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Decoupling of ionic conductivity from structural dynamics in polymerized ionic liquids

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Abstract

Charge transport and structural dynamics in low molecular weight and polymerized 1-vinyl-3-pentylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids (ILs) are investigated by a combination of broadband dielectric spectroscopy, dynamic mechanical spectroscopy and differential scanning calorimetry. While the dc conductivity and fluidity exhibit practically identical temperature dependence for the non-polymerized IL, a significant decoupling of ionic conduction from structural dynamics is observed for the polymerized IL. In addition, the dc conductivity of the polymerized IL exceeds that of its molecular counterpart by four orders of magnitude at their respective calorimetric glass transition temperatures. This is attributed to the unusually high mobility of the anions especially at lower temperatures when the structural dynamics is significantly slowed down. A simple physical explanation of the possible origin of the remarkable decoupling of ionic conductivity from structural dynamics is proposed.

Polymerized ionic liquids (polyILs)[1-13] - a novel class of materials developed within the past two decades - are interesting for many fundamental and technological applications. They combine attractive mechanical characteristics of polymers as well as unique physico-chemical properties of the low molecular-weight ionic liquids (ILs) in the same material. This special mix of features might help to circumvent the key limitations of low molecular weight ionic liquids, namely, leakage and poor mechanical properties while utilizing their outstanding characteristics such as low vapor pressures, wide liquidus ranges, high thermal stability, high ionic conductivity, and wide electrochemical windows. PolyILs have shown remarkable advantages when employed in electrochemical devices such as dye-sensitized solar cells, lithium batteries, actuators, field-effect transistors, light emitting electrochemical cells, and electrochromic devices, among others[2, 7]. Despite the promising prospects as ideal polymer electrolytes, the interplay between ion transport and structural (segmental) dynamics in PolyILs remains poorly understood. According to classical theories, the self-diffusion and ion transport in electrolytes are controlled by structural relaxation. These approaches predict similar temperature dependence for the dc conductivity and for the structural dynamics. Although this prediction has been shown to hold reasonably well for aprotic ionic liquids, it fails for many polymers. It is unclear, however, if it holds for polyILs.

In the current article, the interplay between charge transport and structural dynamics in low molecular weight and polymerized bis(trifluoromethylsulfonyl)imide-based ionic liquids is studied using broadband dielectric spectroscopy, dynamic mechanical spectroscopy and differential scanning calorimetry. Our analysis reveals strong decoupling of ionic conductivity from structural relaxation in the polymerized ionic liquid, while dc conductivity follows structural dynamics well in the low-molecular weight ionic liquid based on the same constituent ions. This is ascribed to the different contributions of the cations and the anions in determining the two processes. The cations dominate structural dynamics since they constitute the polymer chains while the anions are smaller and more mobile ionic species thereby controlling the ionic conductivity.

The ionic liquid monomer 1-vinyl-3-pentyl imidazolium bis(trifluoromethylsulfonyl)imide (PVImNTf$_2$) depicted in Figure 1 was synthesized in two steps. All starting materials used for this synthesis (1-vinylimidazole, 1-iodopentane, *t*-butyl methyl ether) were distilled before use. A small excess of 1-iodopentane with respect to 1-vinyl imidazole (1.1 mole : 1mole) and 1-vinyl imidazole dissolved in *t*-butyl methyl ether were stirred under nitrogen at room temperature until the entire starting material was converted to 1-vinyl-3-pentyl imidazolium iodide (PVImI). The chemical structure was confirmed by ^{1}H NMR spectroscopy. The solvent was evaporated in vacuo, and the PVImI was washed with equal volumes of ethyl acetate for at least three times. After drying in vacuo at 40°C, PVImI was obtained in 75 % yield. A small excess on $LiNTf_2$ relative to PVImI (molar ratio $LiNTf_2$: PVImI = 1.05) was dissolved in water and added to an aqueous solution of PVImI under stirring. The 1-vinyl-3-pentyl imidazolium bis(trifluoromethylsulfonyl)imide ($PVImNTf_2$) separated from the aqueous solution. The two phases were isolated, and ethyl acetate was added to the ionic liquid phase. The resulting organic phase was washed with water (seven times) until no halide was detected after addition of a $AgNO_3$ solution to a sample of the washing water. Then, ethyl acetate was evaporated in vacuo. The $PVImNTf_2$ was further dried in vacuo at 80°C for further 2 days resulting the ionic liquid monomer in 65 % yield.

