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COMMUNICATION

Intrapolymer Heck reaction for proton conductive ladder-type aromatic block copolymers

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A novel polymer synthetic method, intrapolymer Heck reaction, provided ladder-type ionomer membranes with excellent proton conductivity (221 mS cm⁻¹ at 80 °C and 90% relative humidity) and mechanical strength over a wide range of humidity (ca. 0%-90% relative humidity) at 80 °C.

Aromatic polymers with acidic functions have gained attention for applications involving energy devices such as batteries, electrolyzers, fuel cells, and sensors. Considerable effort has been devoted in the last decade to develop proton conductive aromatic polymers for fuel cell applications, as alternatives to state-of-the-art perfluorinated ionomer membranes such as Nafion (du Pont).¹ Fluorine-free aromatic polymers are attractive in terms of high thermal stability, low gas permeability, low production cost, and environmental compatibility. Among a number of aromatic polymers, poly(arylene ether)s (PAEs) are probably most studied for proton exchange membranes (PEMs) because of their easy synthesis, versatility in molecular design, and good film-forming capability.²⁻¹⁰ It has been demonstrated that the hydrophilic and hydrophobic multiblock copolymer structure is effective in improving the proton conductivity due to the pronounced phase-separated morphology with interconnected ionic channels.¹¹ Mechanical strength is another crucial property for PEMs. Most PAE-based PEMs have high ion exchange capacity (IEC) values and therefore suffer from poor mechanical stability under humidified conditions.

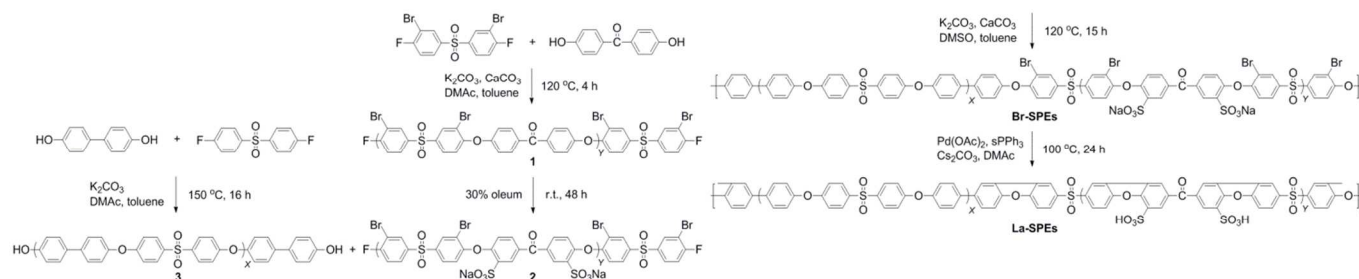
Our strategy to balance these countervailing properties is to include a ladder structure in the hydrophilic blocks. For this purpose, we focus on the intramolecular Heck reaction¹² which can convert quantitatively 2-bromophenyl phenyl ether moieties to the dibenzofuran ones. This reaction has been extensively utilized in organic syntheses as an effective route to numerous complex polycyclic ring systems, providing a wide variety of natural products and synthetically useful materials. It is expected that the application of this reaction to sulfonated PAEs could provide ladder-type aromatic ionomers, which should show much better membrane properties than those of the parent polymers. To the best of our knowledge, there have been

no such attempts. In this paper, we report for the first time an intrapolymer Heck reaction for the synthesis of ladder-type sulfonated aromatic block copolymers. The unique polymer structure, with rigid rod-like ladderized hydrophilic segments, improved both the proton-conducting properties and mechanical stability under conditions similar to those in practical fuel cell operation.

