

SUPPORTING INFORMATION for

Controlling crystallinity in graft ionomers, and its effect on morphology, water sorption, and proton conductivity of graft ionomer membranes

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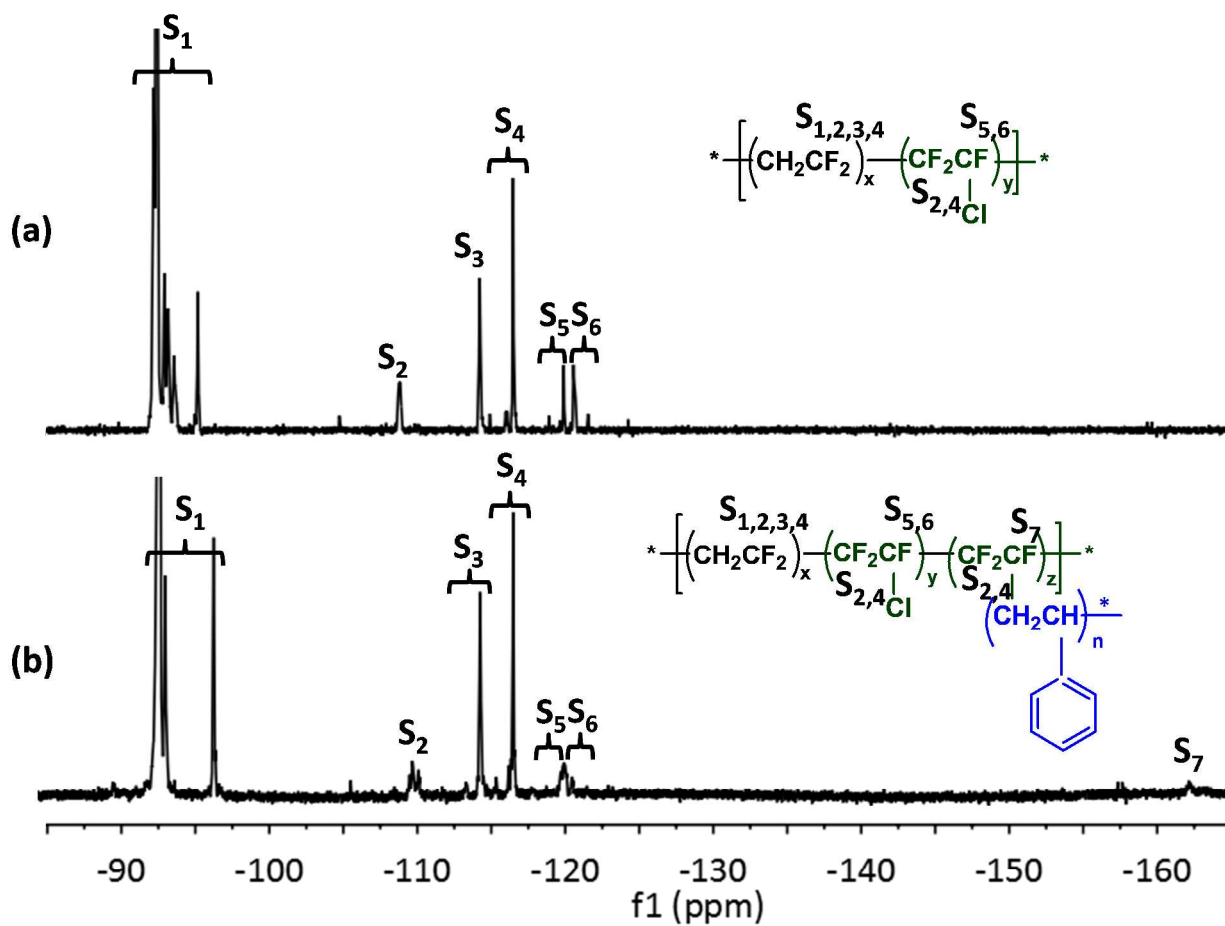


Figure S1: 400 MHz ^{19}F NMR spectra of (a) P(VDF-co-CTFE_{2.6mol%}) and (b) P(VDF-co-CTFE_{2.6mol%})-g-PS₆₂ after 16 h ATRP reaction time.