The glass transition temperature of $PVImNTf_2$ is -76°C determined with a DSC 822e from Mettler-Toledo using heating and cooling rates of 10 K/min. The density of the $PVImNTf_2$ was 1.3313 g/cm^3 measured with a pycnometer at 23 °C. The water content was 830 ppm as determined by Karl Fischer titration. Mass spectrometry revealed an exact mass of 165.14 g/mole in the positive mode, that relates to 1-vinyl-3-pentyl-imidazolium. Mass spectrometry in the negative mode resulted in 280 g/mole corresponding to bis(trifluoromethylsulfonyl)imide. Viscosity of $PVImNTf_2$ was 98.4 mPa.s determined at 23 °C at a rate of 10 s^{-1} with a rheometer AR-G2 (TA Instruments), which was equipped with a Peltier plate and 40 mm cone for 0.3 ml sample volume. It should be noted that $PVImNTf_2$ samples were further dried in vacuum (10^{-5} – 10^{-6} mbar) at 80 °C for about 24 hours prior to dielectric and dynamic-mechanical measurements reported in the current article.

The $PVImNTf_2$ was polymerized in bulk under nitrogen using 1 mole-% azo*bis*isobutyronitrile relative to the monomer at 70°C for 24 h. The polymer (poly(PVIm)NTf_2 (Figure 1)) was dissolved in acetone and precipitated into propanol. After washing the isolated poly(PVIm)NTf_2 with propanol it was dried in vacuo. The glass transition temperature (T_g) of the poly(PVIm)NTf_2 is 55°C (10 K/min for heating and cooling scans during DSC measurements). Solution viscosity measurements on poly(PVIm)NTf_2 were carried out in methyl ethyl ketone containing 0.075 mole/L lithium bis(trifluoromethylsulfonyl)imide with an Ubbelohde capillary viscosimeter iVisc (LAUDA DR. R. WOBSER GMBH & Co. KG) at 25°C as described in literature resulting in a limiting viscosity number of 0.0609 L/g.

Furthermore, poly(PVIm)NTf_2 was also synthesized in an alternative route that starts with polymerization of vinylimidazole, because molecular weight of polyvinylimidazole can be determined for example by solution viscosity measurements using a procedure known from literature[14]. In the second step, polyvinylimidazole was quaternized quantitatively with pentyl iodide. Anion metathesis with lithium bis(trifluoromethylsulfonyl)imide resulted in poly(PVIm)NTf_2. Comparing the viscosity numbers of this sample of poly(PVIm)NTf_2 with the viscosity number of the polymerized ionic liquid gives an estimate about the molecular weight region of the polymerized ionic liquid.

In the first step, polymerization of vinylimidazole dissolved in acetonitrile (wt:wt=1:1, where wt denotes weight) was carried out using 1 mole-% azobisisobutyronitrile at 70°C for 7 h. The resulting polyvinylimidazole was dissolved in methanol and precipitated using acetone. A (1:12 (vol:vol, where vol denotes volume) methanol acetone ratio was used. The polymer was purified twice by re-precipitation using the same solvents (yield 94 %). The viscosity average molecular weight of the polyvinylimidazole was 9260 g/mole determined in methanol containing 0.01 mol/L tetraethylammonium bromide at 25°C according to a procedure described in literature ($K = 4.85\cdot10^{-4}$ and $a = 0.63$)[14]. Assuming that all imidazole structures of this polymer would react with pentyl iodide and all iodide anions would be exchanged by NTf_2 anions, the resulting poly(PVIm)NTf_2 would have a molecular weight of about 44000 g/mole. This is in reasonable agreement with the values reported for a similar polyIL by Nakamura *et al*[5]. The zero shear viscosity at T_g+35 °C for the current polyIL is 7×10^7 Pas which would correspond to a molecular weight of 40000 g/mole. It should however be noted that the two polyILs are not strictly identical, and the difference of one carbon in the side groups of the monomer might result is a slight variation in the quantities compared.

