

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

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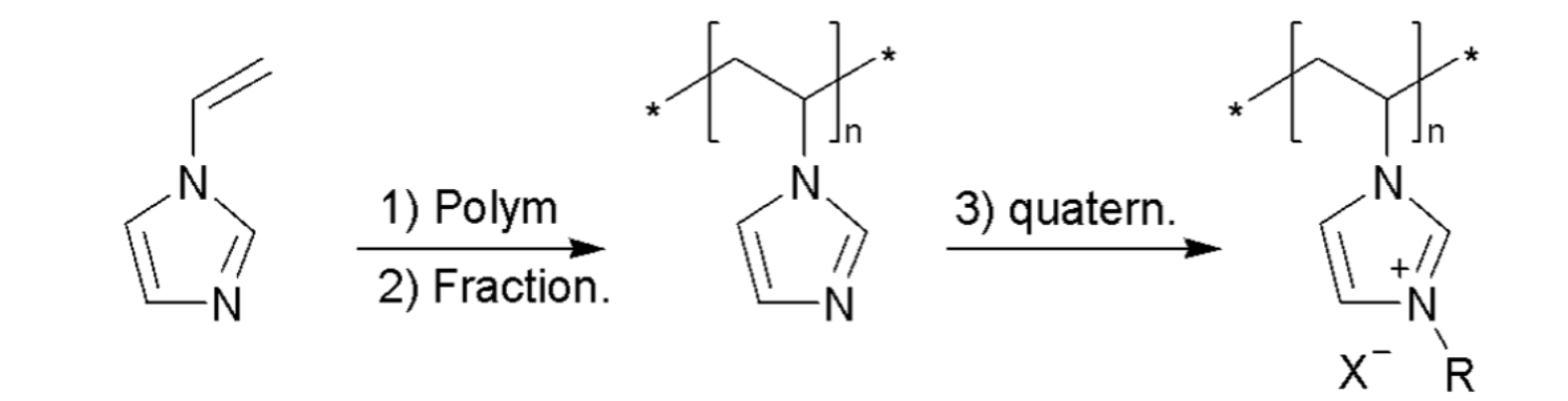
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## Context

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, viscoelasticity, adhesion, and broad macromolecular design...). ILs show 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 dependant on the length of the alkyl side chains. We address this question using neutron scattering, thus probing several lengthscales of the molecular structure.

## Chemistry



Synthesis by Eric Drockenmuller – Laboratoire Ingénierie des Matériaux Polymère, Université de Lyon