The title ladder-type sulfonated aromatic block copolymers (La-SPEs) were synthesized via the intrapolymer Heck reaction of the bromo-containing sulfonated aromatic block copolymers (Br-SPEs), as shown in Scheme 1. The question was whether the intrapolymer reaction proceeds selectively and quantitatively for high molecular weight polymers having sulfonic acid groups. First, the precursor Br-SPEs were synthesized from hydrophilic (sulfonated) and hydrophobic (unsulfonated) oligomers by nucleophilic substitution polymerization.¹³ The degree of polymerization of the hydrophobic block (X) was designed to be 5, and those of the hydrophilic blocks (Y) to be 5 and 10. The numbers of repeat unit in the obtained oligomers (calculated from the ¹H NMR spectra) were approximately the same as those obtained by the feed comonomer ratios. Details of the syntheses and characterization of the oligomers and Br-SPEs are available in ESI† (Figs. S1-S5, Table S1). Gel permeation chromatography (GPC) analyses (calibrated with polystyrene standards) revealed that Br-SPEs had high molecular weights ($M_w > 343$ kDa, Table 1). The apparent molecular weights obtained by GPC analyses with polystyrene standards could be overestimated since Br-SPEs (and the following La-SPEs) as rigid aromatic polymers with electric charges in the main chains would not form typical random coil configuration in the solutions. The IEC values obtained by titration were somewhat lower than those obtained by ¹H NMR spectra (calculated from the integral ratios of hydrophilic parts to hydrophobic parts), indicating that some of the sulfonic acid groups were inactive as ion-exchangeable sites.

Then, we conducted a polymer-type intramolecular Heck reaction of the Br-SPEs. Typical reaction conditions for low molecular weight compounds¹⁴ were applied to our polymer

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Scheme 1 Overall synthetic route to the target block copolymers.

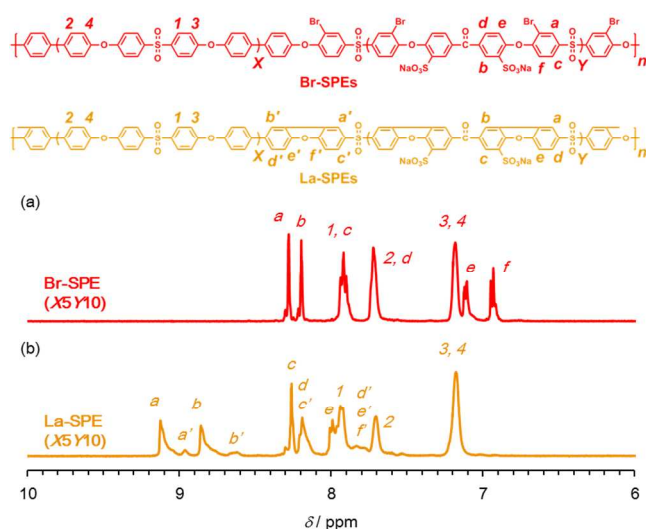


Fig. 1 ^1H NMR spectra of (a) Br-SPE (X5Y10) and (b) La-SPE (X5Y10) in sodium ion form in $\text{DMSO}-d_6$ at $80\text{ }^\circ\text{C}$.

system, where 5 mol% $\text{Pd}(\text{OAc})_2/\text{PPh}_3$ -derivative, Cs_2CO_3 , and DMAc were used as catalyst, base, and solvent, respectively. It should be noted that a water-soluble ligand, sodium-diphenylphosphino benzene-3-sulfonate (sPPh_3), was effective for the efficient removal of by-products derived from phosphine oxide. We have also paid attention to the polymer concentration; low concentration (10 mM for Br) was applied to promote a selective intrapolymer reaction and prevent an unfavorable interpolymer reaction. The chemical structure of the obtained La-SPEs was confirmed by ^1H NMR spectra. While the ^1H signals of the hydrophobic parts (protons 1-4) in La-SPE (Fig. 1b) appeared at the same chemical shifts as those of the precursor Br-SPE (Fig. 1a), those of the hydrophilic parts (protons a-e) in La-SPE were observed at lower field (for reference, the ^1H NMR chemical shift for 2-nitrodibenzofuran in the lowest field region appears at 8.88 ppm¹⁵), suggesting the selective and quantitative formation of fused dibenzofuran rings in the hydrophilic blocks. The dibenzofuran groups at the connecting parts (protons a'-f') can also be well assigned by

Table 1 Molecular weight and ion exchange capacity (IEC) of the block copolymers (Br-SPEs and La-SPEs)

SPEs	M_w^a (kDa)	M_w/M_n^a	IEC (meq g ⁻¹)		
			targeted	^1H NMR	titration
Br (X5Y5)	343	4.34	1.74	1.63	1.42
Br (X5Y10)	435	3.51	2.11	1.97	1.65
La (X5Y5)	317	4.88	1.88 ^b	1.75	1.60
La (X5Y10)	314	3.83	2.35 ^b	2.29	2.12