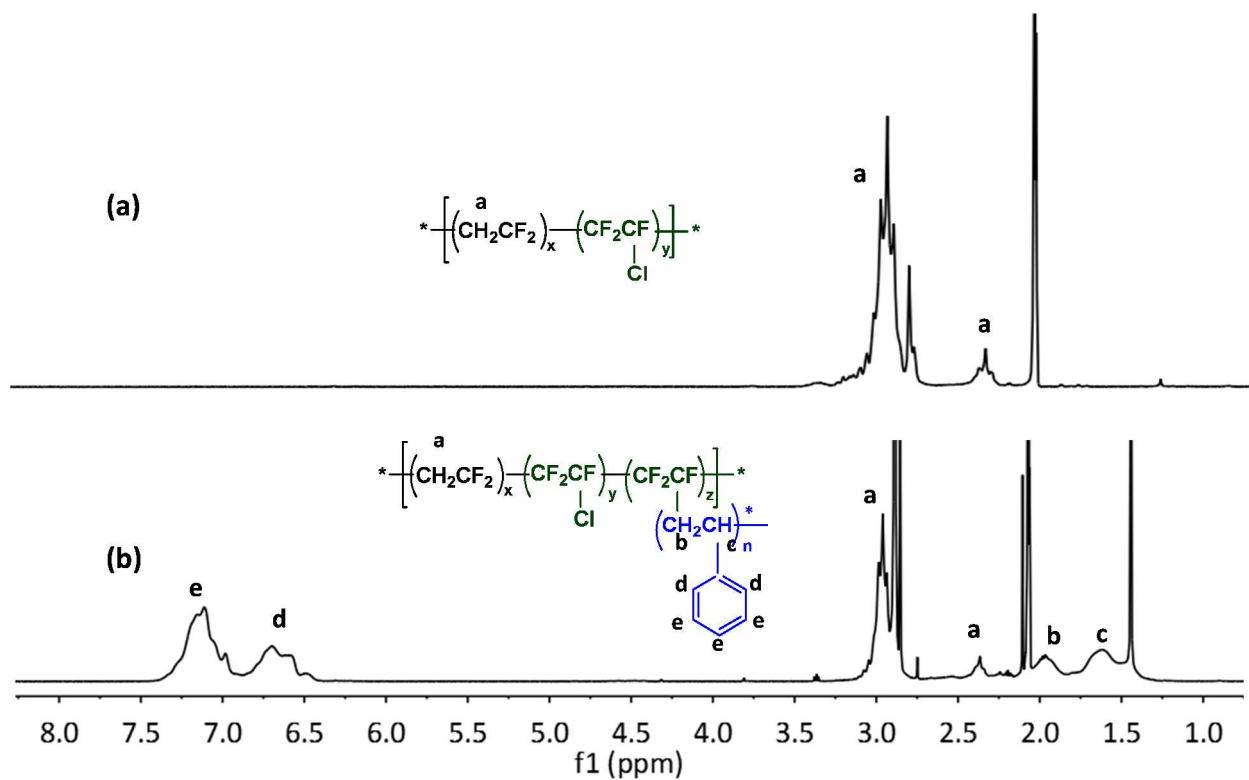


Figure S2: 600 MHz ^1H NMR spectra of (a) P(VDF-*co*-CTFE_{2.6mol%}) (b) P(VDF-*co*-CTFE_{2.6mol%})-*g*-PS₃₉ after 8 h ATRP reaction time. (*d*₆-Acetone)