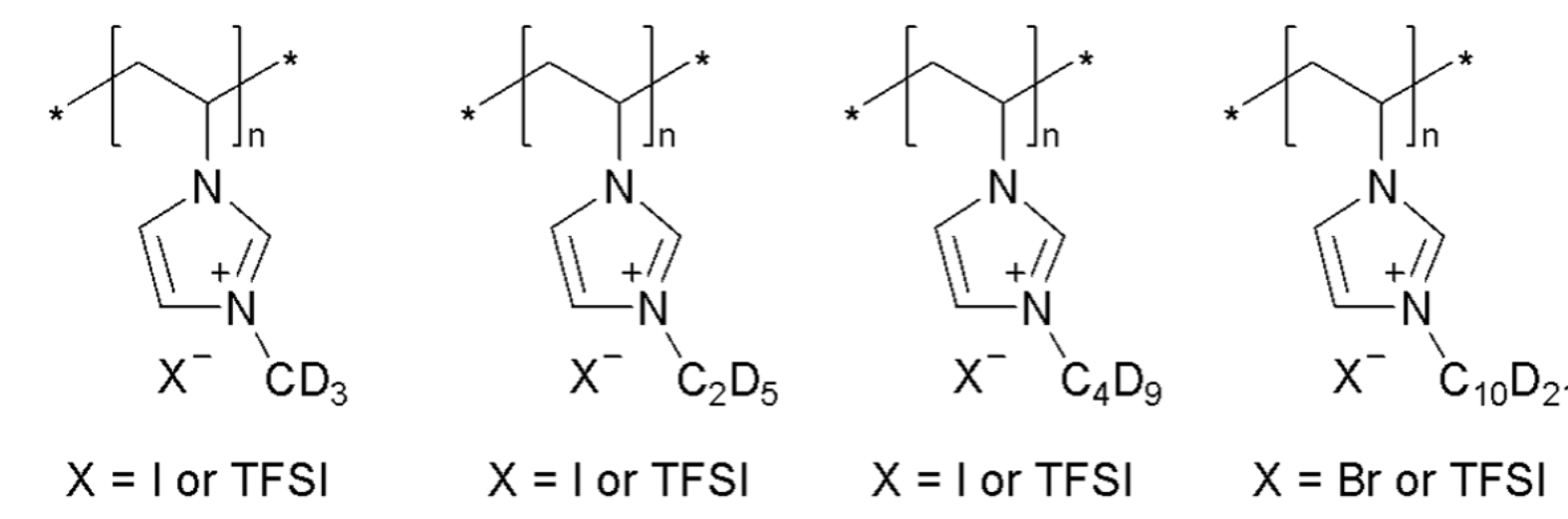
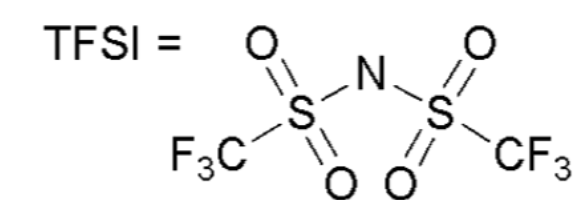
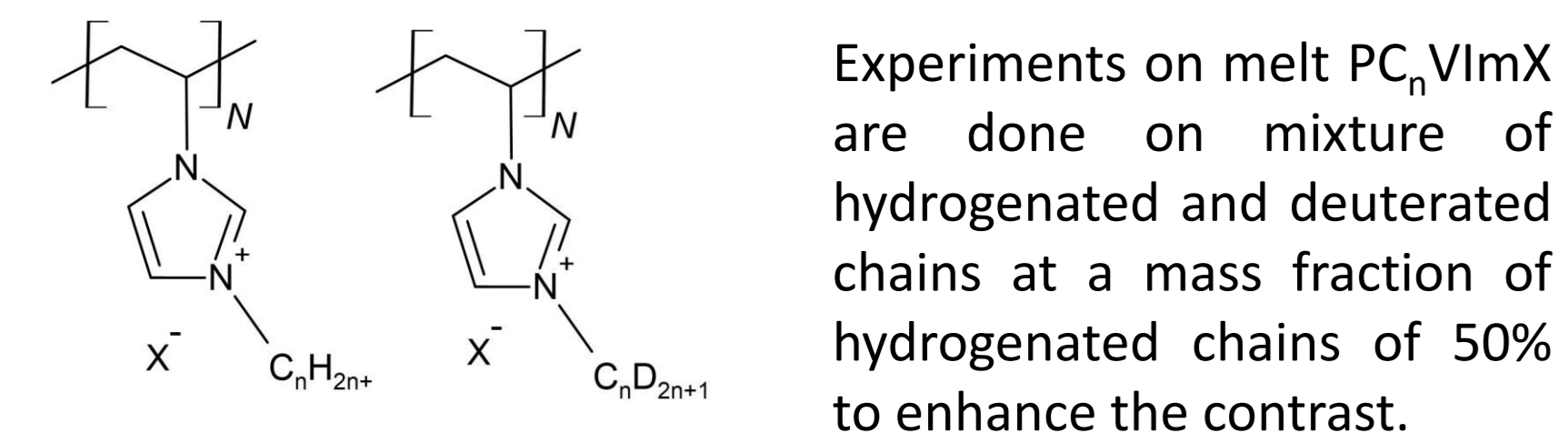


Figure 1: Thick films of PC<sub>n</sub>VImX made by slow evaporation of a concentrated solution, either in THF or DMF respectively for TFSI and halogen counterions



## Small Angle Neutron Scattering experiments

SANS experiments were performed on thick PC<sub>n</sub>VImX films at Laboratoire Léon Brillouin (CEA Saclay) on the PAXY small angle neutron spectrometer.