The polyvinylimidazole (1.9 g) was stirred with pentyl iodide (0.04 mole) in methanol at 70°C for 14 h in the second step. Poly(1-vinyl-3-pentylimidazolium) iodide (poly(PVIm)I) was isolated by filtration. After drying, the poly(PVIm)I was purified by dissolving in an acetone methanol mixture (2:1=vol:vol) and precipitation with *t*-butyl methyl ether. The obtained poly(PVIm)I was washed with *n*-hexane. This purification procedure was repeated, and poly(PVIm)I resulted in 55 % yield. Anion exchange was carried out by dropping a solution of lithium bis(trifluoromethylsulfonyl)imide in methanol water (10:4=vol:vol) to a solution of poly(PVIm)I in methanol and stirring this mixture for 24 h. The dried polymer was dissolved in acetone and precipitated with water. After drying in vacuo, the yield of poly(PVIm)NTf_2 was 74 % in anion metathesis. NMR analysis supports the complete reaction of the vinylimidazole segments, and the absence of any precipitate after addition of $AgNO_3$ solution to the washing water after purification of poly(PVIm)NTf_2 showed that no iodide was remaining in the reaction product. The limiting viscosity number of the resulting poly(PVIm)NTf_2 model polymer, which was obtained via quaternization of polyvinylimidazole followed by anion exchange of the ionic polymer, was 0.01185 L/g. Comparison of the limiting viscosity numbers obtained for the two poly(PVIm)NTf_2 samples shows significant differences. The limiting viscosity number is about 5 times higher for the polymerized ionic liquid compared to the value for poly(PVIm)NTf_2 made from polyvinylimidazole. This indicates that the molecular weight of the polyIL might be higher than 44000 g/mole. It should be noted at this point that the value obtained by solution viscosity reported in this article is just a rough estimate.

Broadband dielectric measurements were carried out using a Novocontrol high resolution alpha dielectric analyzer (0.1 Hz - 10 MHz) and the temperature was stabilized to better than 0.1 K by Quattro controllers using pure nitrogen as a heating agent. An Advanced Rheometric Expansion System (ARES) from TA Instruments was employed to perform dynamic mechanical analyses (rheology) enabling the determination of zero shear viscosity of the low molecular weight and polymerized ILs. The measurements were carried out using 8 mm parallel-plate geometry and the thickness of the sample was about 1 mm. Dynamic frequency sweep measurements were applied at constant deformation and the frequency range was 100 - 0.01 rad/s. The zero shear viscosity was determined by extrapolation of the dynamic viscosity to the low frequency limit. Calorimetric measurements were performed using a Q100 DSC from TA instruments with a cooling/heating rate of 10 K/min. DSC measurements estimated the glass transition to be T_g=197K for molecular IL and T_g=329K for PIL. This corresponds to usual increase in T_g between a monomer and a polymer.

Due to its ability to probe fluctuations of dipolar molecular moieties as well as charge transport in broad frequency and temperature ranges, broadband dielectric spectroscopy (BDS) has proved a versatile experimental technique for probing electrical properties of ionic liquids[15, 16, 17] . BDS measures the complex dielectric function, $\varepsilon^*\left(=\varepsilon'-i\varepsilon''\right)$, as well as the complex conductivity function, $\sigma^*\left(=\sigma'+i\sigma''\right)$. The real part of the complex conductivity function σ' in ionic liquids is characterized on the intermediate frequency regime by a plateau, the value of which directly yields the dc conductivity, σ_0, as well as a characteristic radial frequency, ω_c, at which dispersion sets in and turns into a power law at higher frequencies. At lower frequencies, σ' decreases from σ_0 due to electrode polarization[18, 19]. Figure 2 shows the dielectric spectra of both the low molecular weight and polymerized ionic liquids. On a qualitative level, the values of the dc conductivity are higher for the low molecular weight ionic liquid due to its significantly lower T_g. However, if the temperatures are scaled with respect to T_g, it should be possible to glean further information regarding the differences in the underlying mechanisms of ion transport in the two types of ionic liquids investigated.

According to classical theories, ionic conductivity is defined by ion diffusion D, concentration of free ions n and their charge q, $\sigma_0 \propto Dnq^2$, with the diffusion coefficient inversely proportional to zero shear viscosity $D \propto 1/\eta_0$. It is therefore expected that $\sigma_0 \propto 1/\eta_0$. For polymers, however, the zero shear viscosity is controlled by chain relaxation and not by structural (segmental) dynamics, although the temperature dependence of both is often expected to be similar. It has been found that for many polymers zero shear viscosity has slightly weaker temperature dependence than segmental relaxation[20-22]. Comparison of σ_0 and fluidity, $1/\eta_0$ reveals (Fig. 3) that both exhibit similar Vogel-Fulcher-Tammann (VFT) type temperature dependence for the low molecular weight ionic liquid, while they show clearly different thermal activation in the case of polyIL.

