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Supporting Information:

Increased Ion conduction in Dual Cation [Sodium][Tetraalkylammonium] Poly[4-styrenesulfonyl(trifluoromethylsulfonyl)imide-*co*-ethylacrylate] Ionomers

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Solution nuclear magnetic resonance (NMR) spectroscopy analysis was performed to analyze the composition of the dual-cation ionomers and to shed light on the structure information of these ionomers. Fig. S1 displays the ^1H NMR spectra of **N_{1222}(a)**, **N_{1222}(b)** and **N_{1444}**. It is noted that these ionomers show similar characteristic chemical shifts at around 7.8 ppm for the protons of Ar*H*, 1.5 ppm for $-CHCH_2-$ and $-OCH_2-$ and 4.0 ppm for $-OCH_2-$, and 1.0 - 3.2 ppm for ammonium peaks. The chemical shifts of aryl protons and acrylate protons of the dual-cation ionomers lie close to those of sodium poly(4-styrenesulfonyl)(trifluoromethanesulfonyl)imide based polymers in our previous study and to those of sodium (4-styrenesulfonyl(perfluorobutylsulfonyl)imide, where perflurorobutyl group is a stronger electron with-drawing group compared to the trifluoromethane group in STFSI.[1, 2] It is understandable that those bulky alkylammonium ions are dissociated, as a result of the weak interaction between them and the anionic polymer backbone.[3] Moreover, it is noted that there are upfield shifts for the ammonium protons in **N_{1222}(b)**, compared to those of **N_{1222}(a)**, where the EA has higher concentration. A similar NMR trend was also observed for the quaternary ammonium ions, hosted by sulfonated calixarene derivatives, where there are electrostatic and π-cation interactions between the aryl groups of calixarenes and ammonium cations.[4, 5]

The peaks for aryl protons (Ar*H*) at about 7.8 ppm, acrylate protons ($-OCH_2-$) at 4.0 ppm and ammonium protons ($-OCH_3$) at 2.9 ppm were selected for the integration to compare the relative ratios of each component in the ionomers (Table S1), which has been adopted in our previous work.[6] The calculated ratio for Na^+, N_{1222}^+/N_{1444}^+ and EA are listed in Table S1. Despite of there being possibly at least +/-10% error in this NMR based estimation, it is noted that the polymer compositions are uniformly lower than the monomer batch compositions, suggesting that a fraction of the EA is not polymerized under these conditions, which may be due to a difference in the reactivity ratios as noted in our previous work[6] and by Feng et al. in the copolymerization reaction of lithium poly[(4-styrenesulfonyl)(trifluoromethanesulfonyl)imide] and methoxy-polyethylene glycol acrylate.[7]

Table S1. Mole ratios of each component in the ionomers (normalised by Na^+ content), Na^+ ratio and total cation ratio.

	Na^+	N_{1222}^+/N_{1444}^+	EA	%Na^+	%(Na^++N_{1222}^+/N_{1444}^+)
N_{1222}(a)	1	1.1	6.0	12%	26%
N_{1222}(b)	1	10.5	1.0	8%	92%
N_{1444}	1	9.7	0.9	9%	92%

