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# Phosphonium-based poly(ionic liquid) membranes: the effect of cation alkyl chain length on light gas separation properties and ionic conductivity

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## Abstract

Phosphonium poly(ionic liquid)s (PILs) have been studied as alternatives to more common ammonium and imidazolium PILs for potential transport and separation applications. This work characterizes the CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> single-gas permeability, diffusivity, solubility, and selectivity of free-standing films of poly([(tri-*n*-alkyl)vinylbenzylphosphonium][bis(trifluoromethylsulfonyl)imide]) PILs (i.e., poly([P<sub>nnnVB</sub>][Tf<sub>2</sub>N] where *n* = 4, 6, 8). The gas permeability was found to increase approximately linearly with increasing alkyl chain length on the phosphonium group. To our knowledge, the CO<sub>2</sub> permeability of 186 barrers observed for poly([P<sub>888VB</sub>][Tf<sub>2</sub>N]) is the highest reported for neat PIL materials. In contrast, gas selectivity was observed to decrease with an increase in phosphonium alkyl chain length from *n* = 4 to *n* = 6, then remain approximately constant between *n* = 6 and *n* = 8. Additionally, the ionic conductivity of these materials was observed to increase from ca. 10<sup>-8</sup> to ca. 10<sup>-5</sup> S cm<sup>-1</sup> as the measurement temperature was increased from 25 to 105 °C. At 25 °C, the PIL with the shortest cation alkyl chain (*n* = 4) was observed to have the lowest ionic conductivity. However at ca. 90 °C, the expected trend of increasing ionic conductivity in the order *n* = 4 > *n* = 6 > *n* = 8 was observed.

Keywords: phosphonium, poly(ionic liquid)s, gas separations, ionic conductivity, alkyl chain length

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