Supporting Information for

Anion Exchange Membranes Based on Novel Quaternized Block Copolymers for Alkaline Direct Methanol Fuel Cells

Hsing-Chieh Lee[a], Kun-Lin Liu[a], Li-Duan Tsai,[b] Juin-Yih Lai[c] and Chi-Yang Chao[a]*

a. Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

b. Industrial Technology Research Institute, Material and Chemical Research Laboratories, Hsinchu, 31040, Taiwan

c. Chung Yuan Christian University, Department of Chemical Engineering and R&D Center for Membrane Technology, Chung-Li 32023, Taiwan

E-mail: cychao138@ntu.edu.tw

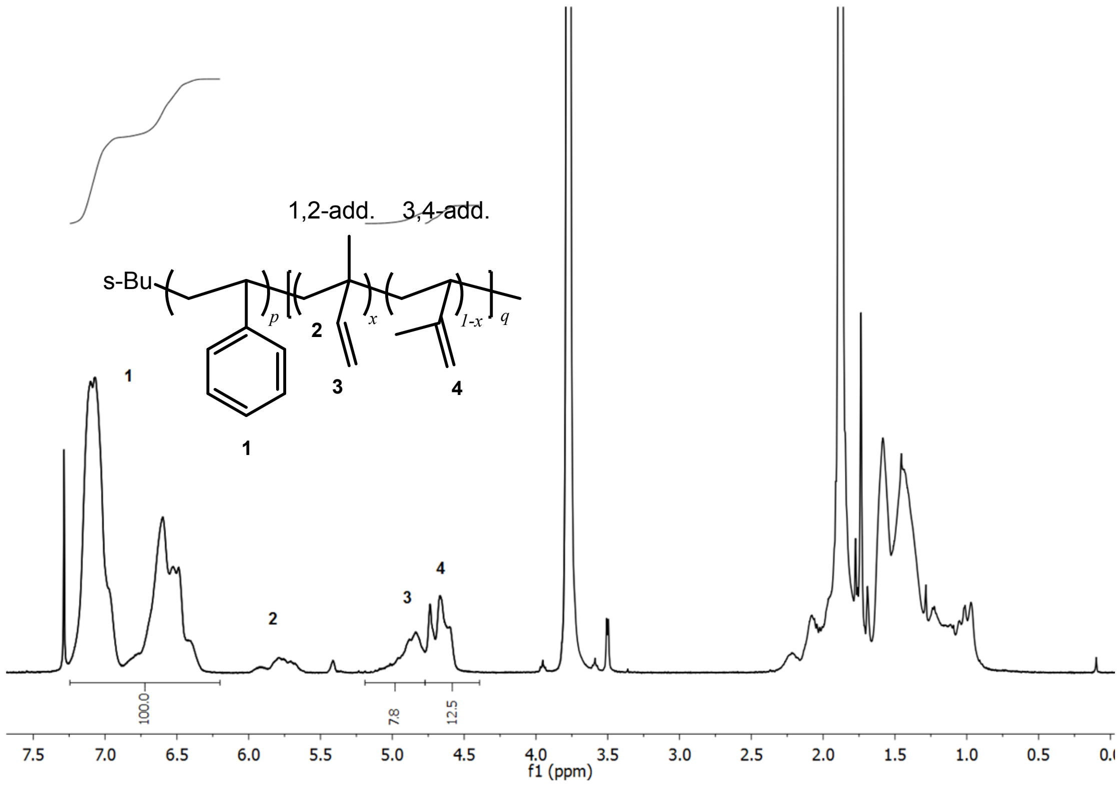

Fig. S1 ^{1}H NMR spectrum of SI21 in $CDCl_3$

Calculate the molecular weight of PI segment of PS-b-PI from ^{1}H NMR spectrum:

p (the number of repeating unit of PS) = 62700(molecular weight of PS obtained from GPC) / 104 (Formula weight of a repeating unit of polystyrene) = 603

Total number of hydrogens on the phenyl ring of the PS repeating units (denoted as hydrogen **1** on the spectrum) = 603 × 5 = 3015

Integral area for one hydrogen = 100 (integrals between 6.1~6.8 ppm for hydrogen **1**) / 3015 = (7.8 + 12.5) (integrals between 4.4~5.2 ppm for the terminal hydrogens of the pendant double bonds in PI, denoted as hydrogens **3** and **4**) / y (total number of hydrogens **3** and **4**)

➔ y = 612

q (the number of repeating unit of PI) = 612 / 2 = 306

Molecular weight of PI = $q \times 68$ = <u>20808</u>

Calculate the ratio of repeating units with 1,2-addition in PI (x) from ^{1}H NMR spectrum:

As shown in Fig. S1, x is the ratio of the number of repeating units with 1,2-addition to the number of all repeating units in PI.

$$x = \frac{\text{intergrals of hydrogen } \mathbf{3}}{\text{intergrals of hydrogen } \mathbf{3} \text{ and } \mathbf{4}} = \frac{7.8}{7.8 + 12.5} = 0.38$$

Calculate degree of quaternization (DQ) from elemental analysis

$$\text{DQ\%} = \frac{\text{experimental nitrogen(wt\%)/carbon(wt\%) from element alanalysis}}{\text{theoretical nitrogen (wt\%)/carbon (wt\%) based on 100\% DQ}} \times 100\%$$

The experimental and theoretical weight ratios of nitrogen to carbon (N/C) are listed in Table S1 where the experimental values were averaging from two elemental analysis experiments while the theoretical numbers were estimated based on 100% DQ as discussed below.

The ratio of the number of repeating units of PS to that of PIN in PS-b-PIN, is identical to the value for the parent PS-*b*-PI, i.e. p/q as p and q are the numbers in the formula shown in Fig. S1. Based on the assumption that all pendant double bonds are successfully converted to the quaternary ammonium groups, every repeating unit in PIN should contain one nitrogen. The molar number of N in PS-*b*-PIN is set to 1 and the molar number of C is the sum of the number of C (11) in a repeating unit of PIN and that of PS (8) times p/q. Hence, the molar ratio of N/C equals to $1/[11 + p/q \times 8]$. The theoretical weight ratio of N/C could be calculated from Eq. (S1):

$$\text{Weight ratio of } \frac{N}{C} = \frac{\text{molar number of N} \times \text{molar weight of N}}{\text{molar number of C} \times \text{molar weight of C}}$$

$$= \text{molar ratio of } \frac{N}{C} \times \frac{14}{12} \qquad \text{(S1)}$$

Table S1 Elemential analysis results and degree of quaternization of PS-*b*-PIN

Sample	Theroetical calculation			Elemental analysis			DQ (%)[c]	$100x$[d]
	Molar ratio of PS/PIN	Molar ratio of N/C[a]	Weight ratio of N/C[b] × 10^2	C (wt %)	N (wt %)	Weight ratio of N/C × 10^2		
SI9-N	4.46	1/46.68	2.50	74.1	0.35	0.47	19	27
SI14-N	2.76	1/33.08	2.84	77.3	0.68	0.88	31	31
SI21-N	1.97	1/26.76	4.36	70.03	1.26	1.81	41	38
SI31-N	1.34	1/21.72	5.37	67.28	1.69	2.51	46	41

[a] The molar ratio of N/C equal to 1N/[11C + (the molar ratio of PS to PIN) × 8C]

[b] Weight ratio of N to C = $\frac{\text{molar number of N} \times \text{molar weight of N}}{\text{molar number of C} \times \text{molar weight of C}} = \text{molar ratio of } \frac{\text{N}}{\text{C}} \times \frac{14}{12}$

[c] Calculated from the division of the weight ratio of N/C from elemental analysis by the theoretical weight ratio of N/C.

[d] x is the ratio of the repeating units in 1,2-addition.

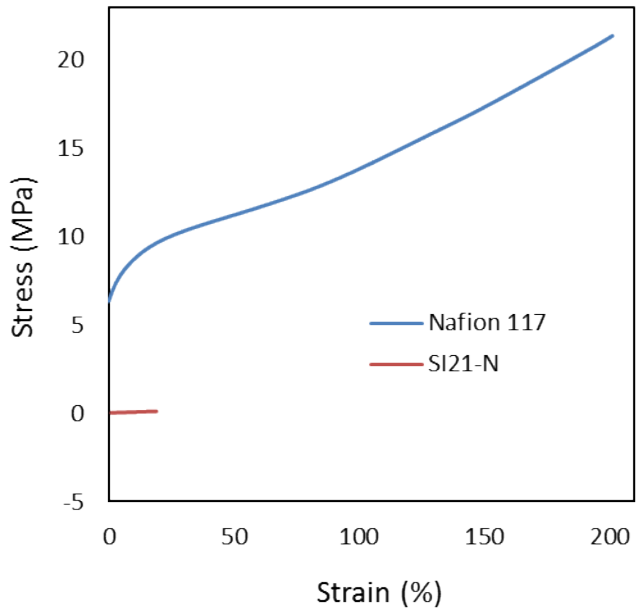

Fig. S2 The stress-strain curves of the membranes of Nafion 117 and SI21-N