SUPPORTING INFORMATION

Structural effects on the nano-scale morphology and conductivity of ionomer blends

Thomas Weissbach,[†] Emily M. W. Tsang,[†] Ami C. C. Yang,[†] Rasoul Narimani,[‡] Barbara J. Frisken[‡] and Steven Holdcroft[*,†]

[†] Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada.

[‡] Department of Physics, Simon Fraser University, Burnaby, BC V5A 1S6, Canada.

[*] To whom correspondence should be addressed. E-mail:

holdcrof@sfu.ca

Synthesis

Materials. Potassium peroxodisulfate ($K_2S_2O_8$, Allied Chemical, reagent grade), sodium disulfite ($Na_2S_2O_5$, Anachemia, anhydrious, reagent grade), sodium pentadecafluorooctanoate ($C_7F_{15}COONa$, Aldrich, 96%), disodium hydrogenorthophosphate (Na_2HPO_4, Sigma, 99+%), sodium dihydrogenorthophosphate (NaH_2PO_4, Sigma, 99+%) vinylidene difluoride (VDF, Aldrich, 99+%), hexafluoropropylene (HFP, Synquest Lab Inc, 98.5%), α-α‘-bipyridine ($C_{10}H_8N_2$, bpy, Aldrich, 99+%), copper(I) chloride (CuCl Aldrich, 99%), acetic anhydride ($(CH_3CO)_2O$, Aldrich, 99.5%), sulfuric acid (H_2SO_4, Anachemia, 95-98%) were used as received. Styrene (C_8H_8, Aldrich, 99+%) was washed twice with aqueous 5% NaOH and twice with water. After drying overnight with $MgSO_4$, styrene was distilled over CaH_2 under reduced pressure and stored under N_2 at -20 °C.

Synthesis of PVDF by Emulsion Polymerization. Polyvinylidene difluoride was prepared by emulsion polymerization of vinylidene difluoride (VDF) following an adapted synthetic route from the literature.[1] The reaction was performed in a 160 mL pressure vessel (Parr Instruments) equipped with a pressure relief valve and a magnetic stir bar. A mixture of 90 ml water, 0.8 g $K_2S_2O_8$, 0.58 g $Na_2S_2O_5$, 0.4 ml $C_7F_{15}COONa$, 10 ml of an aqueous 0.29M NaH_2PO_4 / 0.47M Na_2HPO_4 buffer solution, and 0.75 ml $CHCl_3$ was added. The reactor was filled with 300 psi of VDF. The reaction was started by heating to 60 °C. The pressure loss was compensated by adding new VDF. After the total pressure loss reached 300 psi, the reaction was stopped by removing the emulsion from the vessel. The product was coagulating in the freezer, washed four times with water and once with anhydrous ethanol and dried in the vacuum oven at 80 °C for 24 hours. Mn (2180 DA) and Mw (3200 DA) were determined by GPC.

Synthesis of P(VDF-*co*-HFP) Macroinitiator by Emulsion Polymerization. The synthesis was previously reported:[1] a 160 ml pressure vessel (Parr Instruments) was equipped with a pressure relief valve and a magnetic stir bar. A mixture of 90 ml water, 0.8 g $K_2S_2O_8$, 0.58 g $Na_2S_2O_5$, 0.4 ml $C_7F_{15}COONa$, 10 ml of an aqueous 0.29M NaH_2PO_4 / 0.47M Na_2HPO_4 buffer solution, 0.3 ml chloroform and a monomer mixture of 14 mol% HFP and 86 mol% VDF were added. The reaction was started by heating to 55 °C and the pressure was kept constant at 300 psi by supplying a monomer mixture of 14 mol% HFP and 86 mol% VDF. After a total pressure drop of 350 psi, the reaction was stopped by removing the polymer from the vessel. The polymer latex was coagulated by freezing, washed with water and ethanol, purified by repeated dissolution in acetone and precipitation in ethanol, and drying at 55 °C under vacuum. ^{19}F NMR (470 MHz, D_6-acetone) δ (ppm): -70.8 CH_2-CF_2-$CF(CF_3*)$-CF_2-CH_2, -75.9 CH_2-CF_2-$CF(CF_3*)$-CH_2-CF_2, -90 - -92.8 CF_2-CH_2-CF_2*-CH_2-CF_2, -93.3 CF_2-CH_2-CF_2*-CH_2-CH_2, -111.2 CF_2-CH_2-CF_2*-CF_2-CH_2, -114.7 CH_2-CF_2-CF_2*-CH_2-CH_2, -116.9 CF_2-CH_2-CF_2*-CF_2-CH_2, -185.1 CF_2-$CF*(CF_3)$-CF_2.

^1H NMR (500 MHz, D6-acetone) δ (ppm): 6.10 - 6.40 (f, chain end), 3.65 – 3.80 (f', methylene, CCl3 adjecent, 2.80 - 3.10 (f'', methylene, head-to-tail VDF sequences), 2.05 - 2.50 (f''', methylene, head-to-head or tail-to-tail VDF sequences).