It has been demonstrated from numerous studies[15, 17, 18, 23-25] that charge transport in aprotic ionic liquids is characterized by two central quantities, namely, the dc conductivity, σ_0 and some characteristic diffusion rate ω_c. In these systems, structural relaxation is controlled by dynamics of the same ions that transport charge, which implies a strong coupling of ion motion to structural dynamics. It is therefore not surprising that the dc conductivity and the zero shear viscosity exhibit similar temperature dependence for the molecular IL.

The dc conductivity of the polymerized ionic liquid exhibits a VFT-type of thermal activation above T_g and transitions to Arrhenius-type of temperature dependence below T_g (Fig.3). Direct comparison of σ_0 and $1/\eta_0$ shows (Fig.4) that indeed dc conductivity variations follow those of the fluidity (inverse zero shear viscosity) in the case of molecular IL above the calorimetric glass transition temperature. Moreover, fluidities of molecular IL and polyIL exhibit identical trend when expressed with respect to T_g/T (Fig.4). However, the temperature variation of ionic conductivity in polyIL is significantly weaker than that of fluidity. It is interesting that ionic conductivity in PIL is consistently higher than that of the molecular IL when compared at the same values of T/T_g (Fig.4). The difference is ~10 times at higher T and reaches almost 10^4 times at T_g. Qualitatively similar trend was recently observed for ammonium as well as phosphonium-based polyILs[26]. This suggests that ion transport is more effective in the polyIL at the same T/T_g ratio. In addition, the dc conductivity is systematically higher for the polyIL at identical characteristic diffusion rates (inset of Fig. 4 (a)) by about an order of magnitude at the same characteristic diffusion rates. As previously mentioned above, classical theories of charge transport predict that the term $\sigma_0\eta_0$ should be constant with temperature down to T_g. This is indeed observed for molecular IL (Fig.4b). This term, however, increases drastically as the T_g is approached for the polyIL (Fig.4b). The dc conductivity remarkably decouples from chain dynamics, reflected in the zero shear viscosity of the polyIL. Given that the cations form the polymer chains, it is easy to understand the fact that they are much slower than the smaller anions. This would qualitatively explain the origin of the decoupling of ionic conductivity from structural dynamics. With decreasing temperature, segmental and chain dynamics of the polymer slow down, while the anions are still highly mobile thereby contributing to ionic conductivity.

To obtain a deeper insight into the nature of ionic transport in polymerized ionic liquids, it is instructive to compare the respective roles of the cations and anions in determining the overall measured dc conductivity. By definition, the measured conductivity is a sum of the contributions of the constituent charge carriers, i.e. $\sigma_0=\sigma_{cations}+\sigma_{anions}$[27]. Assuming that all the available ions participate in charge transport, one can estimate the highest possible contribution of the cations to the total dc conductivity if their diffusivity is known. For the current polymerized ionic liquid, the diffusivity was determined by pulsed field gradient (PFG) NMR measurements at 400 K. Since only ^{1}H was probed, the diffusivities relate to the mobility of the polymer chains relating to the motion of the cations. For a molecular weight of 44 kg/mole and mass density of 1500 kg/m^3, the stoichiometric number density of the cations is 2×10^{25} m^{-3}. The diffusion coefficient at 400 K as measured by PFG NMR is $1.5\pm0.3\times10^{-13}$ m^2/s. Thus, if all the available cations participate in ionic conduction, then the highest possible contribution to the dc conductivity at 400 K would be 1.4×10^{-7} S/cm, which is 540 times lower than the actual value measured by broadband dielectric spectroscopy at the same temperature. This implies that the cation mobility is too slow to provide significant contribution to the observed dc conductivity and it should be dominated by the anions contribution. Their mobility should be significantly higher than cations mobility. This result is consistent with rather high ionic conductivity at Tg in polyIL, where mobility of cations is essentially frozen on our experimental time scale.

The physical picture that emerges from studies of low molecular weight aprotic ionic liquids is that ion transport is strongly coupled to structural dynamics. In contrast, for the polyILs, we conjecture that the chain connectivity of the cations results in an increase of the available free volume due to repulsive interaction between the neighboring covalently bound cations. It can be expected that even below T_g, when polymer segmental dynamics is essentially frozen on the relevant experimental time-scales, the anions are still considerably mobile due to their small sizes and available free volume. Ion transport in this case might be analogous to that in inorganic glasses with traditional Arrhenius temperature dependence below T_g[28].