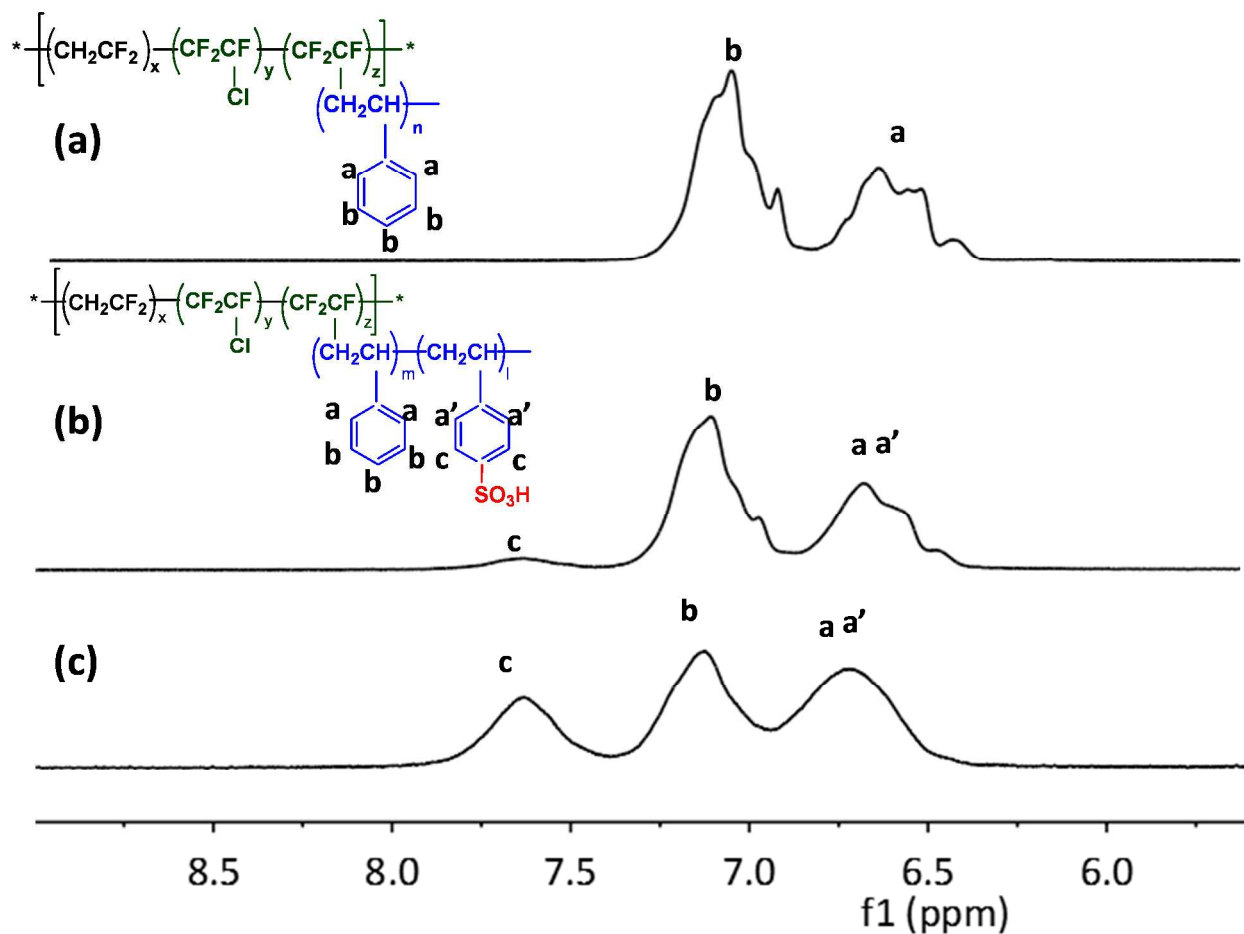


Figure S3: 600 MHz ¹H NMR spectra corresponding to graft polystyrene of (a) P(VDF-co-CTFE_{2.6mol%})-g-SPS₇₉ after 24 h ATRP reaction time and its partially sulfonated graft copolymers: (b) P(VDF-co-CTFE_{2.6mol%})-g-SPS₇₉ DS= 12% ; (c) P(VDF-co-CTFE_{2.6mol%})-g-SPS₇₉ DS= 48% (d₆-Acetone)