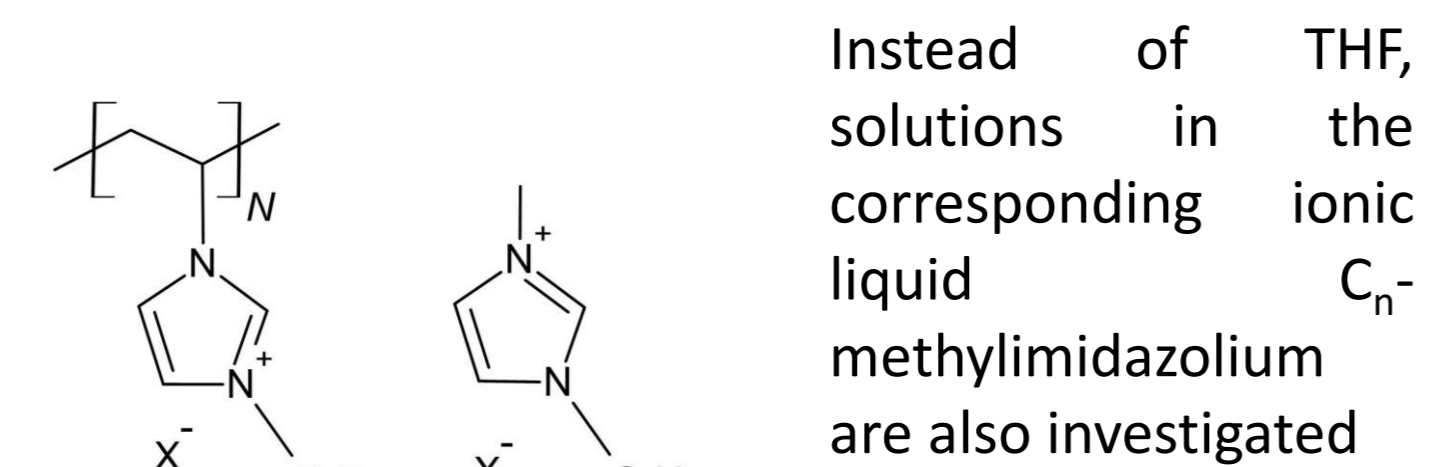
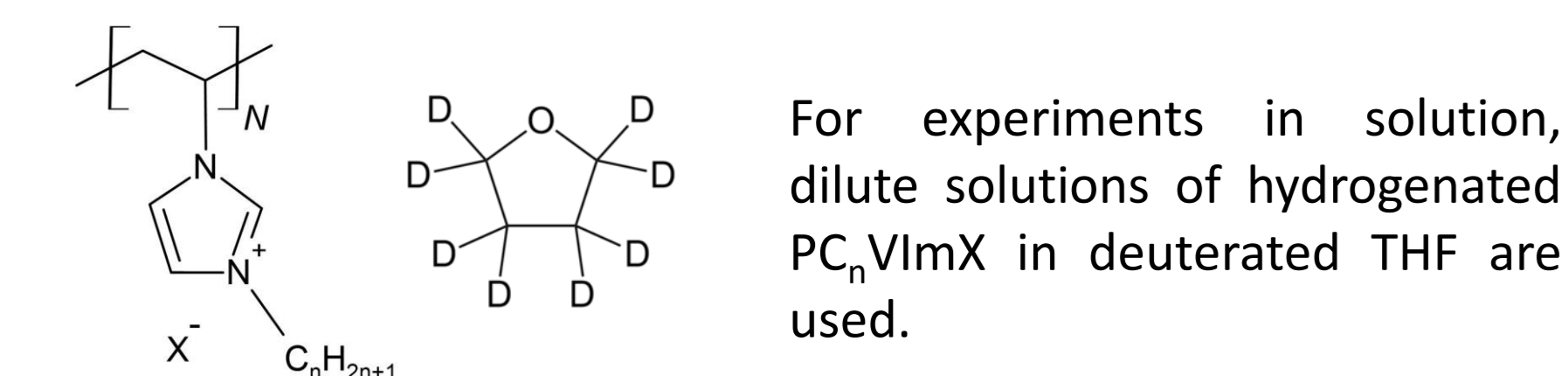


