STRUCTURE OF IONOGELS BASED ON POLYMER AEROGELS OBTANIED FROM POLYAMIDE 6,6

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Ionogels are soft-matter two-phase composites, synergising the properties of ionic liquids and solid porous matrices. In their composition, ionic liquids (IL) are the organic salts with a melting point below 100°C, which possess a set of unique properties including ionic conductivity, non-volatility, dissolving ability, as well as excellent chemical, thermal and electrochemical resistance. A solid component of ionogels endows them with a stable shape and valuable mechanical performance – mechanical strength or elasticity and flexibility. The interest to ionogel materials is related to their emerging properties, which are not inherent in both bare IL and a solid phase alone, such as self-healing or stimuli-responsive behaviour.

The most impressive ionogels' functionality were observed for the polymer-based ionogels. These include the design of switchable adhesives, ionic skins, thermoelectric devices, cuttable electric batteries, photo-, mechano- and thermochromic materials, etc.

These findings induced the structural research by small-angle scattering methods on ionic liquid-polymer systems including poly-ionic liquids, molecular or colloidal polymer-in-IL solutions, liquid crystals, IL-impregnated membranes. At the same time, the SAXS/SANS studies of polymer-based ionogels are mostly focused on the characterisation of the structure of a solid (polymer) component of ionogels, while the assessment of the confinement-dependent structure of ionic liquids is virtually ignored.

In the authors' previous work [1], a very strong distortion of the structure of the confined C8MIm BF_4 ionic liquid was shown in highly porous silica. Most probably, this effect was due to the specific sorption of BF_4 anions onto the silica surface thus resulting in chemically-driven confinement effect. It was hypothesised that such an effect could be far less pronounced for the ionogels obtained on base of polyamide 6,6 aerogels which is relatively inert towards ionic fluorine-containing species. In this view, the current work was aimed at the comparison of the structural parameters in the bare 1-methyl-3-octyl-imidazolium-tetrafluoroborate (C_8MIm BF_4) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C_4MIm TFSI) confined in porous polyamide 6.6, obtained by dissolution polymer in dimethylacetamide in the presence of lithium chloride and subsequent critical drying in CO_2 [2].

For the preparation of ionogels, the polyamide 6,6 aerogels were carefully cut into ~100 mg tablet-shaped fragments and placed into the excess volume (~5 ml) of ionic liquids C_8MIm BF_4 and C_4MIm TFSI, respectively. Next, the samples were left overnight at 50°C to ensure the IL uptake by the porous solids. After the impregnation, ionogels were removed from the IL and the liquid was dabbed away with paper towel. The structure of obtained ionogels was studied using helium pycnometry, low-temperature nitrogen adsorption, WAXS and SAXS.

The analysis of experimental data showed that ionogels based on polyamide 6,6 aerogels and ionic liquids C8MIm BF4 and C4MIm TFSI are two-phase systems in which the structure

of the solid phase remains unchanged upon impregnation with ILs, which sequentially fill the micro- and mesopores of porous polyamide 6,6. Unlike silica-based ionogels [1], the structure of ionic liquids enclosed in porous polyamide 6,6 remains practically unchanged, meaning no confinement effect is observed.

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