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ARTICLE TYPE

Supporting information

Enhancing the Phase Segregation and Connectivity of Hydrophilic Channels by Blending Highly Sulfonated Graft Copolymers with Fluorous Homopolymer

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Synthesis

Materials

The chemicals were purchased from Aldrich and used as received unless otherwise stated: vinylidene fluoride (VDF, +99%), chlorotrifluoroethylene (CTFE, 98%), pentadecafluorooctanoic acid (96%), 2,2-bipyridyl (bpy, +99%), Acetic anhydride (Aldrich, 99.5%), potassium persulfate (KPS, Allied Chemical, reagent grade), sodium metabisulfite ($Na_2S_2O_5$, Anachemia, anhydrous, reagent grade), 1,2-dichloroethane (DCE, Caledon, reagent grade), N-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%), sulfuric acid (Anachemia, 95-98%, ACS reagent). Copper(I) chloride (CuCl, 99%), copper(II) chloride ($CuCl_2$, 99.999%) were purified according to literature[31]. Styrene (St, +99%) was washed twice with 5% aqueous NaOH and twice with water, dried overnight with $MgSO_4$, distilled over CaH_2 under reduced pressure, and stored under N_2 at -20 °C.

Synthesis of fluorous macroinitiators

The macroinitiator P(VDF-*co*-CTFE) was previously prepared by emulsion copolymerization of VDF and CTFE. In brief, the polymerization procedure is: To a 160 mL pressure vessel (Parr Instruments) equipped with a 4.14 MPa (600 psi) pressure relief valve and a magnetic stir bar was added a mixture of 100 mL water, 0.40 g KPS, 0.29 g $Na_2S_2O_5$ and 0.04 g pentadecafluorooctanoic acid. A mixture of VDF and CTFE of predetermined composition was then introduced to the reactor, thereby reaching a constant pressure of 2.07 MPa (300 psi) at 60 °C. The polymerization was carried out for 60 to 90 minutes. Freezing, followed by washing with water and ethanol, coagulated the resulting polymer latex. The crude polymer was purified by repeated dissolution in THF and re-precipitation in ethanol, followed by drying at 80 °C under vacuum for 24 hours.

ATRP-grafting of styrene

P(VDF-*co*-CTFE)-*g*-PS was synthesized by ATRP, with the chlorines of the macroinitiator serving as initiating sites for the monomer. P(VDF-*co*-CTFE)-*g*-PS with 1.1 mol % CTFE was synthesized as follows. 0.9996 g P(VDF-*co*-CTFE) was dissolved in 40 mL NMP in a predried round bottom flask, then 3.0009 g bpy, 40 mL styrene, 0.6406 g CuCl, and 0.0887 g $CuCl_2$ were added. The flask was sealed tight with a septum and degassed over three freeze-pump-thaw cycles to remove oxygen and water from the reactor. The reaction mixture was heated in oil bath under a blanket of nitrogen at 110 °C for a total reaction time of 45 hours. The resulting brown polymer mixture was precipitated in methanol to yield solid polymers. Soxhlet extraction with cyclohexane was performed to remove PS homopolymer. Hereafter followed a final precipitation from methanol.

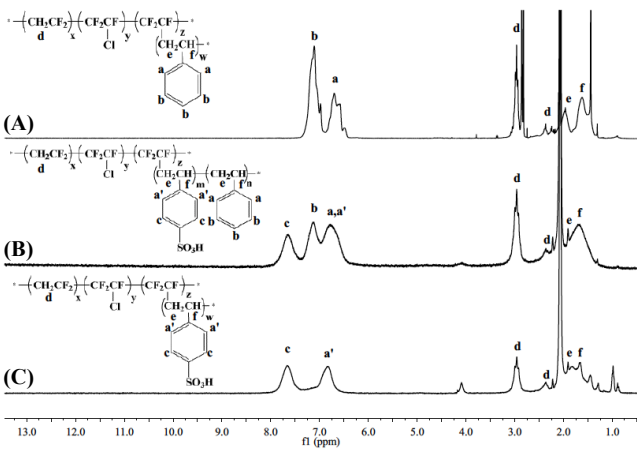

Fig. S1 ^{1}H NMR spectra of graft polystyrene of (A) pristine $Graft_{2.6\text{-}L}$ (B) partially sulfonated $Graft_{2.6\text{-}L}$ (DS = 56%) and (C) fully sulfonated $Graft_{2.6\text{-}L}$.

Membrane Properties

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Table S1 Properties of $Graft_{1.1}$ and blend membranes.

Sample	IEC (mmol g^{-1})	Water uptake (wt%)	[H2O]/[SO_3^-]	Conductivity (mS cm^{-1})	[-SO_3H] (M)	$\mu_{estx1000}$ (cm^2 sV^{-1})
$Graft_{1.1}$	1.10±0.07	192±28	62	46±3	0.77±0.04	0.63
SB40-60	1.22±0.18	66±2	30	63±3	0.71±0.02	0.92
MB40-60	1.31±0.10	98±3	41	62±1	0.68±0.08	0.95
LB40-60	1.15±0.09	91±9	44	62±4	0.72±0.01	0.89
SB25-75	0.60±0.02	32±10	29	48±6	0.97	0.51
MB25-75	0.75±0.09	40±3	30	49±5	0.90	0.57
LB25-75	0.64±0.02	25±3	21	51±6	0.90	0.59

Table S2 Properties of partially and fully sulfonated $Graft_{2.6}$. Data has previously been reported.[28]

Sample	IEC[a] (mmol g^{-1})	DS (%)	Water uptake[b] (wt%)	Water content[b] (wt%)	[H2O]/[SO_3^-]	Conductivity[c] (mS cm^{-1})	[-SO_3H] (M)	$\mu_{estx1000}$ (cm^2 sV^{-1})
P(VDF-*co*-CTFE)-*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
	$3.52_{theoretical}$	99	1790±55	96±1	283	41±3	0.30±0.08	1.42±0.03
P(VDF-*co*-CTFE)-*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
	$4.05_{theoretical}$	99	Partially dissolve in water		-	-	-	-
P(VDF-*co*-CTFE)-*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
	$4.29_{theoretical}$	99	Partially dissolve in water		-	-	-	-

[a] By titration. [b] Room temperature. [c] Soaked in H_2O overnight and dabbed with tissue prior to measurements at room temperature* Errors were calculated as standard deviations over multiple measurements.