans} [m^2/s] slope	rel.err [%]
283	$2.76 * 10^{-9}$	2.95	3.32×10^{-13}	$3.19 * 10^{-13}$	8.4
288	$2.30 * 10^{-9}$	2.89	5.03×10^{-13}	$4.97 * 10^{-13}$	7.8
294	$1.97 * 10^{-9}$	2.86	5.16×10^{-13}	$5.07 * 10^{-13}$	9.8
303	$1.49 * 10^{-9}$	2.82	1.33×10^{-12}	$1.15 * 10^{-12}$	9.5

Independently of this analysis, the diffusion coefficient has also been obtained from the low frequency slope (Fig.2) using Eq.4. The values are included into Table I; they are in very good agreement with those obtained from the full analysis.

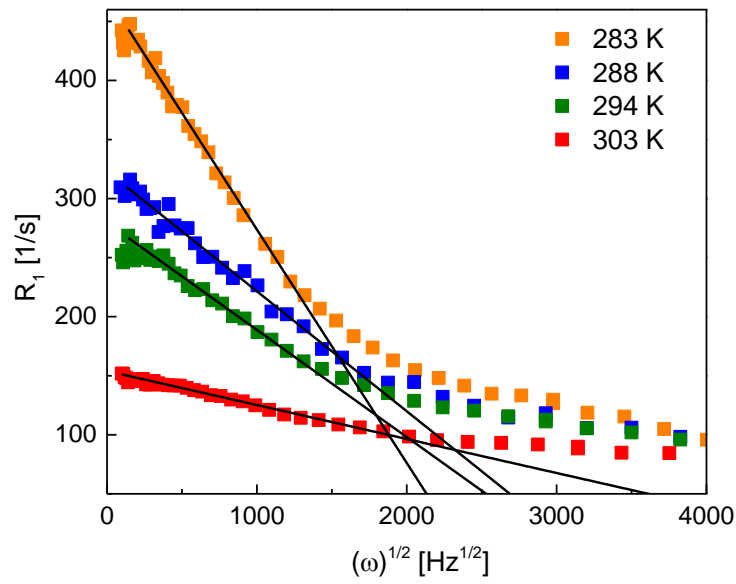
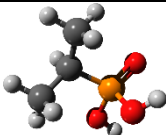
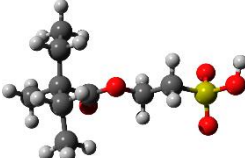
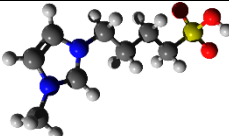
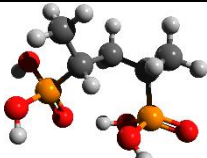
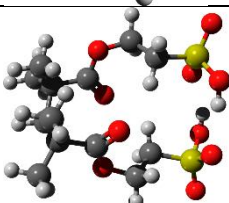
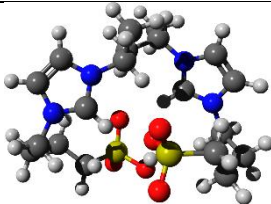
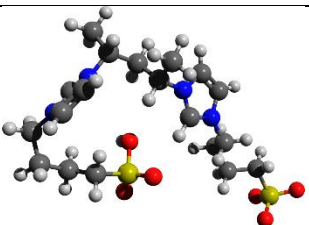


Fig.2. ^1H spin-lattice relaxation rates versus square root of frequency. Solid lines – linear fits in the low frequency range

DFT results

Table II. In table, pKa values have been gathered for all the studied compounds. For SBMIm dimers two conformations have been studied.

molecule	pKa	Conformation snapshot
HPO3	9.02 ; 25.18**	
SEM	-2.16	
SBMIm	-1.42	
Poly-HPO3*	13.94	
Poly-SEM*	-4.76	
Poly-SBMIm* (C1)	2.23	
Poly-SBMIm* (C2)	-4.56	

* In order to simulate proton dissociation in the polymeric compounds, pKa for dimer has been evaluated. Polar side groups have been positioned on the one side of chain which corresponds to the isotactic formation. In case of syndiotactic positioning, pKa should be close to the acidity of monomer.

** For HPO3 molecule first two pKa have been calculated (pKa₁;pKa₂)

Dielectric data of monomer SBMIm SEM

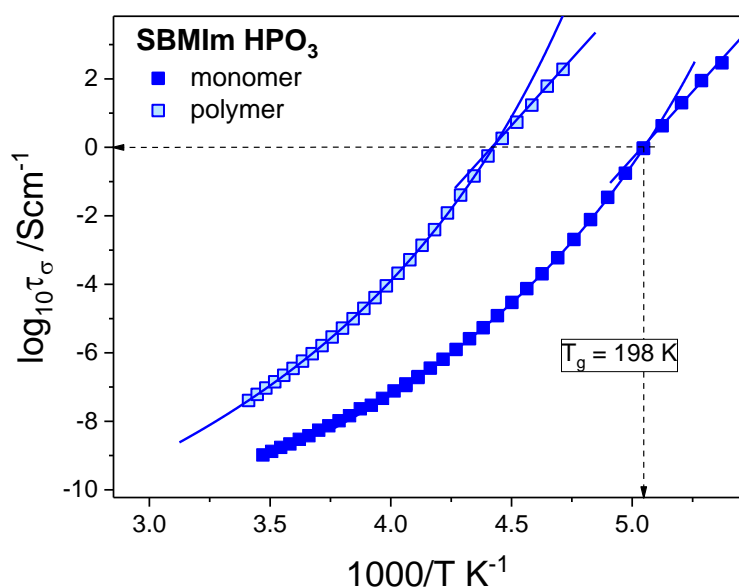


Fig. 3 The dielectric relaxation data of polymer SBMIm poly-HPO₃ and monomer SBMIm vinyl-HPO₃

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