Efficient metal-free strategies of polymerization of sterically hindered ionic monomer through the application of hard confinement and high pressure

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Supplementary Materials

Properties of AAO templates

| Parameter               | Value   |
|-------------------------|---------|
| Pore diameter [nm]      | 35      |
| Pore density [cm⁻²]     | 6·10⁹   |
| Pore period [nm]        | 143     |
| Thickness of membranes  | 50µm    |

Table 1. Details concerning porosity, pore diameter and distribution of AAO membranes.
NMR measurements

$^1$H NMR of P[OVIM][NTf$_2$] (600 MHz, DMSO-d$_6$) $\delta$ ppm = 8.40-9.10 (m, H$_{C'}$), 7.40-7.78 (m, H$_{D'}$), 6.75-7.20 (m, H$_{E'}$), 3.60-4.50 (m, H$_{B',F'}$), 1.80-2.30 (m, H$_{A'}$), 1.50-1.72 (m, H$_{G'}$), 1.10-1.45 (m, H$_{H',L'}$), 0.75-0.95 (m, H$_{M'}$).

Each monomer conversion was calculated by comparing the integrations of vinyl protons of the remaining monomers (5.42 and 5.95 ppm) with the integration of methyl protons for P[OVIM][NTf$_2$] at $\delta$=0.75-0.95 ppm.

Figure 1. $^1$H NMR spectrum of the sample taken from the reaction mixture; p=800 MPa, example of XI.
GPC-LALLS measurements

Figure 1. Panel (a): GPC-LALLS chromatograms of P[OVIM][NTf₂] produced by free-radical high pressure polymerization at p = 500 MPa (gray line), p = 800 MPa (black line) and at p = 1200 MPa (dashed line); Panel (b): GPC-LALLS chromatograms of P[OVIM][NTf₂] obtained under confinement by RAFT (blue line) and free-radical polymerization (black line).

Measurements of samples prepared by polymerization at macroscale were carried out in THF containing 10 mM LiNTf₂ as the solvent at 35 °C and a flow rate of 1 mL/min. Note that in case of GPC measurements of polymers produced under nanoconfinement, the polymer sample recovered from the AAO templates by wash with THF was first freeze-dried under vacuum, then washed with water and again freeze-dried under vacuum. Measurements were carried out in 250 µL vial inserts with a flow rate 0.9 ml/min.