Supplementary Material (ESI) for Polymer Chemistry

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Supporting Information for RAFT polymerization and thermal behavior of trimethylphosphonium polystyrenes for anion exchange membranes†

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NMR Characterization of polymers

Polymers were isolated by precipitation into a solution of 30% isopropanol in n-hexane, and were further purified by dialysis in methanol using a 3500 Da cutoff membrane (MFR). The polymers were isolated and dried in a vacuum dessicator, and were then taken into deuterated methanol (MeOD, ca. 100 mg/mL). Spectra were recorded on a Bruker 600 MHz Avance spectrometer, referenced to the residual solvent peak (3.34 ppm), 256 scans with 2 d1 delay. Spectra were analyzed using MestReNova from MestreLab Research.

Sample	Raw Integrations				Calculated Contribution					
	Methyl	Aliphatic	Benzyl	Arom.	n_{benzyl} [1]	CF_{aro} [2]	CF_{aliph} [3]	n_{aro} [4]	n_{aliph} [5]	M_n kDa
10%	3.00	116.48	7.99	132.02	3.99	15.98	47.94	23.21	22.85	3.3
20%	3.00	257.96	24.40	223.18	12.20	48.80	146.40	34.88	37.19	6.6
30%	3.00	379.86	41.79	270.70	20.90	83.58	250.74	37.42	43.04	9.2
40%	3.00	519.82	64.10	313.65	32.05	128.20	384.60	37.09	45.07	12
50%	3.00	711.45	94.08	376.87	47.04	188.16	564.48	37.74	48.99	15
100%	3.00	1200.76	187.42	386.55	93.71	374.84	1124.52	2.34	25.41	21

1. Number of ionic repeat units, determined from Benzyl integration , divided by 2H.
2. Ionic repeat unit contribution to aromatic signal, obtained by multiplying n_{benzyl} by 4H.
3. Ionic repeat unit contribution to aliphatic signal, obtained by multiplying n_{benzyl} by 12H (3H from backbone, 9H from phosphonium salt).
4. Styrene repeat units, obtained from the Aromatic Raw Integration less the CF_{aro}, divided by 5H (aromatic protons).
5. Styrene repeat units, obtained from the Aliphatic Raw Integration less the CF_{aliph}, divided by 3H (backbone protons).

Average ion content, average degree of polymerization, and average M_n were obtained by calculating the ion content, DP, and M_n from the aromatic signal, from the aliphatic signal, and then averaging the two contributions. This results a slight discrepancy in each calculated value. The average deviation from the mean is reported below as an approximate measure of error in the ion content, DP, and M_n. Due to discrepancies in the measured aromatic and aliphatic

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contributions for the 100% sample, only the ion content calculated from the aromatic and benzylic signals is reported below.

Average ion content (mol %)	Average DP	Average M_n (kg/mol)
14.8 ± 0.10	27 ± 0.18	3.3 ± 0.019
25.0 ± 0.52	48 ± 1.0	6.5 ± 0.10
34.5 ± 1.7	61 ± 3.0	8.9 ± 0.31
44.0 ± 2.4	73 ± 4.0	12 ± 0.42
52.1 ± 3.2	91 ± 5.5	15 ± 0.57
97.6	108 ± 11	23 ± 1.2

A spectral plot for each polymer is provided on the following pages.