In conclusion, broadband dielectric spectroscopy, rheology and differential scanning calorimetry are employed to investigate the interplay of structural dynamics and ion conductivity in low molecular weight and polymerized bis(trifluoromethylsulfonyl)imide-based ionic liquids. The analysis indicate that while the two processes are coupled for the low molecular weight ionic liquids, a strong decoupling is observed for the polymerized ionic liquid implying a failure of the classical theories in describing charge transport and molecular dynamics in these systems. In addition, it is found that ionic transport at temperatures close to T_g is significantly more effective for polymerized IL. This demonstrates the different impact of polymer chain connectivity on the motion of the cations and anions constituting the polyIL.

References

1. Ohno, H.; Yoshizawa, M.; Ogihara, W. *Electrochim Acta* 2004, 50, (2-3), 255-261.

2. Matsumi, N.; Sugai, K.; Miyake, M.; Ohno, H. *Macromolecules* 2006, 39, (20), 6924-6927.

3. Tudryn, G. J.; Liu, W.; Wang, S.-W.; Colby, R. H. *Macromolecules* 2011, 44, (9), 3572-3582.

4. Nakamura, K.; Saiwaki, T.; Fukao, K. *Macromolecules* 2010, 43, (14), 6092-6098.

5. Nakamura, K.; Saiwaki, T.; Fukao, K.; Inoue, T. *Macromolecules* 2011, 44, (19), 7719-7726.

6. Ye, Y.; Choi, J.-H.; Winey, K. I.; Elabd, Y. A. *Macromolecules* 2012, 45, (17), 7027-7035.

7. Mecerreyes, D. *Progress in Polymer Science* 2011, 36, (12), 1629-1648.

8. Ueki, T.; Watanabe, M.; Lodge, T. P. *Macromolecules* 2009, 42, (4), 1315-1320.

9. la Cruz, D. S.-d.; Green, M. D.; Ye, Y.; Elabd, Y. A.; Long, T. E.; Winey, K. I. *Journal of Polymer Science Part B: Polymer Physics* 2012, 50, (5), 338-346.

10. Nakamura, K.; Fukao, K.; Inoue, T. *Macromolecules* 2012, 45, (9), 3850-3858.

11. Yuan, J.; Antonietti, M. *Polymer* 2011, 52, (7), 1469-1482.

12. Yuan, J.; Mecerreyes, D.; Antonietti, M. *Progress in Polymer Science* 2013, 38, (7), 1009-1036.

13. Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. *Nat Mater* 2009, 8, (8), 621-629.

14. Tan, J. S.; Sochor, A. R. *Macromolecules* 1981, 14, (6), 1700-1706.

15. Krause, C.; Sangoro, J. R.; Iacob, C.; Kremer, F. *J Phys Chem B* 2010, 114, (1), 382-6.

16. Sangoro, J.; Iacob, C.; Serghei, A.; Naumov, S.; Galvosas, P.; Karger, J.; Wespe, C.; Bordusa, F.; Stoppa, A.; Hunger, J.; Buchner, R.; Kremer, F. *J Chem Phys* 2008, 128, (21), 214509.

17. Sangoro, J. R.; Iacob, C.; Serghei, A.; Friedrich, C.; Kremer, F. *Phys Chem Chem Phys* 2009, 11, (6), 913-916.

18. Sangoro, J. R.; Serghei, A.; Naumov, S.; Galvosas, P.; Karger, J.; Wespe, C.; Bordusa, F.; Kremer, F. *Phys Rev E* 2008, 77, (5), 051202.

19. Serghei, A.; Tress, M.; Sangoro, J. R.; Kremer, F. *Phys. Rev. B* 2009, 80, (18), 184301-5.

20. Kremer, F., and Schoenhals, A., *Broadband Dielectric Spectroscopy*. Springer, Berlin: 2003.

21. Ding, Y.; Sokolov, A. P. *Macromolecules* 2006, 39, (9), 3322-3326.

22. Plazek, D. J. *Journal of Rheology* 1996, 40, (6), 987-1014.

23. Sangoro, J. R.; Mierzwa, M.; Iacob, C.; Paluch, M.; Kremer, F. *RSC Advances* 2012, 2, (12), 5047-5050.

24. Sangoro, J. R.; Kremer, F. *Accounts Chem Res* 2012, 45, (4), 525-532.

25. Sangoro, J. R.; Iacob, C.; Naumov, S.; Valiullin, R.; Rexhausen, H.; Hunger, J.; Buchner, R.; Strehmel, V.; Karger, J.; Kremer, F. *Soft Matter* 2011, 7, (5), 1678-1681.