ATRP of Polystyrene onto P(VDF-*co*-HFP) Macroinitiator. 1.005 g trichloromethyl-terminated P(VDF-co-HFP) macroinitiator were dissolved in 4.8 ml butylacetate in a 25 ml flask with magnetic stir bar. 0.28 g bpy, 5.2 ml styrene and 0.06 g CuCl were added. The air in the flask was removed by three freeze-pump-thaw cycles with liquid nitrogen. The reaction was started by heating the flask to 110 °C under nitrogen atmosphere. The reaction was stopped by cooling and exposing to air after 13 hours. The polymers were precipitated in 500 ml of an 1:1 ethanol / hexane mixture (by volume), washed five times with ethanol / hexane, purified by dissolving the polymer in tetrahydrofurane and filtering through a silica gel 60 (EM Science) column. ^{19}F NMR (470 MHz, D_6-acetone) showed similar signature peaks to P(VDF-co-HFP) macroinitiator. ^{1}H NMR (500 MHz, D^6-acetone) δ (ppm): 6.40 - 7.40 (b, b', c, aryl), 6.10 - 6.40 (f, chain end), 3.65 – 3.80 (f', methylene, CCl_3 adjecent), 2.80 - 3.10 (f'', methylene, head-to-tail VDF sequences), 2.05 - 2.50 (f''', methylene, head-to-head or tail-to-tail VDF sequences), 1.80 - 2.10 (e, benzylic), 1.10 - 1.80 (d, methylene, styrene).

Sulfonation of P(VDF-*co*-HFP)-*b*-PS. The sulfonation reaction was performed as described:[2] 0.3 g P(VDF-co-HFP)-b-PS were dissolved in 8 ml 1,2-dichlorethane in a 50 ml three-neck flask equipped with a condenser by heating to 50 °C under nitrogen atmosphere. The sulfonation reagent acetyl sulfate was prepared by mixing 1.8 ml acetic anhydride with 3 ml 1,2-dichlorethane in a nitrogen-purged test tube. After cooling the test tube with the mixture to 0 °C with 10 % calcium chloride ice bath, 0.6 ml 95-97 % sulfuric acid were added. Half of that mixture was added to the polymer solution at 45 °C with a Pasteur pipette. In order to obtain polymers with different degrees of sulfonation, the reaction was performed with reaction times of 17, 34, 51, 60 and 90 minutes. The polymers were precipitated in 50 ml of a 1:1 ethanol / hexane mixture (by volume), washed five times with water and dried overnight in the vacuum oven at 80 °C. ^{19}F NMR (470 MHz, D_6-acetone) showed similar signature peaks to P(VDF-co-HFP) macroinitiator. ^{1}H NMR (500 MHz, D^6-acetone) δ (ppm): 7.40 - 7.90 (a, aryl, adjacent to SO_3H), 6.40 - 7.40 (b, b', c, aryl). All other peaks are similar to P(VDF-*co*-HFP)-*b*-PS.

Polystyrene Content. The PS content of the unsulfonated polymer was calculated using the molar weight of the PS side chains/block ($M_{w,PS}$) and the macroinitiator ($M_{w,Macro}$).

$$PS\ content = \frac{M_{w,PS}}{M_{w,Macro} + M_{w,PS}} \times 100\%$$

The PS content of ionomer blends was calculated by the ionomer content, the degree of sulfonation (DS), and the molecular weight of the macroinitiator, the PS side chains/block ($M_{w,PS}$), the styrene monomer ($M_{w,Styrene}$) and the SO_3 fragment (M_{SO3}).

$$PS\ content = \frac{Ionomer\ content}{100\ \%} \cdot \frac{M_{w,PS}}{M_{w,Macro} + M_{w,PS} + \frac{DS}{100\%} \cdot \frac{M_{w,PS}}{M_{w,Styrene}} \cdot M_{SO_3}} \times 100\%$$

Volume contents of PS were calculated estimating a density of ρ_{PS}= 1.05 g/cm^3 and ρ_{PVDF} = 1.78 g/mol^3. Additionally, the density of PVDF was estimated to be similar to the macroinitiators. The density of the SPS was estimated to be similar to the PS.

$$PS\ content = \frac{\frac{Ionomer\ content}{100\ \%} \cdot \frac{M_{w,PS}}{\rho_{PS}}}{\frac{M_{w,Macro}}{\rho_{PVDF}} + \frac{Ionomer\ content}{100\ \%} \cdot \frac{M_{w,PS}}{\rho_{PS}}} \times 100\%$$

Membrane Characterization. The membranes were soaked in a 2 M aqueous sodium chloride solution for five hours to exchange the protons inside the membrane with sodium ions. The number of released protons was detected by acid-base end-point titration with 0.001 M aqueous sodium hydroxide solution and Phenolphthalein. The membranes were stored in 1 M hydrochloric acid over night to retransform them to the protonic form, washed every 40 minutes five times with deionized water in five hours to remove HCl and afterwards dried in the vacuum oven at 80 °C overnight. The dry weight (W_{dry}) and the dry dimensions of the membranes were determined after the membranes cooled down in a desiccator. The ion exchange capacity (IEC, mmol/g) was calculated by