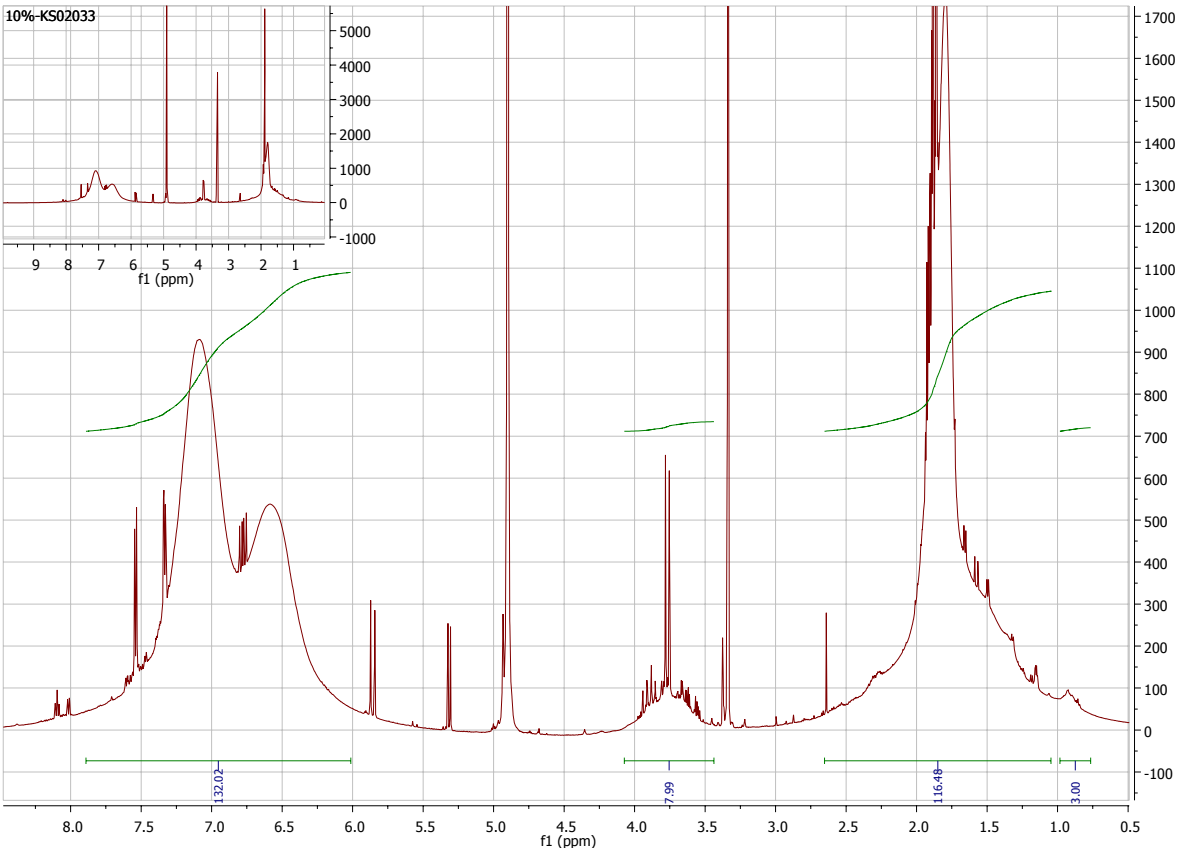

Figure 1: Polymer 3a, 10% ion content spectral scan.

