New trends in development of highly conductive poly(ionic liquid)s

D.R. Nosov^a

L.F. Lepre^b, A.S. Shaplov^a and E. Drockenmuller^b

 Luxembourg Institute of Science and Technology (LIST), 5 avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg
Univ Lyon, Université Lyon 1, CNRS, Ingénierie des Matériaux Polymères, UMR 5223, F-69003, Lyon, France daniil.nosov@list.lu

The achievement of high ionic conductivity in poly(ionic liquid)s (PILs) is of great interest as all-solid-state electrolytes are becoming increasingly popular due to their processability, viscoelasticity and extreme safety. Although attempts to enhance the ionic conductivity of PILs applying various approaches have been made previously, the influence of the repeat unit charge density (Fig.1, I) and the nature of the cation's substitutes (Fig.1, II) on the bulk conductivity of PILs has been scarcely addressed [1].

To date the maximum number of ion pairs per monomer unit reported to date is three and the structure/conductivity relationships remain sometimes contradictory [2]. To fill this gap eight poly(ionic liquids)s were synthesised and structure/property correlations were established. The different repeat units contain one to four ion pairs, with one to four bis(trifluorosulfonyl)imide (TFSI) anions and one or two types of ammonium, imidazolium or 1,2,3-triazolium counter-cation. Generally, the higher the repeat unit charge density of PILs the higher their T_a and the lower their ionic conductivity and thermal stability. The observed dependences passed through a maximum when PILs had two cations per monomer unit that were separated by alkyl or oxyethylene chains. The highest conductivity $(1.8 \times 10^{-5} \text{ S cm}^{-1} \text{ at } 25^{\circ} \text{C})$ was reached when PILs contain two 1,2,3-triazolium cations that are separated by an oxyethylene spacer.

The presence of the oxyethylene fragments in the backbone or in the side chains of PILs significantly improves the solubility of ionic species, facilitates their

dissociation, and promotes an increase in the conductivity of PILs [1]. Thus, in the second approach (Fig. 1, II) the PEO based chosen polymers were to undergo quaternization reaction and to form novel class of cationic PILs [3]. Eight different substitutes were selected to form the side chain in PILs: from alkyl and silyl, to siloxane and perfluorinated groups. As a result, almost all PILs with alkyl side chains showed values and higher ionic lower Ta conductivities in comparison with PILs bearing silyl-containing and fluorinated chains. The highest conductivity (7.3×10-6 S cm⁻¹ at 25°C) was reached in PIL with ethyl side chain.

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References

- Shaplov, A. S.; Marcilla, R.; Mecerreyes, D. Electrochim. Acta 175 (2015) 18–34.
- [2] Cotessat, M.; Nosov, D.; Schmidt, D. F.; Drockenmuller, E.; Shaplov, A. S. New J. Chem. 45 (1) (2021)53–65.
- [3] Jia, Z.; Yuan, W.; Zhao, H.; Hu, H.; Baker, G. L. J. Polym. Sci. Part A: Polym. Chem. 53 (11) (2015) 1339– 1350.



