Supplemental Information

Synthesis and Characterization of Poly(vinylidene fluoride)-g-sulfonated polystyrene Graft Copolymers for Proton Exchange Membrane

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GPC curves of VDF/CTFE Copolymers Prepared by Borane/Oxygen Initiator

Figure S1 shows the GPC curves of three VDF/CTFE terpolymers prepared by control broane/oxygen radical initiator, which increase their molecular weight with the conversion of monomers. The long-life propagating site leads to a linear polymer structure with a molecular weight distribution $M_w/M_n \sim 2.5$. In addition to the relatively narrow molecular weight and composition distributions, this bulk process also produces fewer impurities (boric acid and butanol) that can be easily removed by methanol washing.

Figure S1. GPC curves of three VDF/CTFE terpolymers prepared by a borane/oxygen initiator and various reaction times, (a) 4, (b) 7, and (c) 10 hours.

¹H and ¹⁹F NMR spectra of PVDF-g-PS and PVDF-g-SPS graft copolymers

Figure S2 compares the ¹H NMR spectra of a set of PVDF-g-PS (II) and PVDF-g-SPS (III) graft copolymers, with starting low molecular weight P(VDF-co-CTFE) copolymers (I). In addition to the chemical shifts at 2.1-3.3 ppm for VDF units, Figure S2,b shows several new chemical shifts at 7.4-6.4 ppm (aryl, 5H), 1.3-1.7 ppm (methylene, 2H), and 1.80-2.0 ppm (benzylic, 1H), indicating the incorporation of polystyrene (PS) grafts in the resulting PVDF-g-PS graft copolymer. There is no proton chemical shift for CTFE units. Figure S3 shows an ¹⁹F NMR spectra of the corresponding P(VDF-co-CTFE) (I) and PVDF-g-PS (II). In Figure S3,a, the chemical shifts at 91-96, 109-111, and 120-122 ppm, correspond to three fluorine species (CH₂-CF₂, CF₂-CFCl), respectively. The reduction of the CFCl peak intensity at 120-122 ppm (Figure S3,b) indicates about 40% of C-Cl groups in the P(VDF-co-CTFE) copolymer (I) involved in the ATRP graft-from polymerization. In other words, the graft density (graft number per 100 VDF units in the backbone) of the PVDF-g-PS (II) graft copolymer is estimated to be about 40% of the CTFE content in the P(VDF-co-CTFE) (I). The subsequent sulfonation reaction was carried out to achieve various degrees of sulfonation (DS). Figure 1c shows a complete sulfonated PVDF-g-SPS (III) graft copolymer, which exhibits a new set of aromatic proton peaks at 6.6-7.0 ppm—corresponding to the protons on *meta/para* disubstituted phenyl rings—and at 7.5-7.9 ppm for protons adjacent to the sulfonate group.

Figure S4 shows a similar ¹H NMR spectral comparison between a starting high molecular weight P(VDF-ter-TrFE-ter-CTFE) terpolymer (I') and two corresponding PVDF-g-PS (II') and PVDF-g-SPS (III') graft copolymers. Essentially, all the spectra are very similar to the corresponding ones in Figure 1, except for an additional minor peak at 5.1-5.8 ppm, attributed to the existence of TrFE units in the backbone.

Figure S2, ^1H NMR spectra of (a) P(VDF-co-CTFE) (I) (VDF/CTFE mole ratio= 99/1), (b) PVDF-g-PS (II) (VDF/styrene mole ratio= 99/31), and (c) PVDF-g-SPS (III) (VDF/sulfonated styrene mole ratio= 99/31).

Figure S3, ^{19}F NMR spectra of (a) P(VDF-co-CTFE) (I) (VDF/CTFE mole ratio= 99/1),
(b) PVDF-g-PS (II) (VDF/styrene mole ratio= 99/31),

Figure S4, ^1H NMR spectra of (a) P(VDF-ter-TrFE-ter-CTFE) (I') (VDF/TrFE/CTFE mole ratio= 94/5.2/0.8), (b) PVDF-g-PS (II') (VDF/styrene mole ratio= 94/36), and (c) PVDF-g-SPS (III') (VDF/sulfonated styrene mole ratio= 94/36).

TGA Analysis of PVDF-g-PS and PVDF-g-SPS graft copolymers

Figure S5 (top) compares the TGA curves (temperature range: 25 - 600 °C) of a P(VDF-co-CTFE) copolymer and three corresponding PVDF-g-PS graft copolymers with various PS contents. The onset of degradation temperatures is very similar at ~350 °C, but the slope is somewhat different. The degradation is clearly accelerated by the high PS content. At 500 °C, the PS-rich graft copolymer shows about a 20 wt% yield, about half of the corresponding P(VDF-co-CTFE) copolymer. The thermal degradation of the PVDF-g-PS graft copolymer must start at the PS grafts. It is especially interesting to understand the stability of the sulfonated graft copolymers. Figure S5 (bottom) compares the TGA curves of a set of PVDF-g-SPS graft copolymers, having various sulfonic acid concentrations, and the corresponding PVDF-g-PS with 0.8 mol% graft density and Nafion 117. Based on the trend, four regions of mass loss are identified, including moisture desorption, elimination of sulfonic acid groups, the degradation of the polystyrene segment, and the decomposition of the PVDF backbone. The mass loss due to the absorbed moisture starts from about 50 °C and ends at around 200 °C. The weight percentage of mass loss due to water absorbed is relative to the content of sulfonic acid or IEC. Up to 7 % of mass loss (double that of Nafion 117) comes from water residual when IEC is 2.70 mmol/g. The elimination of sulfonate acid is initiated at 250 °C, which is about 50 °C lower than that of Nafion 117. The mass loss from the degradation of polystyrene grafts begins at around 350 °C, followed by the decomposition of the PVDF backbone at higher temperature. It is interesting to note that all PVDF-g-SPS graft copolymers show a similar high yield (~40 wt%) at 550 °C, higher than the corresponding PVDF-g-PS and Nafion 117.

Figure S5. (top) TGA comparison of (a) a starting P(VDF-co-CTFE) copolymer (I) and three corresponding PVDF-g-PS graft copolymers (II) with 0.4 mole% graft density and various PS graft length (b) 13.2, (c) 44.3, and (d) 78.8 styrene units per graft, respectively; (bottom) TGA curves of Nafion 117, PVDF-g-PS in run set A2, and corresponding PVDF-g-SPS runs A2-2, A2-3, A2-4, and A2-6 having increasing sulfonic acid contents.

Proton conductivity semi-log plots of PVDF-g-SPS graft copolymer

Figure S6 shows the semi-log plots of proton conductivity vs. relative humidity (RH) under various environmental conditions (i.e. temperature and humidity), which is the same results shown in Figure 6.

Figure S6. Comparison of semi-log plots of proton conductivity vs. relative humidity between B1-2 and Nafion 112 PEMs at 30, 80, and 120 °C.