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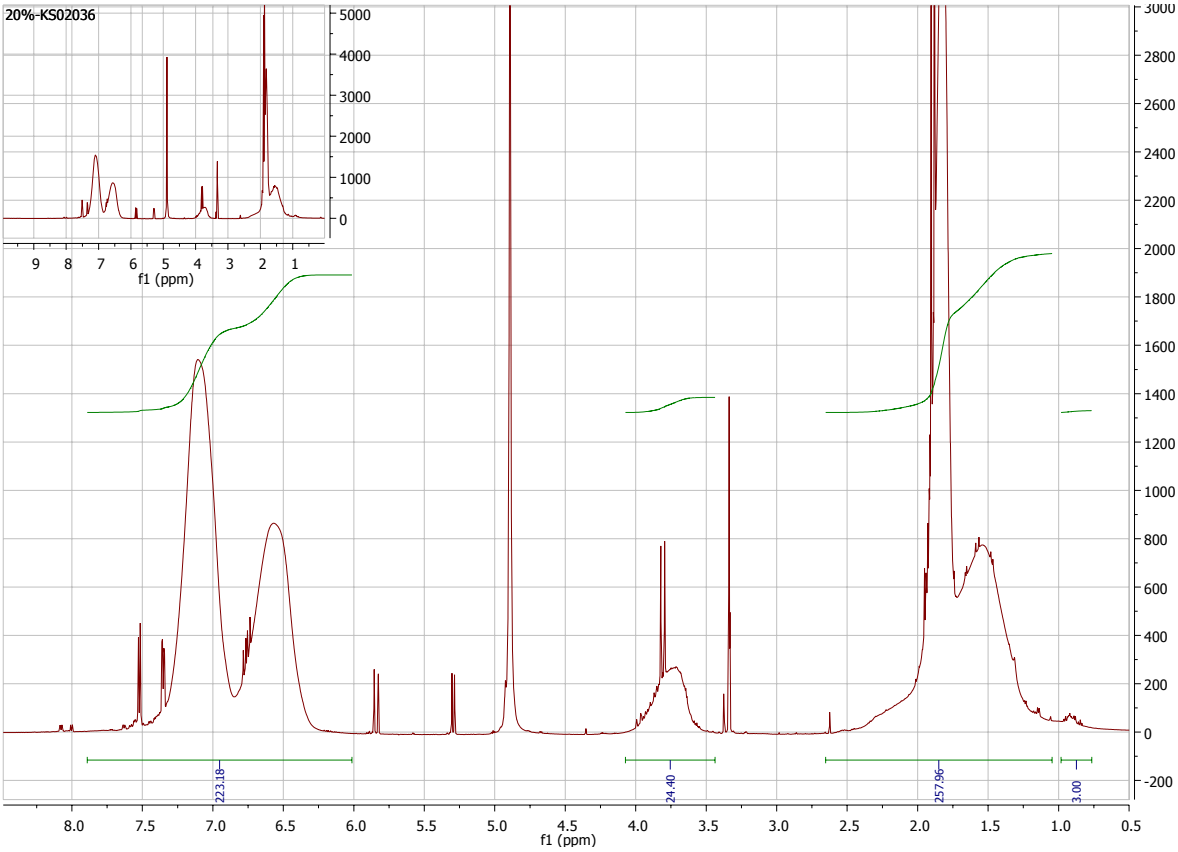

Figure 2: Polymer 3b, 20% ion content spectral scan.

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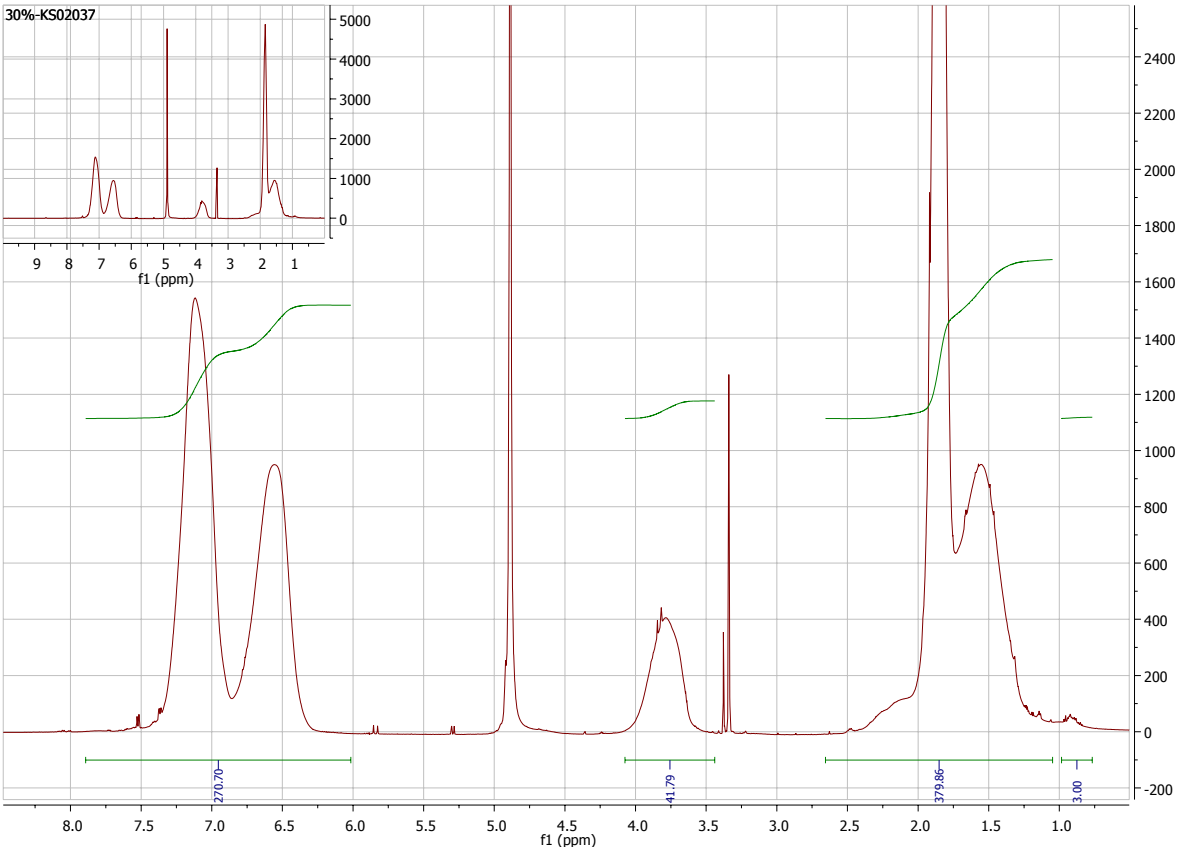