$$IEC = \frac{V_{NaOH} \times [NaOH]}{W_{dry}}$$

where V_{NaOH} is the blank corrected volume of the sodium hydroxide solution and [NaOH] is the sodium hydroxide concentration. The membranes were stored in water overnight. The surface water was removed from the wet membranes with Kimwipes without removing the water from inside of the membrane to determine the wet weight (W_{wet}) of the membrane. The water uptake was calculated by

$$water\ uptake = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

where W_{wet} and W_{dry} are the wet and the dry weights. The water content was calculated by

$$water\ content = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100\%$$

and represents the weight related content of the water in the wet membrane. In contrast, the water volume fraction was calculated by

$$X_V = \frac{Vol_{wet} - Vol_{dry}}{Vol_{wet}} = \frac{\left(W_{wet} - W_{dry}\right) / \rho_{H_2O}}{Vol_{wet}}$$

and represents the volume fraction of the water in a wet membrane. Due to the difficult measurable dimensions of the dry membrane, the contained volume of water was simplified by using the weight of the incorporated water and its density (ρ_{H2O}).

The length and width of the membranes were measured with Mitutoyo Digimatic calipers; thickness was measured with Series 293 Mitutoyo Quickmike calipers. Each value was measured five times and the average was used for the calculation.

In order to get a relation between the ion content and the water content, the number of water molecules per ionic group, λ, was calculated:

$$[H_2O]/[-SO_3H] = \lambda = \frac{W_{wet} - W_{dry}}{M_{H_2O} \times V_{NaOH} \times [NaOH]}$$

M_{H2O} represents the molar weight of water. The conductivity of the polymer was calculated using

$$\sigma = \frac{L}{R\,A}$$

where L is the distance between the electrodes, R the by AC impedance measured resistance and A, the cross-sectional area of the fully hydrated membrane.

Diagramms

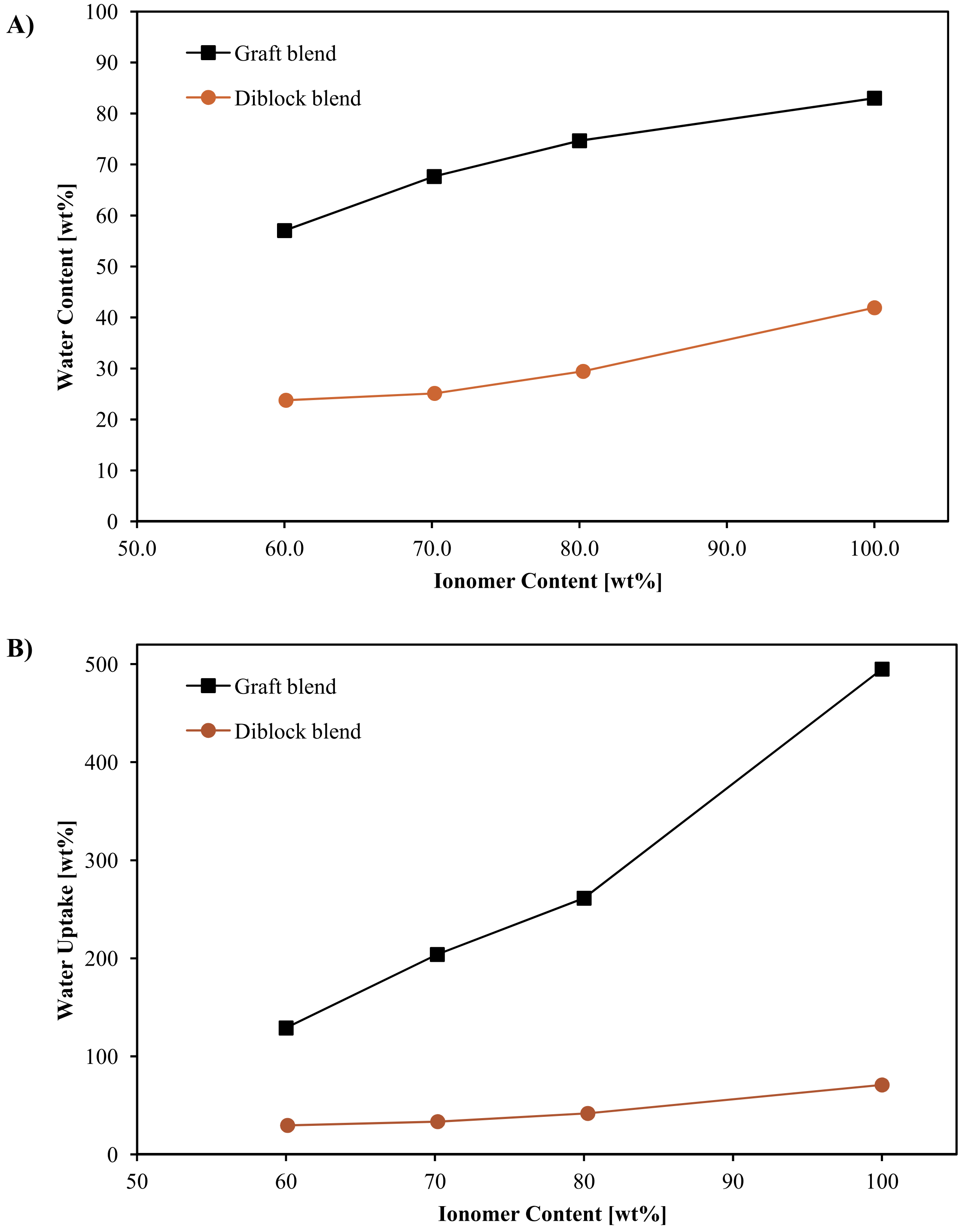


Fig. S1 A) Water content vs. ionomer content and B) water uptake vs. ionomer content of ionomer blends