26. Hemp, S. T.; Zhang, M.; Allen, M. H.; Cheng, S.; Moore, R. B.; Long, T. E. *Macromolecular Chemistry and Physics* 2013, 10.1002/macp.201300322.

27. Bruce, P., *Chemistry of solid state materials : Solid state electrochemistry*. Cambrigde University Press: 1995; p 360.

28. Dyre, J. C.; Maass, P.; Roling, B.; Sidebottom, D. L. *Reports on Progress in Physics* 2009, 72, (4), 046501.

29. Bockris, J. O. M., and Reddy, A. K. N., *Modern Electrochemistry 1: Ionics*. Second ed.; Plenum Press: New York, 1998; p 769.

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Figures and figure captions:

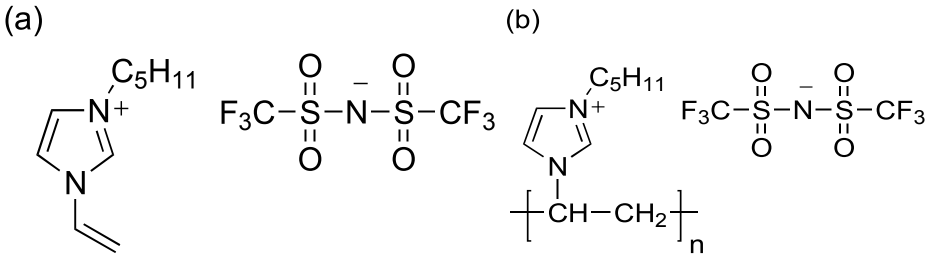

Fig. 1: Chemical structure of (a) low molecular weight PVIM NTf_2 and (b) polymerized PVIM NTf_2.