Figure 3: Polymer 3c, 30% ion content spectral scan.

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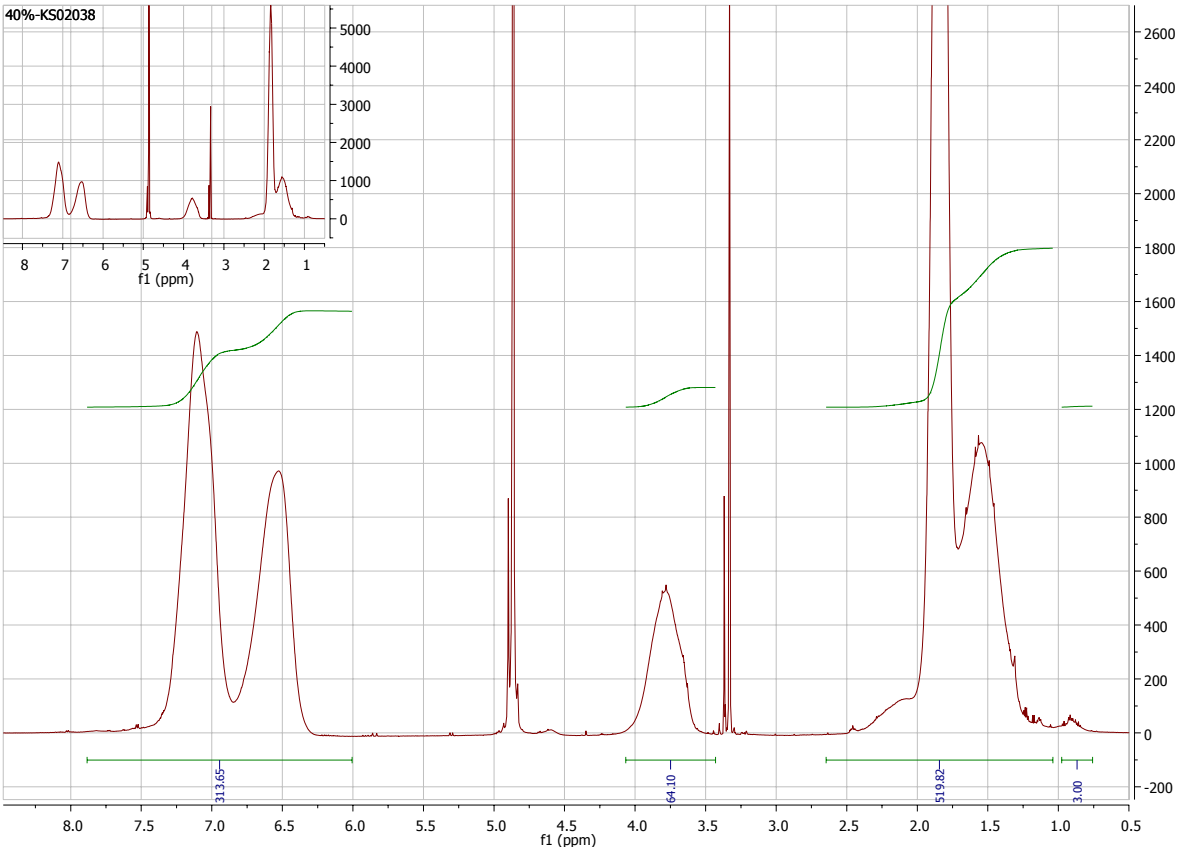