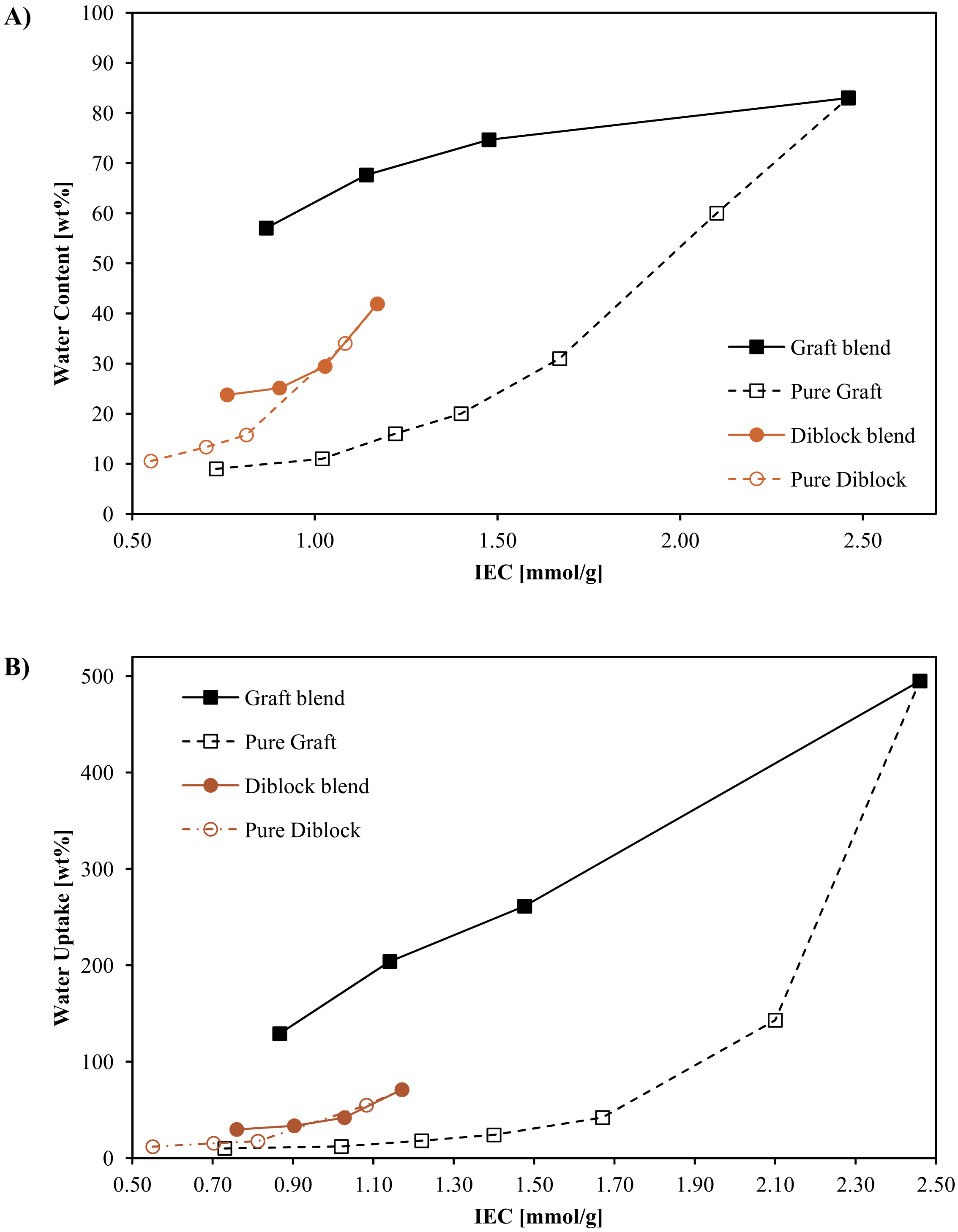


Fig. S2 A) Water content vs. ion exchange capacity and B) water uptake vs. ion exchange capacity of ionomer blends and ionomers with different DS