For very dilute solutions of polymer, at a volume fraction  $\phi$ :

$$I(q) = \phi N v (\Delta\rho)^2 P(q)$$

For a polymer melts, with a fraction  $x$  of hydrogenated chains:

$$I(q) = x(1-x) N v (\Delta\rho)^2 P(q)$$



## SANS data

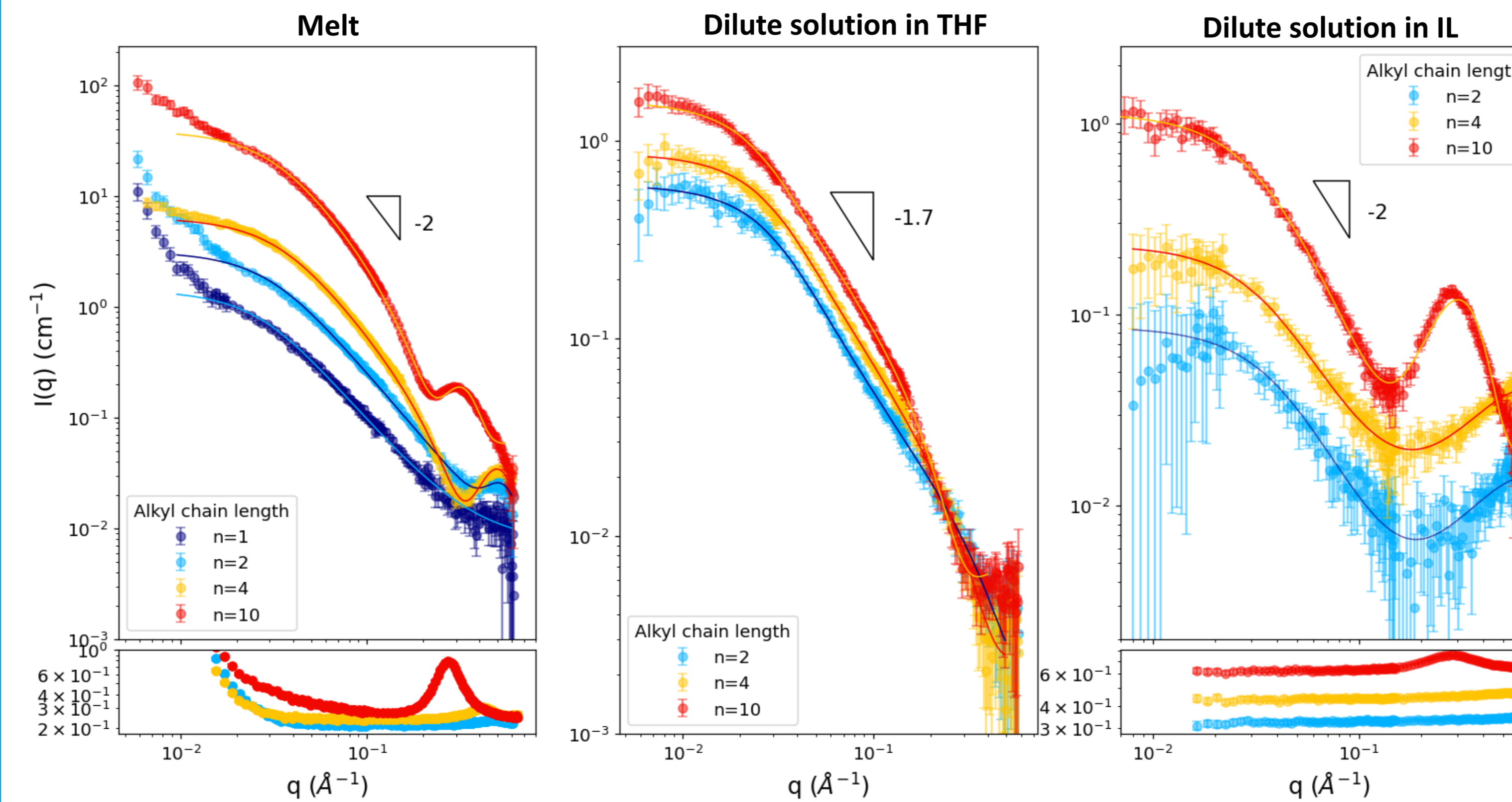


Figure 2: SANS results for PC<sub>n</sub>VImTFSI from left to right in melt, dilute solution in deuterated THF, in dilute solution in corresponding ionic liquid. Insets on the left are SANS data for fully deuterated chains and on the right for deuterated ionic liquid alone.

