# Polyethylene Based Block Copolymers for Anion Exchange Membranes

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## Supporting Information:

### Bromination of P4MS homopolymer

The bromination of the poly(4-methylstyrene) was accomplished using NBS and BPO following a modified literature procedure.[1-3] P4MS (0.3556 g, 3.00 mmol 4-methylstyrene repeat units) was weighed into a two neck 50 mL round bottom flask equipped with a magnetic stirbar, a condenser, and an argon bubbler. Carbon tetrachloride (15 mL) was added to form a suspension. The reaction flask was immersed in an oil bath and heated to 72 °C. The mixture was stirred until the copolymer dissolved. AIBN (0.0075 g, 0.045 mmol) was added followed by NBS (0.481 g, 2.70 mmol, 90 mol% to the amount of 4-methylstyrene) under argon flow. The solution was refluxed and allowed to stir for 24 hrs during which the solution turned yellow. The hot solution was precipitated into excess methanol, filtered, and the yellow powder was washed with deionized water to remove byproducts. The product was filtered and dried in the vacuum oven at 80 °C overnight.

### Results

Bromination of the backbone tertiary benzylic carbon could be in competition with the bromination of the 4-methyl group of the P4MS as previous research has demonstrated that polystyrene can be brominated at the tertiary benzylic site.[4] A model reaction to brominate the P4MS homopolymer was examined in order to determine the conditions for the bromination of 4-MS repeat units in the block copolymer. The reaction was carried out in the presence of AIBN with less than the stoichiometric amount for full conversion ([NBS]/[4-methyl group] = 0.9/1

molar ratio) in order to ensure selective bromination of the 4-methyl group without reacting at the tertiary benzylic protons on the backbone. $^{1}$H NMR spectroscopy was used to evaluate the reaction (Figure S1). The intensity of the peak corresponding to the 4-methyl groups at 2.07-2.51 ppm reduces after bromination while a new peak appears at 4.20-4.76 ppm representing the formation of benzyl bromide groups. The degree of bromination reaction can be calculated based on the integration ratio between benzyl bromide groups and aromatic groups. Furthermore, the integration ratio between methylene protons (1.34 – 1.64 ppm) and the tertiary benzylic proton (1.64 – 2.05 ppm) on the backbone remained the same after the bromination reaction. We speculate that the less sterically hindered 4-methyl group is the preferred site for hydrogen atom abstraction with a less than equivalent amount of NBS. From the results, it is expected that the reaction could be used to quantitatively synthesize the PE-b-PVBBr block copolymers with only 4-methyl groups brominated.