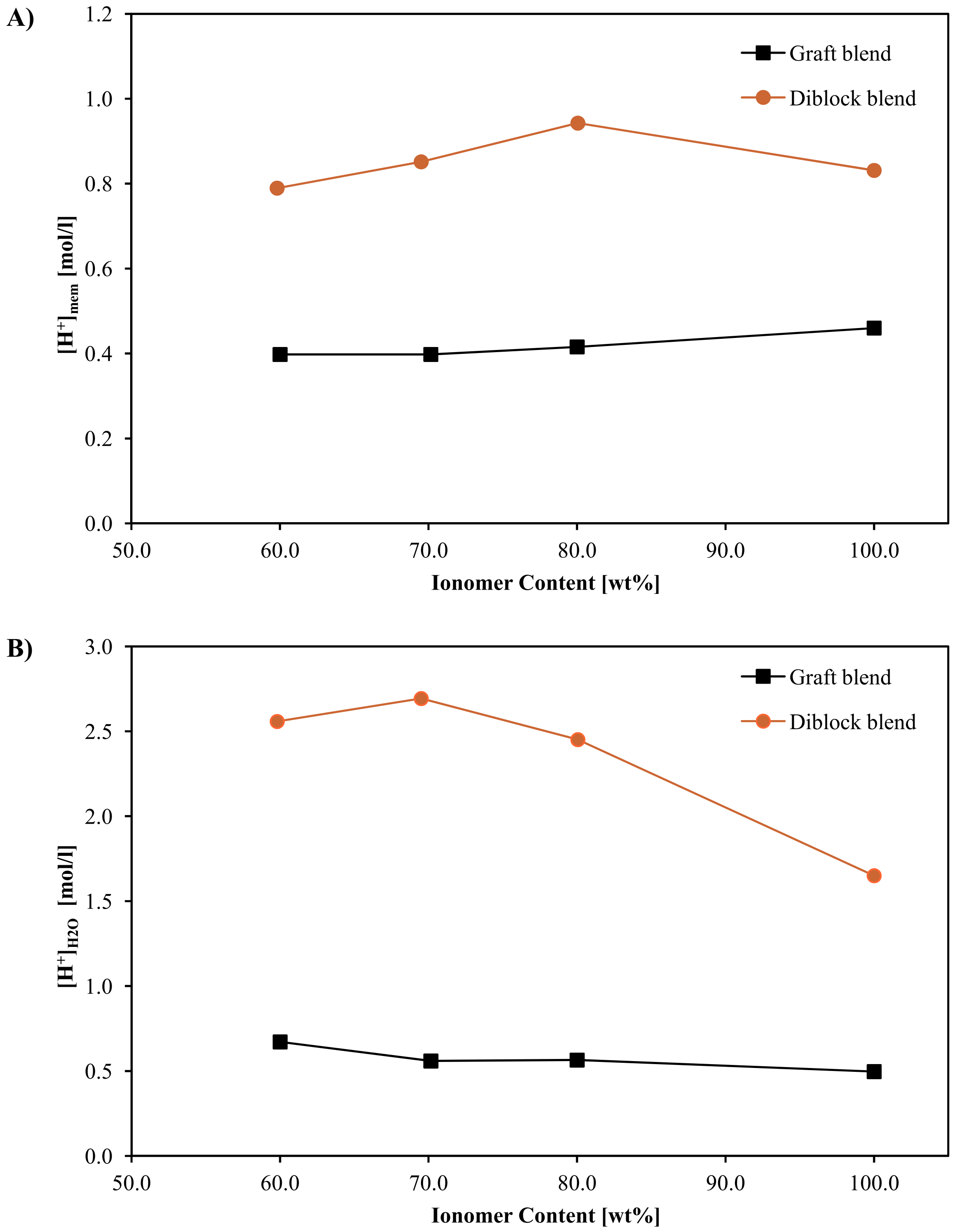


Fig. S3: A) $[H^+]_{mem}$ vs. ionomer content and B) $[H^+]_{H2O}$ vs. ionomer content of ionomer blends.

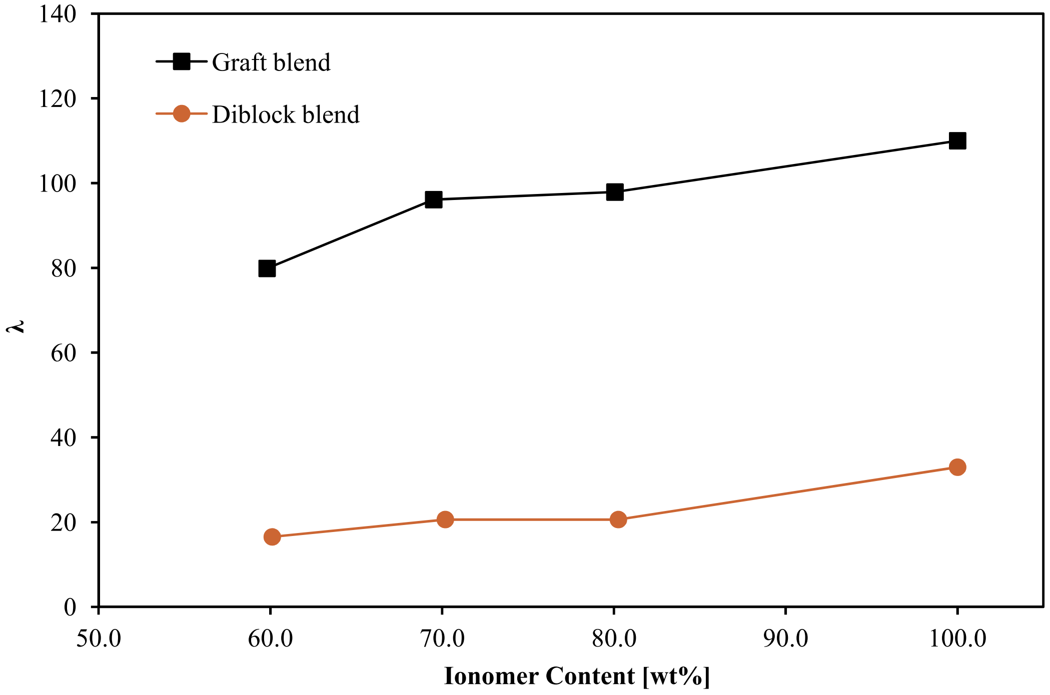


Fig. S4: Water molecules per sulfonic acid group, λ vs. ionomer content of ionomer blends.