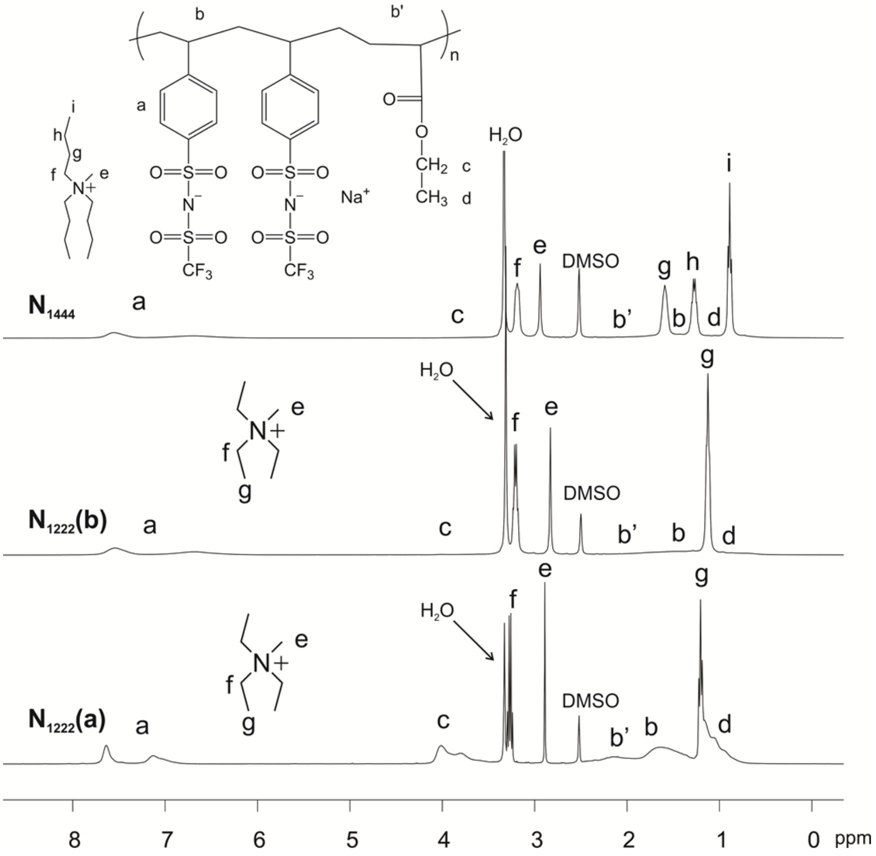

Fig. S1 ^{1}H NMR of the ionomers in DMSO-*d*6.

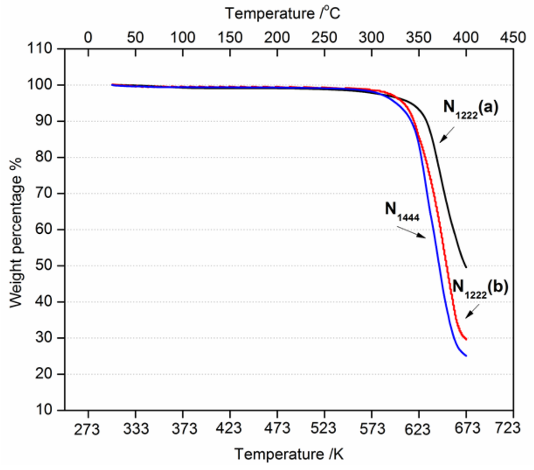

Fig. S2 Thermogravimetric analysis plots of the ionomers.

Thermogravimetric analysis was performed to study the ionomers in Fig. S2. It is noted that the ionomers show similar thermal stability over 573 K, which are quite thermally stable.

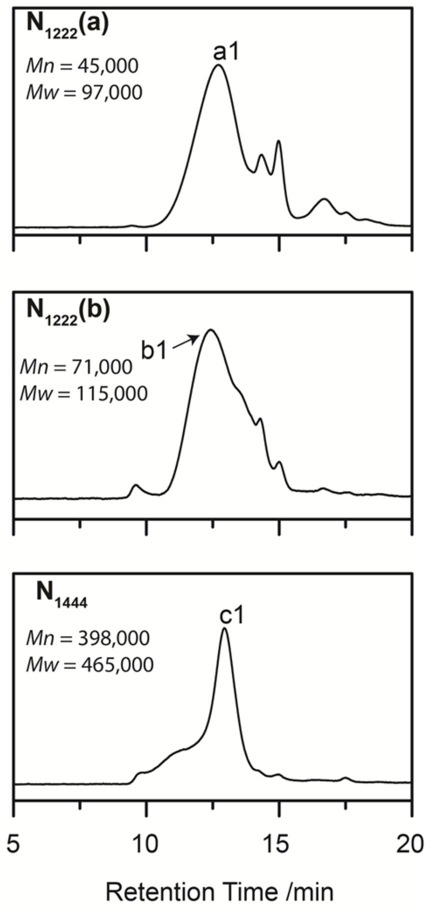

Fig. S3 Gel permeation chromatography results for the ionomers.

The mass average molecular weight (Mw) and number average molecular weight (Mn) of the ionomers were measured as illustrated in Fig. S3. The ionomers show wide molecular weight dispersity.

References:

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