Observation of the slope in the intermediate regime (0.05 to 0.1 Å<sup>-1</sup>) reveals:

- PC<sub>n</sub>VImTFSI chains behave as ideal chains in melt.
- THF is a good solvent for PC<sub>n</sub>VImTFSI in which it behaves as a polymer with excluded volume effects.
- Ionic liquids are theta solvents for their corresponding PC<sub>n</sub>VImTFSI.

Moreover, the correlation peak is characteristic of the distance between backbones in melt [2] or the alkyl chain length for ionic liquids [1]

## Model

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

$$P_{\text{Guinier}} = \exp\left(-\frac{q^2 R_g^2}{3}\right)$$

- Intermediate regime (0.05 to 0.1 Å<sup>-1</sup>):

$q^{-2}$  decay for melts, characteristic of ideal chains.

$$P_{\text{Debye}}(q) = 2 \frac{\exp(-q^2 R_g^2) - 1 + q^2 R_g^2}{q^4 R_g^4}$$

$q^{-1,7}$  decay for solutions in THF, characteristic of polymers with excluded volume effects.

$$P_{\text{excl}}(q) = 2 \int_0^1 dx (1-x) \exp\left(-\frac{q^2 a^2}{6} N^{2\nu} x^{2\nu}\right)$$

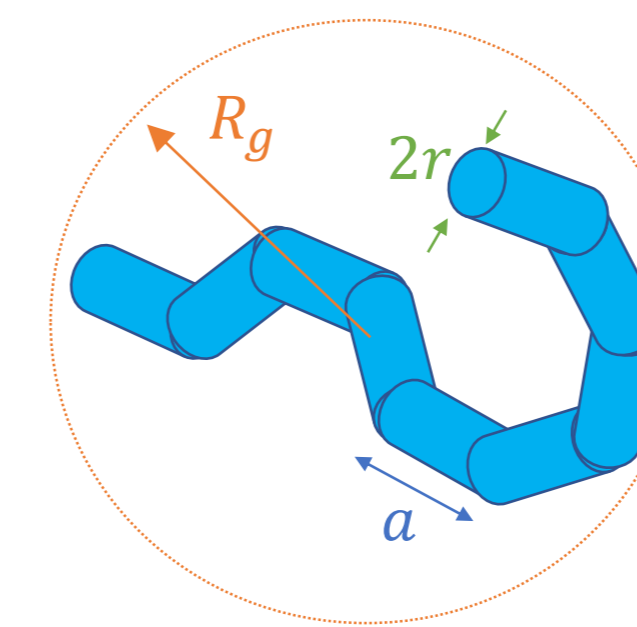
- Change of slope around 0.2 Å<sup>-1</sup>, probing the local characteristic length: the cross section  $r(n)$

$$I(q) = I_0 P_{\text{Debye}}(q) \times P_{\text{cross}}(q) + I_1 P_{\text{correl}}(q)$$