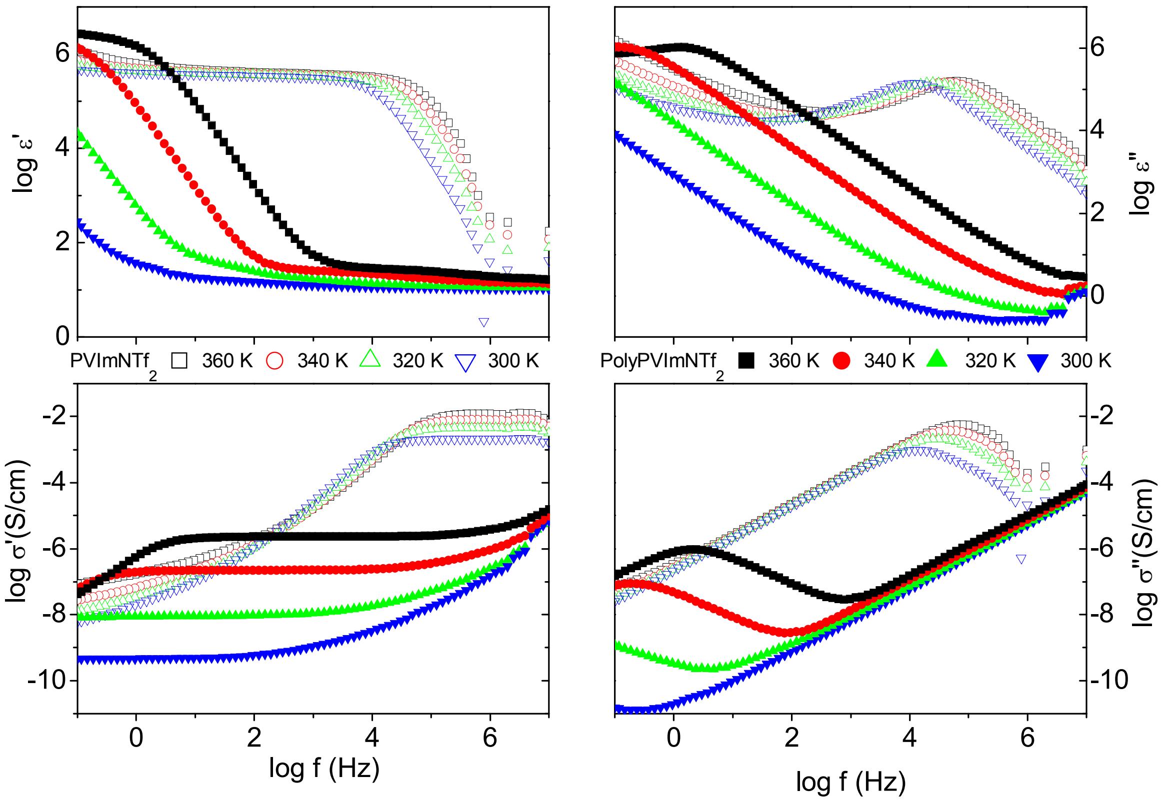

Fig.2. The complex dielectric function ε *(ε ′ − *i*ε ″) and the complex conductivity function σ *(σ ′ + *i*σ ″) *versus* frequency at different temperatures as indicated for the polymerized ionic liquid (poly (PVIM) NTf2) (closed symbols) and the corresponding low molecular weight ionic liquid (open symbols) at selected temperatures. The error bars are comparable to the size of the symbols, if not specified otherwise. The logarithm is to base 10.

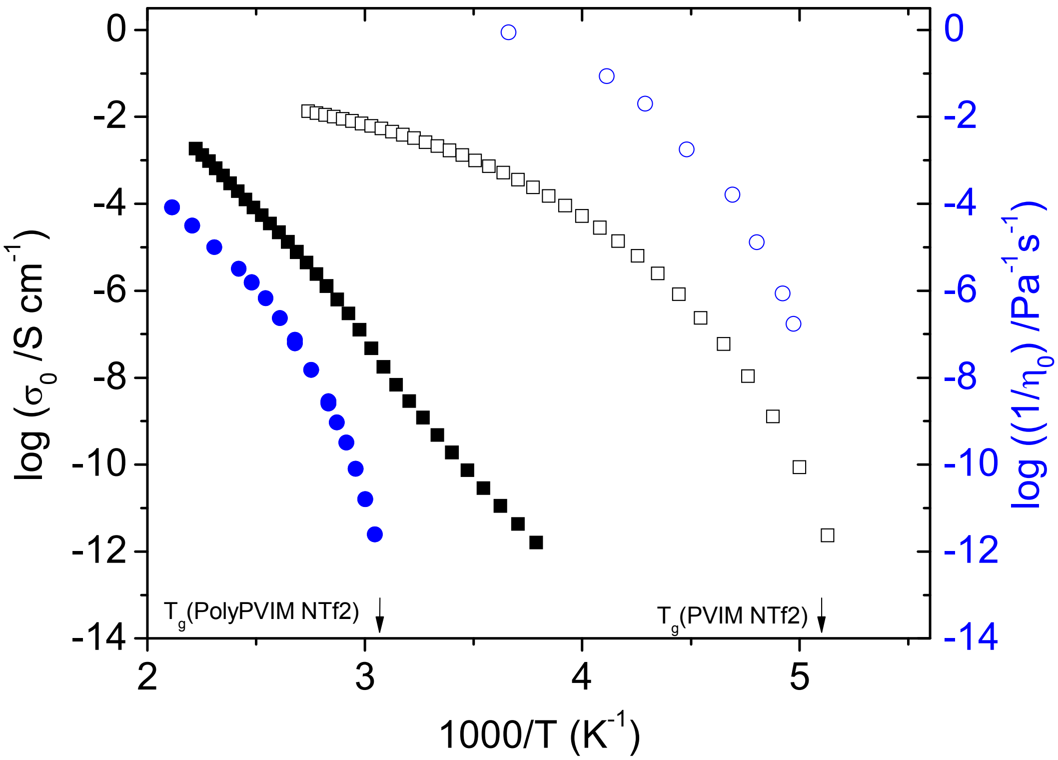

Fig.3: Thermal activation plots of the dc conductivity, σ_0 (black symbols), as well as the inverse zero shear viscosity, $1/\eta_0$ (blue symbols), for the polymerized ionic liquid (poly (PVIM) NTf_2 – full symbols) and the low molecular weight ionic liquid PVIM NTf_2 (open symbols). T_g denotes the calorimetric glass transition, experimentally found to be 197 K and 329 K for the low molecular weight and polymerized PVIM NTf_2 respectively.