Tables

Table S1: Chemical composition of graft copolymers.[3]

	DS [%]	Ionomer Content [wt%]	P(VDF-co-CTFE) Mn, GPC [g/mol]	PS Mn, NMR [g/mol]	PS Content [wt%]	PS Content [vol%]
Graft Copolymer	0	100	312000	1048000	77.1	85.1
Graft Ionomer	10	100	312000	1048000	72.7	85.1
	15	100	312000	1048000	70.8	85.1
	18	100	312000	1048000	69.6	85.1
	21	100	312000	1048000	68.5	85.1
	26	100	312000	1048000	66.8	85.1
	34	100	312000	1048000	64.1	85.1
	41	100	312000	1048000	62.0	85.1
Graft Blend	41	80	312000	1048000	49.6	82.0
	41	70	312000	1048000	43.4	79.9
	41	60	312000	1048000	37.2	77.4

Table S2: Chemical composition of diblock copolymers.

	DS [%]	Ionomer Content [wt%]	P(VDF-co-CTFE) Mn, GPC [g/mol]	PS Mn, GPC [g/mol]	PS Content [wt%]	PS Content [vol%]
Diblock Copolymer	0	100	12060	4680	28.0	39.7
Diblock Ionomer	20	100	12060	4680	26.8	39.7
	25	100	12060	4680	26.5	39.7
	31	100	12060	4680	26.2	39.7
	34	100	12060	4680	26.0	39.7
	36	100	12060	4680	25.9	39.7
Diblock Blend	36	80	12060	4680	20.8	34.5
	36	70	12060	4680	18.2	31.5
	36	60	12060	4680	15.6	28.3

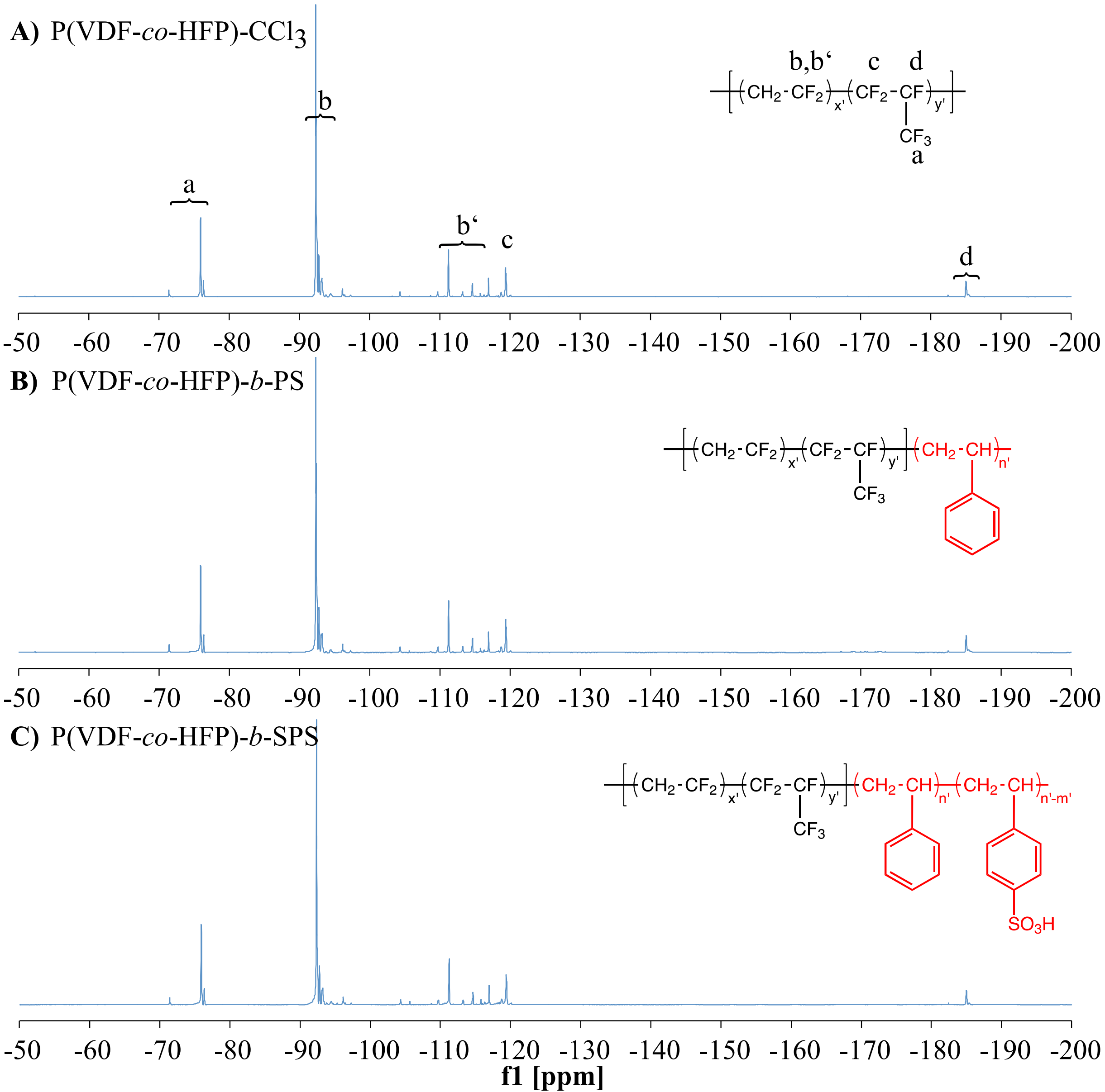
Table S3: Properties of graft and diblock copolymer blends