^a Determined by GPC analyses (calibrated with polystyrene standards). ^b Calculated from the observed IEC values (^1H NMR) of the corresponding precursor Br-SPEs.

comparing the normalized ^1H NMR spectra between two La-SPEs with different hydrophilic block lengths (Fig. S6a). There were no peaks that would indicate cross-linked structures via interpolymer reactions. The purity of the La-SPEs was confirmed by ^{31}P NMR spectra. It is known that triarylphosphine oxide derived by-products often contaminate the products and are difficult to remove in similar reactions (*e.g.*, Wittig¹⁶ and Mizoroki-Heck¹⁷ reactions). Such contaminants typically show peaks at ca. 25 ppm in the ^{31}P NMR spectra. The ^{31}P NMR spectra of La-SPEs after purification showed no phosphine species (Fig. S6c), indicating the complete removal of such compounds. The GPC profiles of La-SPEs were similar to those of the parent Br-SPEs, suggesting negligible interpolymer cross-linking reaction (Fig. S6d). As a reference, when the model oligomer **2a** was reacted under similar conditions, additional shoulders were observed at earlier retention times in the GPC profile (Fig. S7a). It is assumed that these shoulders of higher molecular weights are attributable to the interpolymer reactions of the terminal bromo groups. This was not the case for the Br-SPEs, because the terminal bromo groups were negligible in the high molecular weight polymers. Compared to other compounds, such high selectivity and conversion is rather surprising. It was reported

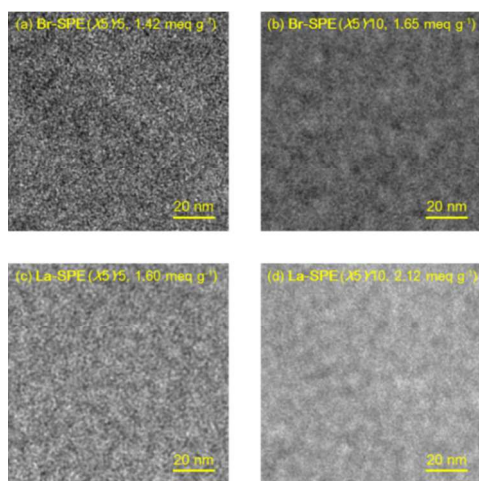


Fig. 2 TEM images of the membranes in lead ion form; (a) Br-SPE (X5Y5, 1.42 meq g⁻¹), (b) Br-SPE (X5Y10, 1.65 meq g⁻¹), (c) La-SPE (X5Y5, 1.60 meq g⁻¹), and (d) La-SPE (X5Y10, 2.12 meq g⁻¹).

that the modification of triarylphosphine with bulky electron-deficient ligands such as CF₃ groups preferred the intramolecular Heck reaction of low molecular weight compounds.¹⁸ In the present case, hydrophilic sPPh₃ with a sulfonic acid group might have functioned similarly, resulting in the excellent selectivity and conversion for the high molecular weight Br-SPEs. The obtained La-SPE polymers possessed high molecular weights ($M_w > 314$ kDa, GPC analyses, calibrated with polystyrene standards), slightly lower than those of the parent Br-SPEs. Despite containing a ladderized structure, the La-SPEs were soluble in polar organic solvents such as DMF, DMAc, and DMSO, and provided transparent membranes by solution casting. The IEC values of the La-SPEs obtained from the ¹H NMR spectra were in good agreement with those expected from the structure and copolymer composition. Similar to the Br-SPEs, the IEC values obtained by titration were slightly lower than those estimated from the ¹H NMR spectra.

The morphology of the Br- and La-SPE membranes was observed by transmission electron microscopy (TEM). In Fig. 2 are shown cross-sectional TEM images of the membranes in lead ion form, in which the dark areas correspond to hydrophilic domains. Hydrophilic–hydrophobic phase separation was observed for all membranes on the nanometer scale. In the image of Br-SPE (X5Y5, 1.42 meq g⁻¹) membrane, nearly spherical hydrophilic domains with diameters of ca. 1 nm were distributed throughout the field of view. In the image of Br-SPE (X5Y10, 1.65 meq g⁻¹) with higher IEC, the hydrophilic domains were larger, with diameters up to ca. 5 nm. The La-SPE membranes also showed phase-separated morphology, with attendant IEC dependence, similar to those of the Br-SPE membranes. Compared to our previous sulfonated aromatic block copolymer membranes,¹⁹ the La-SPE membranes showed somewhat less-developed phase separation, with smaller hydrophilic domains and less distinct interfaces between hydrophilic and hydrophobic domains, probably due to the rigid ladderized structure of the hydrophilic blocks. The results are essentially consistent with the IEC data mentioned above, in which the titration values were smaller than those obtained from the ¹H NMR spectra. It is considered that the phase-separated morphology could be more pronounced with increasing the humidity.