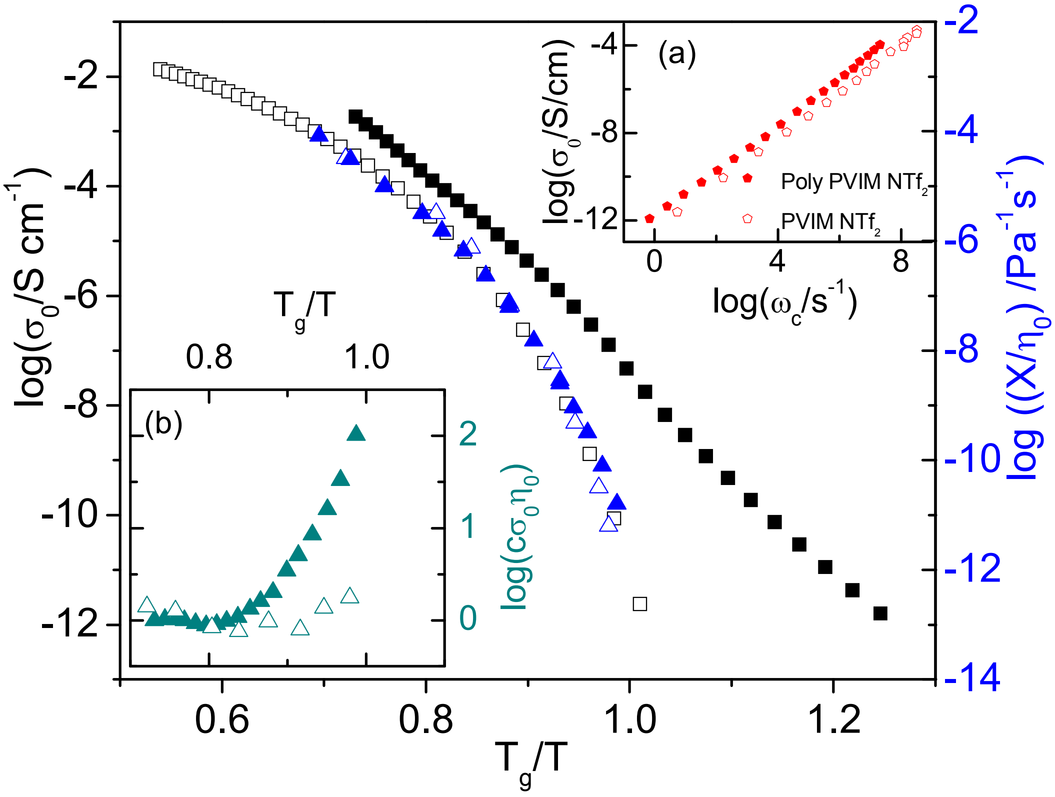

Fig. 4: The dc conductivity, σ_0 (black symbols), as well as the inverse shear viscosity $1/\eta_0$ (blue symbols) *versus* T_g/T for the polymerized ionic liquid (poly (PVIM) NTf_2 – full symbols) and the low molecular weight ionic liquid PVIM NTf_2 (open symbols). The constant X with values 1 and $10^{4.43}$ is employed for the low molecular weight and polymerized ionic liquid, respectively, for direct comparison of the temperature dependence of $1/\eta_0$. The disparity in the values of X presumably stems from the differences in the molecular weights of the two materials. Inset: (a) BNN plot; dc conductivity, σ_0, *versus* the characteristic frequency, ω_c, for the materials under study as indicated, and, (b) product of the dc conductivity and the zero shear viscosity normalized with respect to the high temperature values for the materials investigated versus T_g/T. *c* is a normalization factor.

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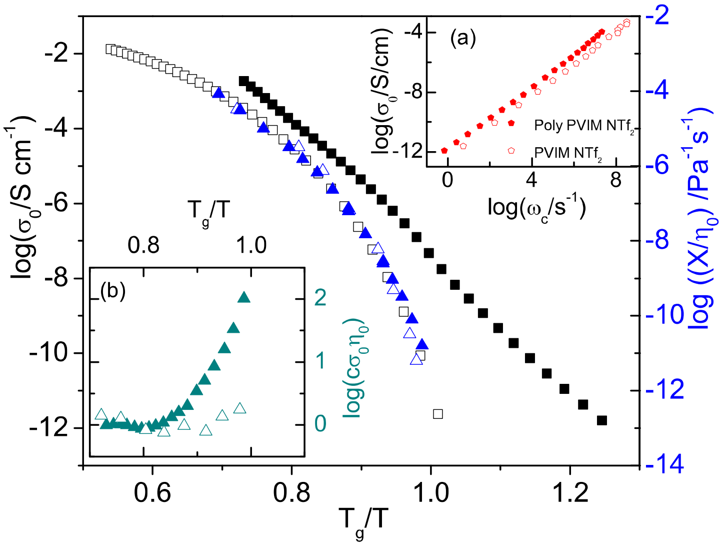

Charge transport is more efficient in polymerized than molecular ionic liquids