Table S1: Properties of P(VDF-co-CTFE_{2.6mol%})-g-SPS Graft Copolymer Membranes

Membrane	IEC ^a (mmol/g)	DS (%)	Water uptake ^b (%)	Water content ^b (%)	λ	Conductivity (mS/cm) ^c	[-SO ₃ H](M)	$\mu_{\text{est}} \times 1000$ (cm ² /sV)
PCV-g-SPS ₃₉	1.12 ± 0.01	18	18 ± 1	15 ± 1	9 ± 1	8 ± 1	1.07 ± 0.01	0.07 ± 0.01
	1.72 ± 0.04	31	47 ± 6	32 ± 1	15 ± 1	47 ± 2	1.34 ± 0.04	0.37 ± 0.03
	2.27 ± 0.07	53	155 ± 8	61 ± 1	38 ± 2	72 ± 2	1.04 ± 0.07	0.77 ± 0.09
	2.66 ± 0.06	60	211 ± 6	67 ± 1	45 ± 2	84 ± 11	0.89 ± 0.02	0.96 ± 0.04
	3.02 ± 0.05	70	278 ± 25	73 ± 1	53 ± 4	77 ± 9	0.77 ± 0.02	1.03 ± 0.03
	3.33 ± 0.08	85	788 ± 33	89 ± 1	136 ± 7	44 ± 2	0.39 ± 0.02	1.12 ± 0.09
	3.52 _{theoretical}	100	1790 ± 55	96 ± 1	283	41 ± 3	0.30 ± 0.08	1.42 ± 0.03
PCV-g-SPS ₆₂	1.23 ± 0.04	19	15 ± 1	13 ± 1	7 ± 1	1 ± 0.1	0.82 ± 0.01	0.01 ± 0.00
	1.79 ± 0.04	23	36 ± 1	26 ± 1	11 ± 1	21 ± 1	1.21 ± 0.07	0.18 ± 0.02
	2.00 ± 0.05	28	48 ± 2	32 ± 1	13 ± 1	34 ± 2	1.38 ± 0.05	0.26 ± 0.03
	2.74 ± 0.04	49	298 ± 11	75 ± 1	62 ± 3	68 ± 4	0.66 ± 0.02	1.01 ± 0.04
	3.07 ± 0.05	58	835 ± 66	89 ± 1	158 ± 8	33 ± 1	0.33 ± 0.01	1.04 ± 0.06
	4.05 _{theoretical}	100	Partially dissolve in water		-	-	-	-
PCV-g-SPS ₇₉	0.74 ± 0.03	12	11 ± 1	10 ± 1	9 ± 2	3 ± 2	0.45 ± 0.07	0.06 ± 0.04
	1.35 ± 0.02	23	29 ± 3	22 ± 2	12 ± 1	15 ± 2	1.07 ± 0.05	0.14 ± 0.02
	1.48 ± 0.04	27	38 ± 2	27 ± 1	14 ± 1	23 ± 1	1.11 ± 0.03	0.24 ± 0.02
	1.81 ± 0.04	30	65 ± 4	39 ± 2	20 ± 1	45 ± 1	1.19 ± 0.03	0.37 ± 0.02
	2.05 ± 0.09	33	128 ± 12	56 ± 2	33 ± 2	69 ± 4	0.91 ± 0.08	0.80 ± 0.08
	2.35 ± 0.02	48	815 ± 63	89 ± 1	199 ± 14	33 ± 9	0.34 ± 0.03	1.02 ± 0.05
	2.91 ± 0.04	56	1060 ± 94	92 ± 1	211 ± 10	36 ± 7	0.28 ± 0.06	1.23 ± 0.08
	4.29 _{theoretical}	100	Partially dissolve in water		-	-	-	-

a. By titration. b. Room temperature. c. Soaked in H₂O overnight and pat-dried with a Kimwipe paper before measurements at room temperature. *Errors were calculated based on standard deviation of several experiments.

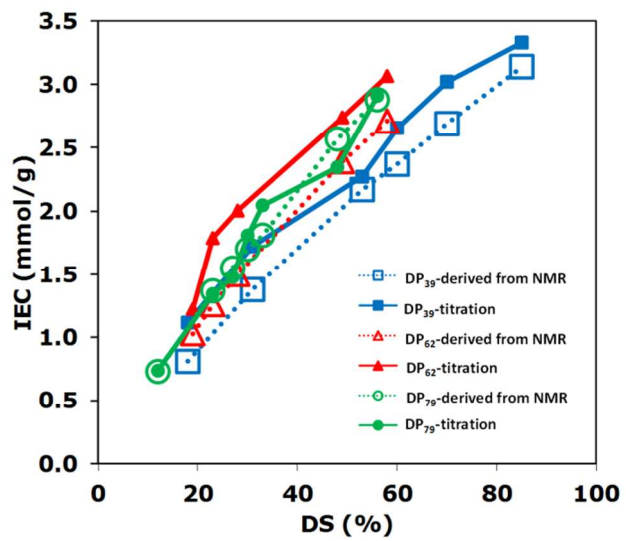


Figure S4: IEC as a function of Degree of sulfonation (DS).