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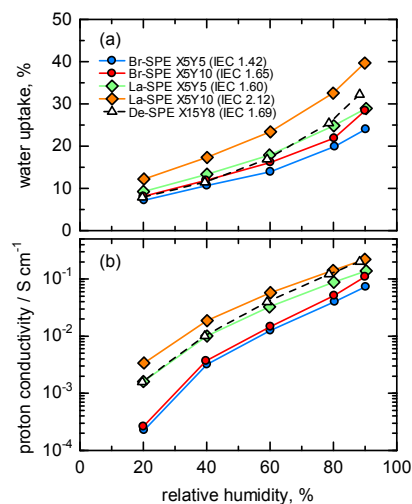
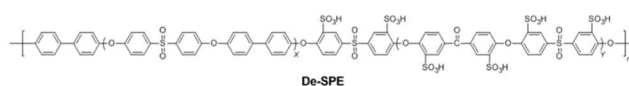


Fig. 3 (a) Water uptake and (b) proton conductivity of membranes at 80 °C as a function of relative humidity (RH). The IEC values are given in meq g⁻¹. De-SPE in the top is a reference polymer.

In Fig. 3 are shown the water uptake and proton conductivity of the Br-SPEs and La-SPEs membranes (in acid form) at 80 °C as a function of relative humidity (RH). Data are also included for our previous sulfonated block copolymer membrane (De-SPE),²⁰ which shares the hydrophobic blocks but does not contain bromo groups or a ladder structure. The water uptake approximately followed the order of the IEC values at all humidities. The numbers of absorbed water molecules per sulfonic acid group, often designated as λ , were 9.4 (Br-SPE X5Y5, 1.42 meq g⁻¹), 9.6 (Br-SPE X5Y10, 1.65 meq g⁻¹), 10.1 (La-SPE X5Y5, 1.60 meq g⁻¹), 10.4 (La-SPE X5Y10, 2.12 meq g⁻¹), and 10.6 (De-SPE X15Y8, 1.69 meq g⁻¹), respectively, at 90% RH (Fig. S8). The λ values were slightly lower for the Br-SPEs, presumably because the bromo groups lower the density of sulfonic acid groups and accordingly the local hydrophilicity in the hydrophilic domains. The proton conductivity of the membranes was dependent on both the structure and IEC value. The general trend is, as expected, that the higher IEC membranes are more proton-conductive. The results are reasonable, taking the higher acid concentration and higher water uptake into account. The proton conductivities decreased in the order La-SPE \approx De-SPE > Br-SPE. It should be noted that the La-SPE membrane showed significantly higher proton conductivity than that of the Br-SPE membrane over a wide range of humidity; compare the conductivity between Br-SPE (X5Y10, 1.65 meq g⁻¹) and La-SPE (X5Y5, 1.60 meq g⁻¹) sharing similar IEC value. The highest proton conductivity obtained for La-SPE (X5Y10, 2.12 meq g⁻¹) was 3.38 mS cm⁻¹ at 20% RH and 221 mS cm⁻¹ at 90% RH. La-SPE membrane showed relatively high proton conductivity at 120 °C (Fig. S9). The slightly lower conductivity at higher temperature was caused by lower water uptake at 120 °C.