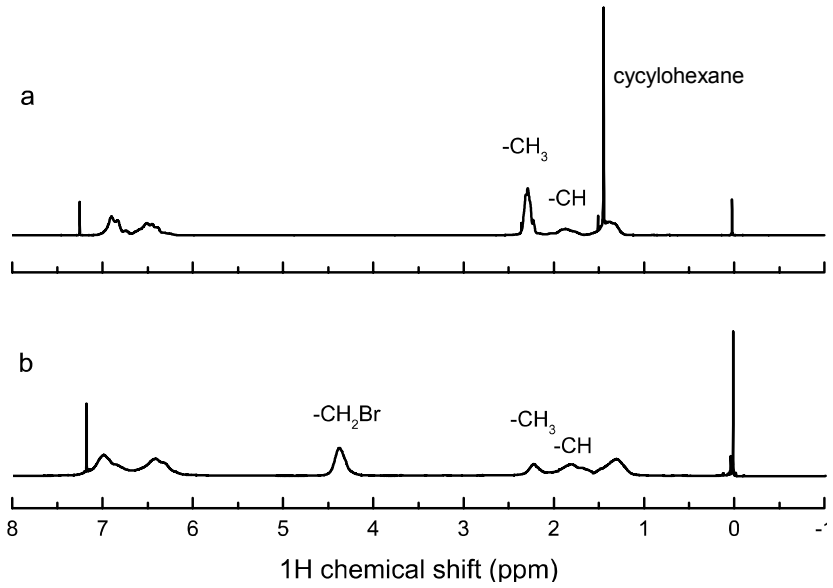


**Figure S1.** $^{1}$H NMR spectra of (a) P4MS homopolymer and (b) P4MS after bromination reaction

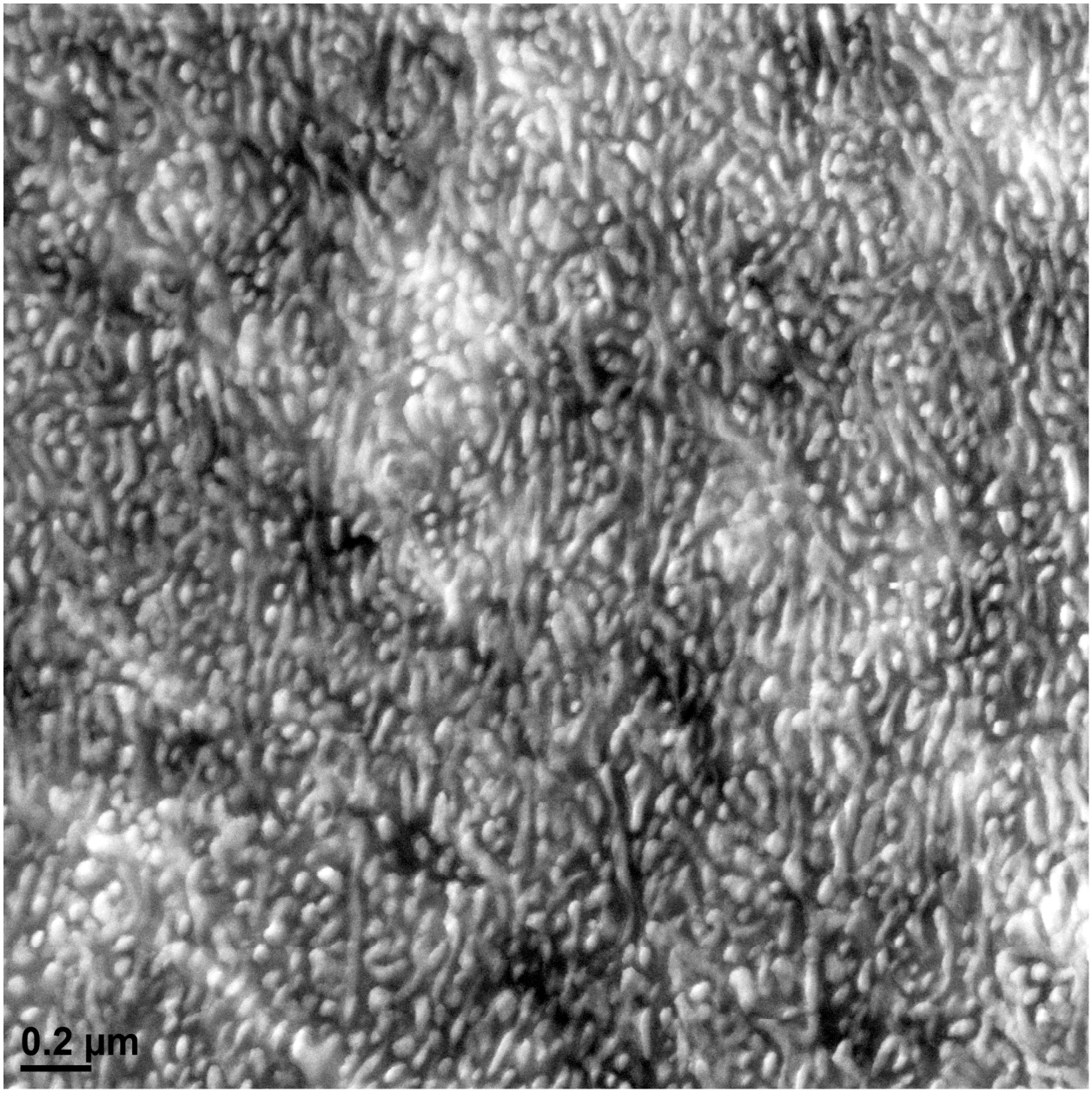


**Figure S2.** Transmission Electron Micrograph of Sample D (scale bar = 0.2 μm)

References

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