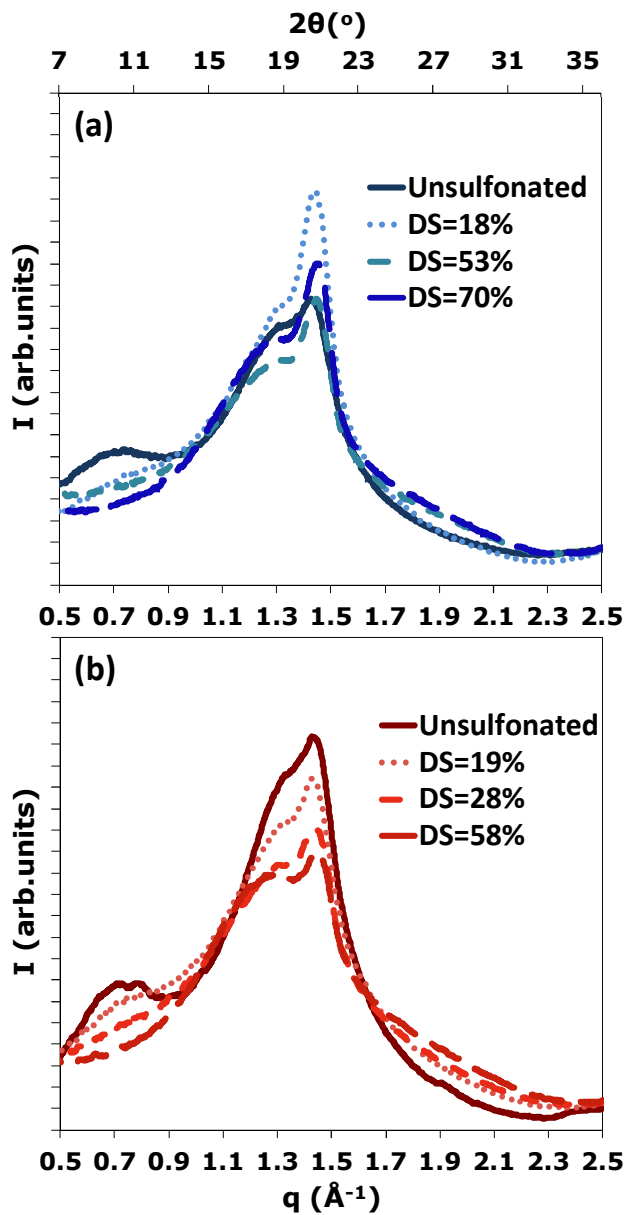


Figure S5: WAXS patterns of (a) $\text{P(VDF-co-CTFE}_{2.6\text{mol}\%})\text{-g-PS}_{39}$ and (b) $\text{P(VDF-co-CTFE}_{2.6\text{mol}\%})\text{-g-PS}_{62}$.

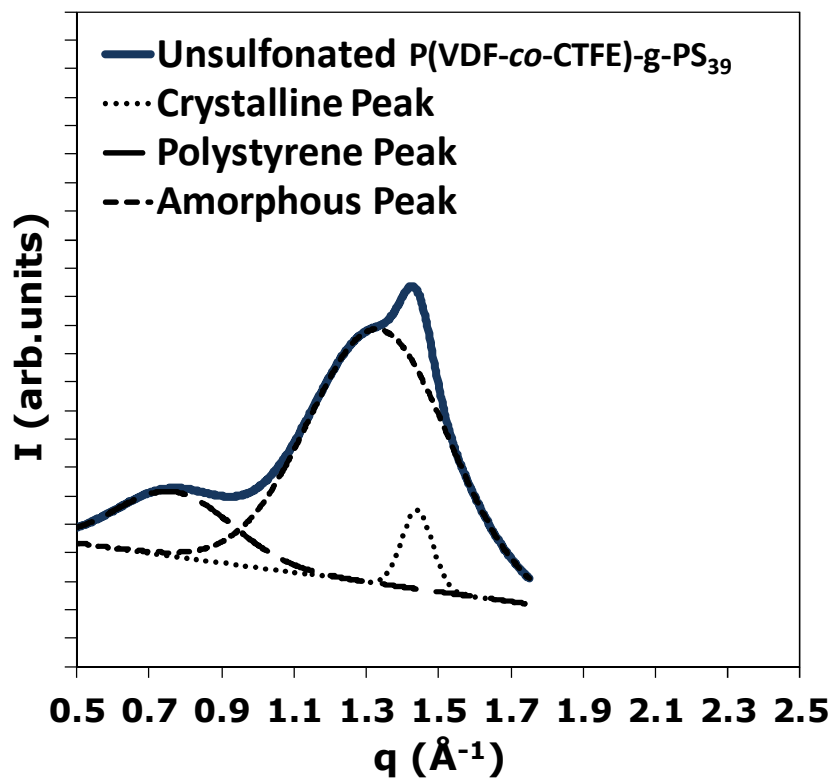


Figure S6: WAXS spectrum of the graft polymer P(VDF-co-CTFE_{2.6mol%})-g-SPS₃₉. Three Gaussian curves were fit to the data in order to estimate the degree of crystallinity.