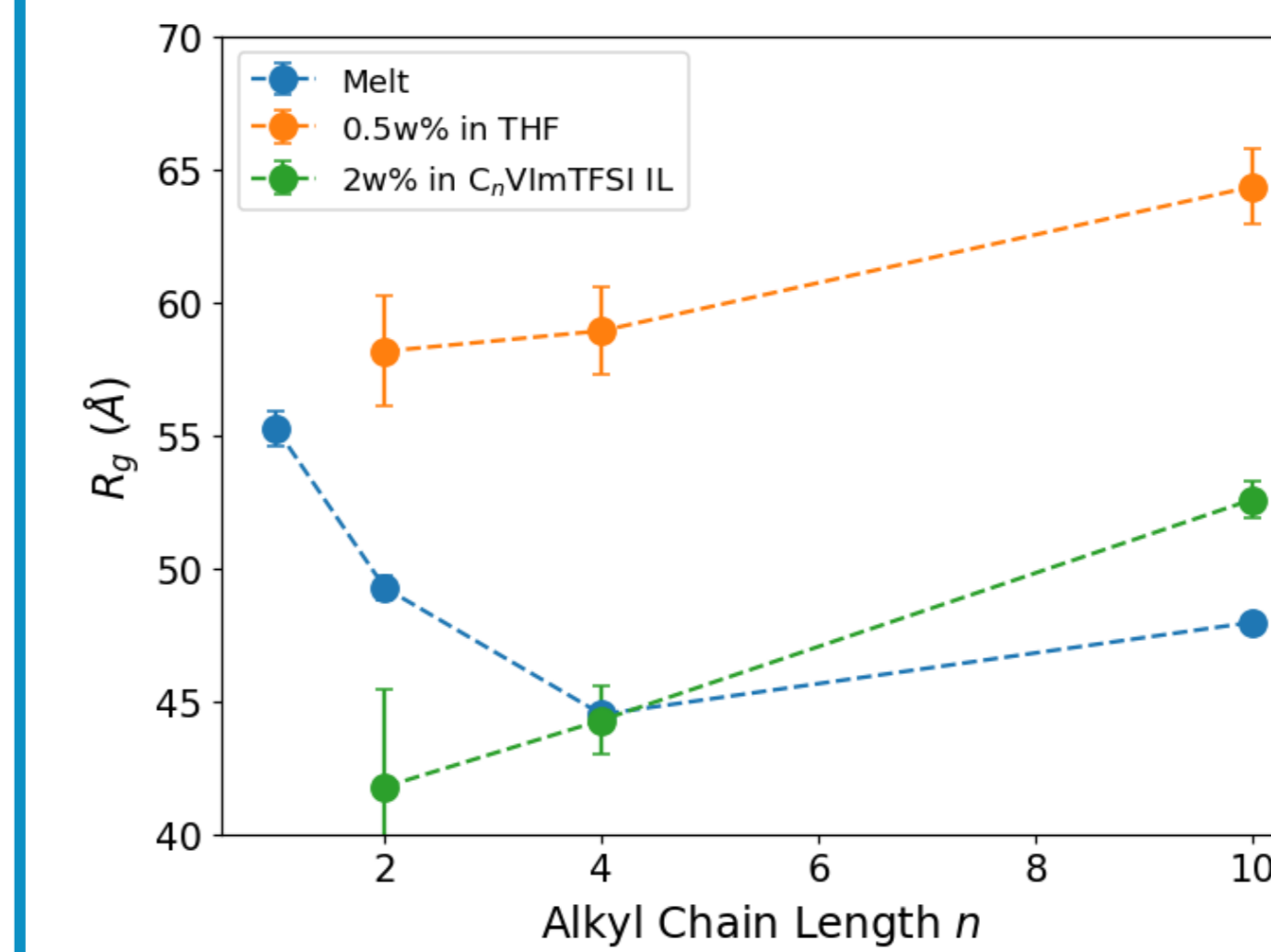
Flexible cylinder models

$$P_{\text{correl}}(q) = \exp\left(-\frac{(q - q_0)^2}{2\sigma^2}\right)$$

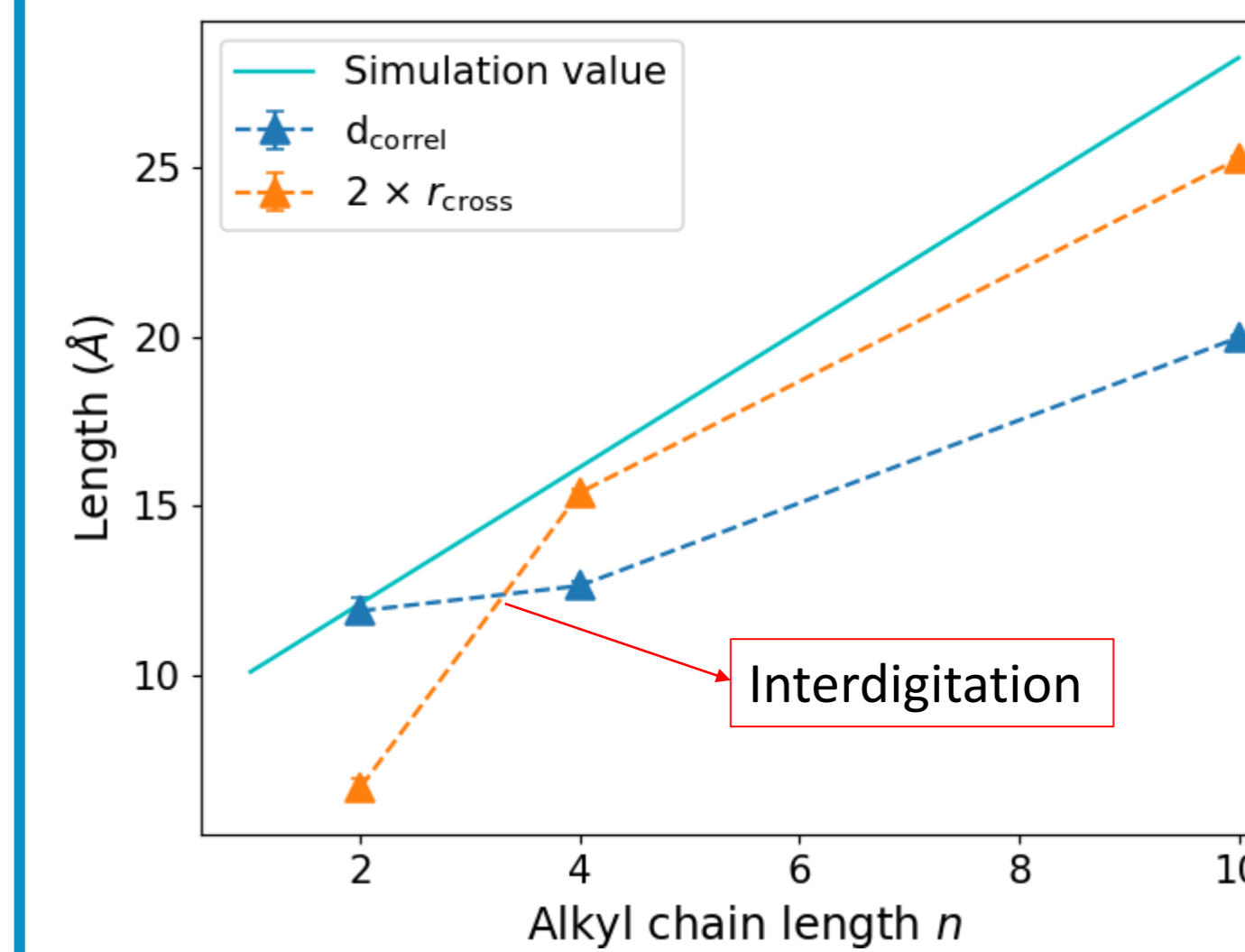