Figure 4: Polymer 3d, 40% ion content spectral scan.

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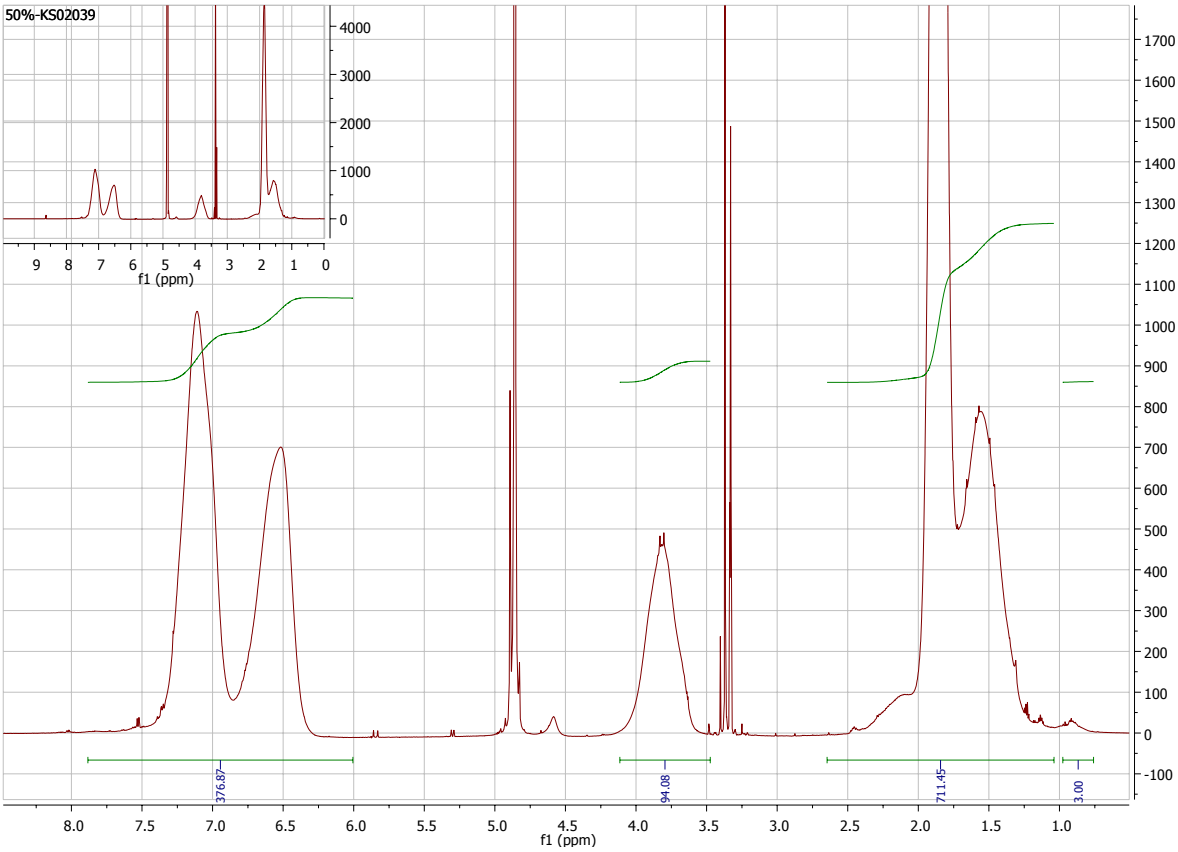

Figure 5: Polymer 3e, 50% ion content spectral scan.

