Multiscale structure of polymerized ionic liquids by small angle neutron scattering.

Poly(ionic liquid) (PILs) refer to a special type of polyelectrolytes in which each monomer unit is composed of an ionic liquid (IL). They have recently drawn significant attention since they present a unique combination of the properties of ILs (e.g., high thermal, chemical, electrochemical stabilities, interfacial adsorption and enhanced ionic conductivity,...) with those of polymer materials (e.g. processability, viscosity, adhesion, and broad macromolecular design). So a local phase separation which confers the bulk with either a globular or a sponge-like structure [1]. Similarly, PILs present structural features which are highly dependent on the length of the alkyl side chains. We address this question using neutron scattering, thus probing several length scales of the molecular structure.

Context
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Chemistry
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Small Angle Neutron Scattering experiments
SANS experiments were performed on thick PC_VImTFSI films at Laboratoire Léon Brillouin (CEA Saclay) on the FRAP spectrometer.

Experiments on melt PC_VImX are done on mixture of hydrogenated and deuterated chains at a mass fraction of hydrogenated chains of 50% to enhance the contrast.

For experiments in solution, dilute solutions of hydrogenated PC_VImTFSI in deuterated THF are used.

For very dilute solutions of polymer, at a volume fraction g:

\[ \langle q \rangle = \rho \chi (1 - g^2) \chi \frac{\langle R^2 \rangle}{3} \]

For a polymer melts, with a fraction g of hydrogenated chains:

\[ \langle q \rangle = \chi (1 - g^2) \chi \frac{\langle R^2 \rangle}{3} \]

Instead of THF solutions in the corresponding ionic liquid C6H12 mesitylmethanol are also investigated.

Model
• Guinier regime at very low q, where the form factor can be approximated by:

\[ F_{\text{Guinier}} = \exp \left( -q^2 \langle R^2 \rangle / 3 \right) \]

• Intermediate regime (0.05 to 0.1 Å−1):

\[ q^2 \langle R^2 \rangle \chi (1 - g^2) \chi \frac{\langle R^2 \rangle}{3} \]

• Change of slope around 0.2 Å−1, probing the local characteristic length: the cross section r (a)

\[ \langle q \rangle = 1 + P_{\text{back}} \left( \frac{2}{\langle R^2 \rangle} \right) + P_{\text{miscell}} \left( \frac{2}{\langle R^2 \rangle} \right) \]

Flexible cylinder models

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Flexible cylinder models

A competition revealed at two scales
Radii of gyration in solution, both in THF and in the corresponding IL, increase with increasing side chains length due to steric effects due to steric effects of the side chains. In melt, both show a first decrease, revealing a dominance of electrostatic repulsion, progressively screened by increasing the side chains length.

Comparison of the correlation length \( d_{\text{correl}} \) twice the cross section \( r_{\text{back}} \) of the chain shows a crossover point, revealing interdigitation of the side chains.

Conclusion / Perspectives
• Radii of gyration of PC_VImTFSI in solution show a monotonous increasing behavior with increasing side chain length.
• In melt, electrostatic and steric contribution are in competition. An increase of the alkyl domain by increasing the side chain length screens the electrostatic interactions and favours steric repulsion of the backbones.
• Interdigitation of the side chains occurs as soon as steric interactions prevail over electrostatic repulsion (\( q > 4 \)).

• Perspectives:

  • Explore their structure at interfaces (specular and off specular X-ray reflectivity).
  • Investigate the rheological properties of these materials with insight of their structure.
  • Measure their slip length using a FRAP experiment (fluorescence recovery after photobleaching).

Figure 2: Expected lamellar structure of PIL at interfaces, resembling that of Lc.