Poly(*para*-phenylene) ionomer membranes containing methyl or trifluoromethyl substituents

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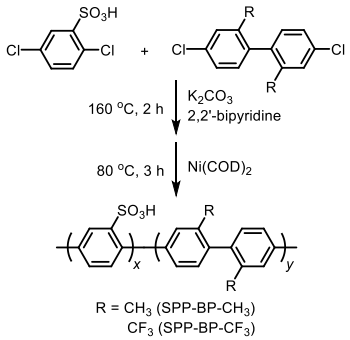
Keywords: Poly(para-phenylene); Proton conductive polymers; sulfonated polymers

Sulfonated poly(*para*-phenylene)s with high molecular weight and membrane forming capability were obtained by using methyl and trifluoromethyl substituents. The linearity of the polymer main chain decreased by introducing these substituents; the persistence length (*lp*, index of linearity, distance required for a polymer chain to bend by 90° on average) of homopolymers for 2,2'-dimethyl-1,1'-biphenyl (BP-CH_3) and 2,2'-bis(trifluoromethyl)-1,1'-biphenyl (BP-CF_3) was ca.350.6 and 87.7 nm, respectively, estimated by numerically averaging backbone conformations. Copolymers with sulfo-*para*-phenylene groups, SPP-BP-CH_3 and SPP-BP-CF_3, were obtained as high molecular weight (Mn = 28–30 kDa and Mw = 88–100 kDa for SPP-BP-CH_3 and Mn = 49–149 kDa and Mw = 161–316 kDa for SPP-BP-CF_3, respectively) to provide flexible membranes by casting from the solution. Despite more hydrophobic nature of the substituents, SPP-BP-CF_3 membranes showed higher water uptake and proton conductivity than those of SPP-BP-CH_3 membranes with comparable ion exchange capacity (IEC). SPP-BP-CF_3 membranes showed slightly higher maximum strain (2.9–5.2%) than SPP-BP-CH_3 membranes (1.1–2.1%), leading to higher rupture energy as expected from the smaller persistence length of BP-CF_3 homopolymers. While SPP-BP-CH_3 decomposed under harsh oxidative conditions, SPP-BP-CF_3 was more oxidatively stable and exhibited negligible changes in the weight, molecular weight, molecular structure and membrane properties (proton conductivity, mechanical properties, etc.)



Scheme 1. Synthesis of SPP-BP-CH_3 and CF_3.

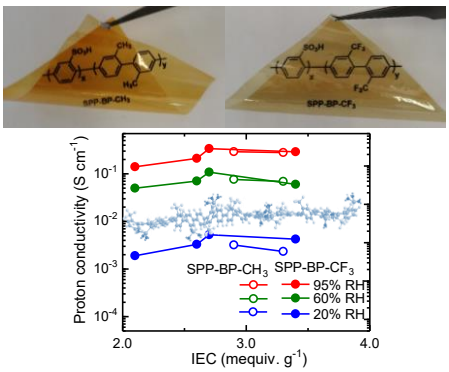


Figure 1. IEC dependence of proton conductivity of SPP-BP-CH_3 and -CF_3 at 80 °C.