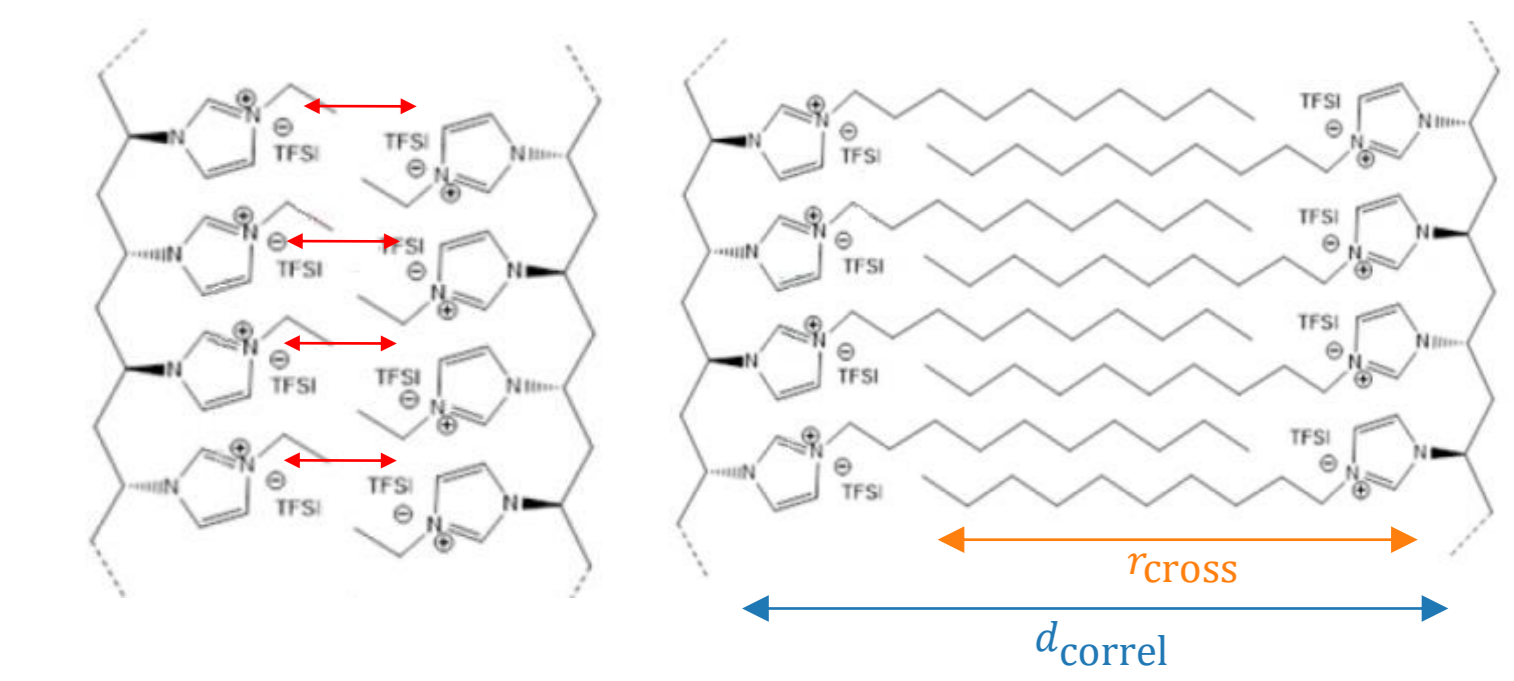
$$P(q) = P_{\text{excl}}(q) P_{\text{cross}}(q) \text{ with } P_{\text{cross}}(q) = \left(2 \frac{J_1(qr)}{qr}\right)^2$$