	Ionomer Content [%]	Calculated IEC [mmol/g]	Measured IEC [mmol/g]	Conductivity σ [S/cm]	Water Content [wt%]	Water Uptake [wt%]	λ	$[-SO_3H]$ [mol/l]	X_V [vol%]	μ_{eff} x 1000 [cm²/Vs]
Graft blend	100	2.46	2.46 ± 0.05	0.057 ± 0.001	83 ± 1	495 ± 20	110 ± 5	0.46 ± 0.02	85 ± 1	1.28
	80	1.97	1.48 ± 0.07	0.057 ± 0.002	75 ± 3	261 ± 10	98 ± 2	0.42 ± 0.01	71 ± 1	1.42
	70	1.73	1.14 ± 0.03	0.050 ± 0.002	68 ± 2	204 ± 6	96 ± 3	0.40 ± 0.06	68 ± 4	1.29
	60	1.48	0.87 ± 0.03	0.046 ± 0.000	57 ± 2	129 ± 3	80 ± 3	0.40 ± 0.02	52 ± 1	1.20
Diblock blend	100	1.17	1.17 ± 0.05	0.055 ± 0.004	42 ± 3	71 ± 3	33 ± 3	0.83 ± 0.01	46 ± 5	0.69
	80	0.94	1.03 ± 0.02	0.054 ± 0.001	29 ± 3	42 ± 6	21 ± 1	0.94 ± 0.04	38 ± 3	0.60
	70	0.82	0.90 ± 0.01	0.038 ± 0.004	25 ± 1	34 ± 1	21 ± 1	0.85 ± 0.02	32 ± 1	0.46
	60	0.70	0.76 ± 0.04	0.026 ± 0.004	24 ± 2	30 ± 2	17 ± 2	0.79 ± 0.01	29 ± 3	0.34

Table S4: Properties of graft and diblock copolymers with varying degree of sulfonation

	DS [%]	Measured IEC [mmol/g]	Conductivity σ [S/cm]	Water Content [wt%]	Water Uptake [wt%]	λ	$[H^+]_{mem}$ [mol/l]	$[H^+]_{H2O}$ [mol/l]	X_V [vol%]	μ_{eff} x 1000 [cm²/V^s]
Pure Graft	10	0.73 ± 0.01	0.003 ± 0.001	9 ± 1	10 ± 1	7 ± 1	0.66 ± 0.01	7.30	9	0.05
	15	1.02 ± 0.03	0.006 ± 0.002	11 ± 1	12 ± 2	7 ± 1	0.93 ± 0.05	8.50	13	0.07
	18	1.22 ± 0.01	0.014 ± 0.004	16 ± 1	18 ± 1	8 ± 1	1.04 ± 0.02	6.78	15	0.13
	21	1.40 ± 0.04	0.023 ± 0.004	20 ± 1	24 ± 1	10 ± 1	1.17 ± 0.02	5.83	21	0.20
	26	1.67 ± 0.02	0.066 ± 0.003	31 ± 2	42 ± 2	14 ± 1	1.22 ± 0.04	3.98	31	0.51
	34	2.10 ± 0.02	0.090 ± 0.001	60 ± 2	143 ± 4	37 ± 2	0.87 ± 0.02	1.47	60	1.07
	41	2.46 ± 0.05	0.057 ± 0.001	83 ± 1	495 ± 20	110 ± 5	0.46 ± 0.02	0.50	85	1.28
Pure Diblock	20	0.55 ± 0.01	0.006 ± 0.001	11 ± 1	12 ± 1	10 ± 1	0.66 ± 0.02	4.67	12 ± 1	0.09
	25	0.70 ± 0.01	0.012 ± 0.002	13 ± 1	15 ± 1	12 ± 1	0.71 ± 0.05	4.56	13 ± 2	0.18
	31	0.81 ± 0.01	0.030 ± 0.001	16 ± 1	18 ± 1	15 ± 2	0.86 ± 0.01	4.64	20 ± 1	0.36
	34	1.08 ± 0.02	0.050 ± 0.002	34 ± 2	55 ± 4	24 ± 3	0.90 ± 0.06	1.97	35 ± 1	0.57
	36	1.17 ± 0.05	0.055 ± 0.004	42 ± 3	71 ± 3	33 ± 3	0.83 ± 0.01	1.65	46 ± 5	0.69

NMR Spectra


A) P(VDF-*co*-HFP)-CCl$_3$

B) P(VDF-*co*-HFP)-*b*-PS

C) P(VDF-*co*-HFP)-*b*-SPS

Fig. S5: ^{19}F NMR spectra of A) P(VDF-*co*-HFP)-CCl$_3$, B) P(VDF-*co*-HFP)-*b*-PS, and C) P(VDF-*co*-HF)-*b*-SPS.