Table S2: Degree crystallinity of P(VDF-*co*-CTFE_{2.6mol%})-*g*-PS copolymers

Sample	DS (%)	IEC (mmol/g)	Degree of Crystallinity (%)
P(VDF- <i>co</i> -CTFE _{2.6mol%})- <i>g</i> -PS ₃₉	0	-	6.7 ± 1.0
	18	1.12	12.6 ± 1.5
	53	2.27	11.5 ± 0.2
	70	3.02	12.5 ± 0.6
P(VDF- <i>co</i> -CTFE _{2.6mol%})- <i>g</i> -PS ₆₂	0	-	6.4 ± 0.3
	19	1.23	6.8 ± 0.1
	28	2.00	6.5 ± 0.5
	58	3.07	5.8 ± 0.1
P(VDF- <i>co</i> -CTFE _{2.6mol%})- <i>g</i> -PS ₇₉	0	-	5.6 ± 0.2
	12	0.74	6.6 ± 0.6
	30	1.81	5.7 ± 0.1
	33	2.05	5.6 ± 0.4
	56	2.91	-

Table S3: Average diameter and 2-D number density of ion-rich domains for representative P(VDF-*co*-CTFE_{2.6mol%})-*g*-SPS membranes

Image label	IEC (mmol/g)	DS (%)	Ionic domain diameter (nm)	2-D cluster number density (per 10 ⁴ nm ²)
P(VDF- <i>co</i> -CTFE _{2.6mol%})- <i>g</i> -SPS ₃₉				
A	1.12	18	2.5 ± 0.4	86 ± 5
B	3.52	100	3.8 ± 0.6	56 ± 3
P(VDF- <i>co</i> -CTFE _{2.6mol%})- <i>g</i> -SPS ₆₂				
C	1.23	19	2.3 ± 0.3	104 ± 7
D	4.05	100	4.1 ± 0.7	55 ± 2
P(VDF- <i>co</i> -CTFE _{2.6mol%})- <i>g</i> -SPS ₇₉				
E	1.35	23	2.5 ± 0.4	126 ± 6
F	4.29	100	4.7 ± 0.6	53 ± 1

Table S4: Properties of P(VDF-*co*-CTFE)-*g*-SPS graft copolymer membranes having different amount of CTFE

Membrane	IEC ^a (mmol/g)	Water uptake ^b (%)	Water content ^b (%)	λ	Conductivity (mS/cm) ^c	[-SO ₃ H] (M)	$\mu_{\text{est}} \times 1000$ (cm ² /sV)
P(VDF- <i>co</i> -CTFE _{2.6mol%})- <i>g</i> -SPS ₃₉	1.12 ± 0.01	18 ± 1	15 ± 1	9 ± 1	8 ± 1	1.07 ± 0.01	0.07
	1.72 ± 0.04	47 ± 6	32 ± 1	15 ± 1	47 ± 2	1.34 ± 0.04	0.37
	2.27 ± 0.07	155 ± 8	61 ± 1	38 ± 2	72 ± 2	1.04 ± 0.07	0.77
	2.66 ± 0.06	211 ± 6	67 ± 1	45 ± 2	84 ± 11	0.89 ± 0.02	0.96
	3.02 ± 0.05	278 ± 25	73 ± 1	53 ± 4	77 ± 9	0.77 ± 0.02	1.03
	3.33 ± 0.08	788 ± 33	89 ± 1	136 ± 7	44 ± 2	0.39 ± 0.02	1.12
P(VDF- <i>co</i> -CTFE _{5.8mol%})- <i>g</i> -SPS ₃₅	0.64 ± 0.02	9 ± 1	8 ± 1	7 ± 1	2 ± 1	0.62 ± 0.02	0.03
	1.03 ± 0.04	21 ± 2	17 ± 1	11 ± 1	10 ± 3	0.82 ± 0.02	0.15
	1.22 ± 0.02	28 ± 1	22 ± 1	13 ± 1	40 ± 2	1.01 ± 0.01	0.41
	1.59 ± 0.02	89 ± 5	47 ± 3	31 ± 2	75 ± 6	0.89 ± 0.03	0.92
	1.98 ± 0.05	176 ± 5	63 ± 1	53 ± 3	83 ± 2	0.73 ± 0.01	1.18
	2.48 ± 0.06	358 ± 17	78 ± 1	80 ± 3	65 ± 1	0.52 ± 0.01	1.30

a. By titration. b. Room temperature. c. Soaked in H₂O overnight and pat-dried with a Kimwipe paper before measurements at room temperature. *Errors were calculated based on standard deviation of several experiments.