## 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,  $R_g$  show a first decrease, revealing a dominance of electrostatic repulsion, progressively screened by increasing the side chains length.



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

## Conclusion / Perspectives

- Radii of gyration of PC<sub>n</sub>VImX 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 ( $n > 4$ ).

### Perspectives:

- Explore their structure at interfaces (Specular and off specular XRay 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)

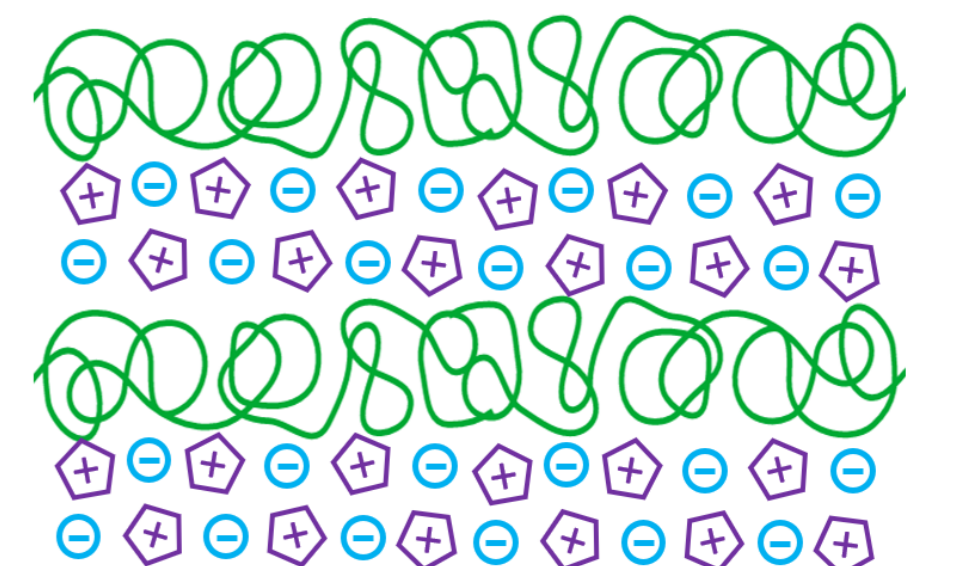


Figure 3: Expected lamellar structure of PIL at interfaces, resembling that of IL

[1] Hayes, R.; Warr, G.G.; Atkin R. Structure and nanostructure in ionic liquids. *Chemical reviews* 115.13 (2015): 6357-6426.

[2] H. Liu and S.J. Paddison. Direct comparison of atomistic molecular dynamics simulations and x-ray scattering of polymerized ionic liquids. *ACS Macro Letters*, 5(4):537-543, (2016)