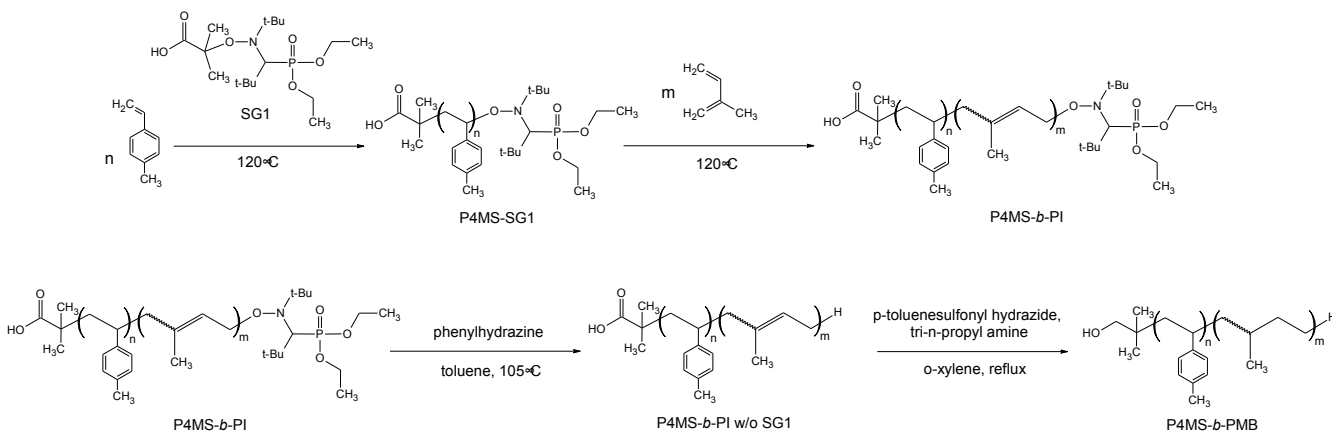


Supporting Information – for review only extracted from [1]

Summary of the preparation of the [PVBTMA] [Br] -b-PMB anion-exchange membranes (AEMs)

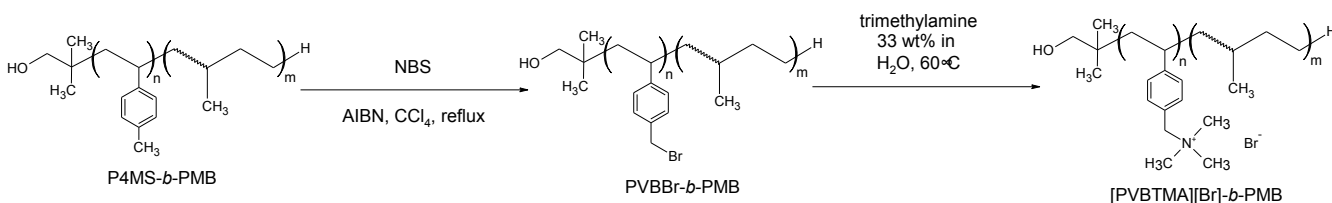
4-methyl styrene (4MS) is homopolymerized through nitroxide-mediated polymerization at 120°C adopting SG1 as the catalyst. The product (P4MS-SG1) is recovered by precipitation in methanol and re-dissolved in isoprene. The reaction mixture is brought to 120°C; P4MS-SG1 undergoes chain extension, yielding poly (4-methyl styrene) -*block*-poly (isoprene) (P4MS-*b*-PI). In a subsequent step, the end groups are removed by reacting P4MS-*b*-PI with phenyl hydrazine in toluene at 105°C; the product is hydrogenated with *p*-toluene sulfonylhydrazide and tri-*n*-propylamine under reflux using *o*-xylene as solvent. Poly (4-methyl styrene) -*block*-poly (methyl butylene) (P4MS-*b*-PMB) is thus obtained. The procedure for the preparation of P4MS-*b*-PMB is shown in Scheme S1.



Scheme S1. Preparation procedure of P4MS-*b*-PMB.

The functionalization of P4MS-*b*-PMB with anion-exchange groups is carried out as follows. P4MS-*b*-PMB diblock copolymer is dissolved in CCl₄; *N*-bromosuccinimide

(NBS) and azo-bis-isobutyronitrile (AIBN) are added as the brominating agent and the radical initiator, respectively. The reaction mixture is refluxed for two hours; the recovered product is recast on a Teflon sheet, yielding a poly (vinylbenzyl bromine) - *block*-poly (methyl butylene) (PVBBBr-*b*-PMB) precursor membrane. The obtained membrane is immersed in 33 wt% aqueous trimethyl amine (TMA) at 60°C, yielding the final poly (vinylbenzyltrimethyl ammonium bromide) -*block*-poly (methylbutylene) [PVBTTMA] [Br] -*b*-PMB AEMs. Scheme S2 outlines the functionalization of P4MS-*b*-PMB with anion-exchange groups to yield the final [PVBTTMA] [Br] -*b*-PMB AEMs.



Scheme S2. Functionalization of P4MS-*b*-PMB with anion-exchange groups.

1. Tsai, T.-H., *Ionic Copolymers for Alkaline Anion Exchange Membrane Fuel Cells (AAEMFCs)*, in *Polymer Science and Engineering*. 2013, University of Massachusetts, Amherst: Amherst, MA.