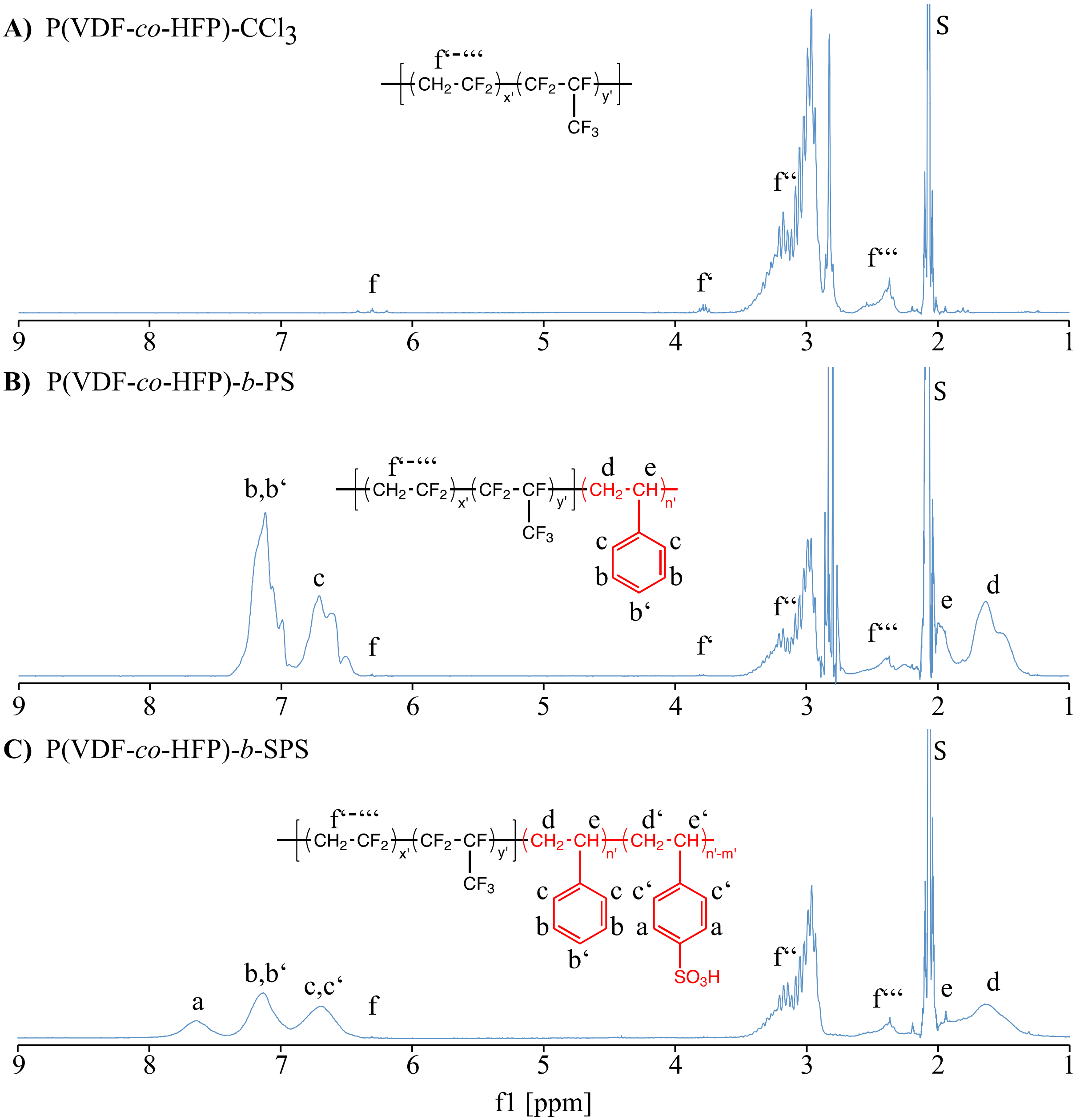


Fig. S5: ^{1}H NMR spectra of A) P(VDF-*co*-HFP)-CCl$_3$, B) P(VDF-*co*-HFP)-*b*-PS, and C) P(VDF-*co*-HF)-*b*-SPS.

References

1. Z. Q. Shi and S. Holdcroft, *Macromolecules*, 2004, **37**, 2084-2089.
2. Z. Q. Shi and S. Holdcroft, *Macromolecules*, 2005, **38**, 4193-4201.
3. E. M. W. Tsang, Z. B. Zhang, A. C. C. Yang, Z. Q. Shi, T. J. Peckham, R. Narimani, B. J. Frisken and S. Holdcroft, *Macromolecules*, 2009, **42**, 9467-9480.