It is anticipated that polymers with rigid rod-like structures such as La-SPE tend to provide brittle membranes. The dynamic mechanical properties of the membranes were investigated under changing humidity conditions at 80 °C (Fig. 4). Sulfonated aromatic polymers often show significant dependence of the dynamic mechanical properties on the

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humidity, because the absorbed water acts as a plasticizer. As a typical example, the De-SPE membrane showed a large drop in storage (E') modulus and a clear peak in $\tan \delta$ (possible glass transition) at ca. 57% RH. In contrast, the Br-SPE membranes showed much higher E' values than that of the De-SPE membrane at high RH and maintained this over a wide range of humidity. The La-SPEs membranes showed even better dynamic mechanical properties, with slight dependence on the humidity. The storage modulus of La-SPE (X5Y5, IEC = 1.60 meq g⁻¹) was 1.2×10^9 Pa at 90% RH, which was 3 times higher than that of Br-SPE (X5Y10, IEC = 1.65 meq g⁻¹) and 12 times higher than that of De-SPE (X15Y8, IEC = 1.69 meq g⁻¹). La-SPE (X5Y10), with a higher IEC (2.12 meq g⁻¹), for which the water uptake was the highest, also showed very little dependence of the mechanical properties on the humidity. These results imply that the ladderization of the hydrophilic blocks makes the polymer main chains rigid and restricts the molecular motion, resulting in the favorable mechanical properties, irrespective of the absorbed water. We have then measured tensile strength of La-SPE membrane at 80 °C and 60% RH by a universal testing instrument (Fig. S10). La-SPE (X5Y5) membrane showed moderate mechanical strength (21 MPa stress at break point, 79% strain at break point, and 0.54 GPa Young's modulus), which was comparable to the existing PAE-based PEMs.

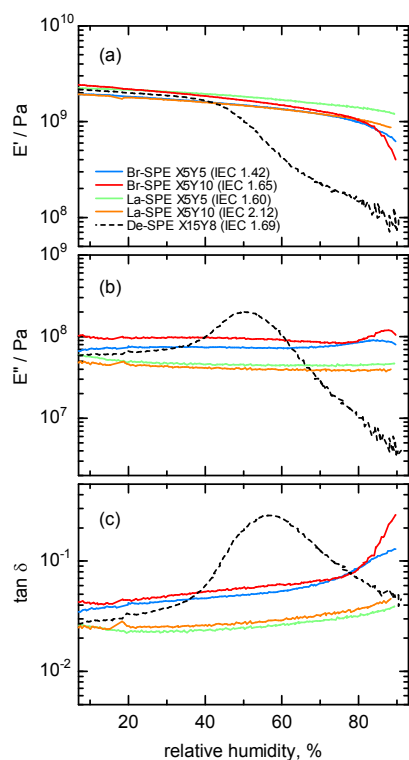


Fig. 4 DMA analyses of the membranes; (a) E' (storage modulus), (b) E'' (loss modulus), and (c) $\tan \delta$ at 80 °C as a function of RH. The IEC values are given in meq g⁻¹.

In conclusion, we have developed a novel synthetic method for ladder-type aromatic polymers via a highly selective and quantitative intrapolymer Heck reaction. The obtained ladder-type ionomers showed good solubility in organic solvents and provided thin, ductile membranes. The ladderized ionomer

membranes showed higher proton conductivity and mechanical properties compared with those of the brominated precursors and our previous ionomer membranes. The newly proposed molecular design proves that the fused structure is highly effective in balancing the proton conductivity and mechanical stability of aromatic ionomer membranes, which is promising for proton exchange membrane fuel cell applications.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedure and characterisation data of oligomers and polymers. See DOI: 10.1039/c000000x/

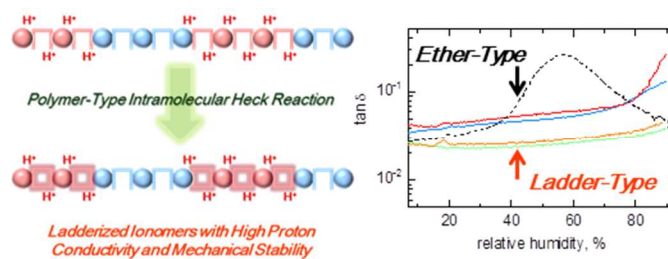
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Graphical Abstract

Intrapolymer Heck reaction for proton conductive ladder-type aromatic block copolymers

Junpei Miyake, Masahiro Watanabe,* and Kenji Miyatake*



A novel polymer synthetic method, intrapolymer Heck reaction, provided ladder-type ionomer membranes with excellent proton conductivity (221 mS cm^{-1} at $80 \text{ }^\circ\text{C}$ and 90% relative humidity) and mechanical strength over a wide range of humidity (ca. 0%-90% relative humidity) at $80 \text{ }^\circ\text{C}$.