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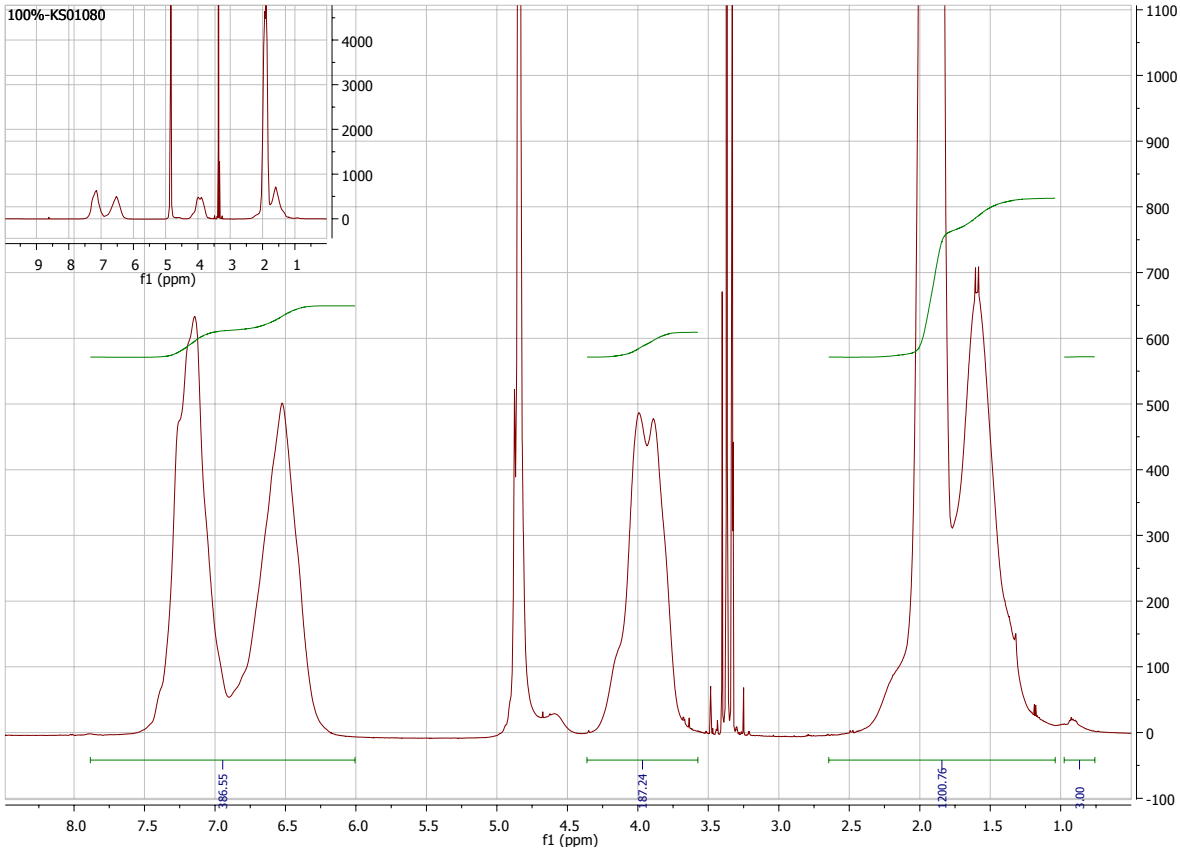

Figure 6: Polymer 3f, 100% ion content spectral scan.

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Analysis of Glass Transition Behavior

The Gordon-Taylor-Wood theory was used to analyze the glass transition behavior of the copolymer. In order to fit the data, a T_g of 82 °C was used for pure polystyrene, consistent with the relative low molecular weights of these materials. Least squares fitting was performed using Wavemetrics Igor Pro 6.2. The following fitting parameters were found: $T_{g,PS} = 79 \pm 7.5$ °C, $T_{g,98\ mol\%\ ionomer} = 272 \pm 7.0$ °C, and K = 3.7852, where K is the constant parameter defined in the Gordon-Taylor-Wood model.