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# Simultaneous Enhancements of Conductivity and Stability for Anion Exchange Membranes (AEMs) through Precise Structure Design

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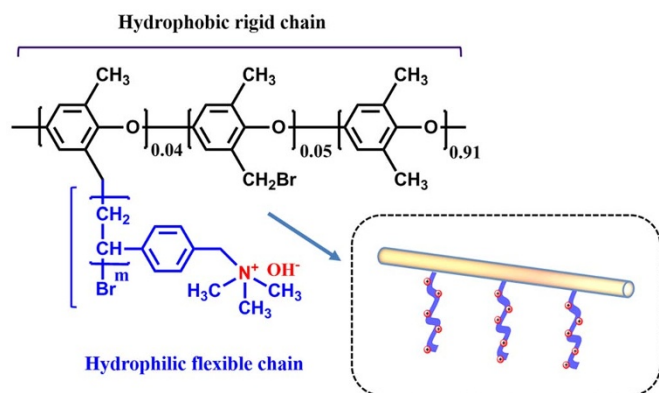
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Polymeric materials as anion exchange membranes (AEMs) play an essential role in the field of energy and environment. The achievement of high performance AEMs by the precise manipulation of macromolecular architecture remains a daunting challenge. Herein, we firstly report a novel rod-coil graft copolymer AEM, possessing rigid hydrophobic main chains and soft hydrophilic graft chains. The low graft density, which can alleviate the adverse influences of ionic graft chains on the main chains, was obtained by using the living polymerization technique. Consequently, the grafted ionic groups which result in the degradation of polymer backbone was decreased to a small degree. Moreover, the relatively long graft chains induced the nanophase separation between the hydrophobic polymer chains and hydrophilic graft chains, which creates a convenient pathway for high hydroxide ion mobility. Such an accurate molecular design simultaneously improves the hydroxide ion conductivity and alkaline stability as well as dimensional stability.

Ion exchange membranes are currently investigated for various applications such as electro dialysis, electrochemical devices<sup>1–4</sup>. Among them, the alkaline fuel cells (AFCs) that utilize solid polymer anion exchange membranes (AEMs) as the electrolytes have received significant interests because of their inherent superiority<sup>5</sup>, including the improved kinetics of the oxygen reduction reaction and more possibilities for cathode catalysts based on nonprecious metals compared with acidic fuel cells<sup>5–7</sup>.

The AEMs, which separate oxidant, fuel chambers and conduct hydroxide ions, are primary limitations for the achievement of inexpensive fuel cell system<sup>8,9</sup>. Ideal AEM candidates should exhibit high hydroxide ion conductivity and low permeability to fuels, while maintaining robust mechanical integrity and chemical stability under fuel cell operating conditions<sup>10,11</sup>. Most AEMs are typically prepared from aromatic polymers with quaternary ammonium groups ( $-NR_3^+$ ) distributed along the polymer backbones, such as quaternized poly(arylene ether sulfone)<sup>12</sup>, poly(phenylene oxide)<sup>13</sup>, poly(phenylene)<sup>14</sup>, and radiation-grafted fluorinated polymers<sup>15</sup>. Low hydroxide ion conductivity was widely observed for these AEMs and impeded the progresses of high performance AEMs. To circumvent this obstacle and pursue higher hydroxide ion conductivity, several researchers have imitated the strategies applied in designing the proton exchange membranes (PEMs). Similar to PEMs, side-chain-type and multiblock polymer structure AEMs, have been proved to be effective for promoting hydroxide ion conductivity, but suffered from deteriorating dimensions<sup>16,17</sup>. However, researches on this class of polymers are still in the initial stages, and the fine control over the topological structure of these polymers and the nanoscale morphology are unsatisfactory<sup>18</sup>. Meanwhile, the alkaline stability is not well improved by the currently developed polymer in AEMs.

Our group also has devoted many efforts to obtaining enhanced performance AEMs from the viewpoint of macromolecular architecture design. As gained knowledge in PEMs, ion exchange membranes derived from graft copolymers, which tolerate much higher ionic contents while limiting excessive swelling and possess highly concentrated, isotropically developed ionic channels<sup>19,20</sup>. We attempted to prepare comb-shaped poly(phenylene oxide) (PPO) AEMs with a combination of a high graft density and short graft chains<sup>21</sup>. One of significant findings is that hydrophilic-hydrophobic phase separation morphology can be produced from the graft copolymers, and thus the hydroxide ion conductivity is improved. However, the other fuel cells related properties, such as chemical stability and dimensional stability, are not so attractive. Hence, the precise regulation of the graft copolymer



**Figure 1** | Synthesis and illustration of the rod-coil graft copolymers (PPO-g-QVBC).

architecture on the molecular scale is needed. The graft copolymer structure parameters generally contain the graft density and graft chain length, which should be carefully designed and regulated to realize the simultaneous improvements of hydroxide ion conductivity, dimensional stability, and chemical stability.

Herein, we report a well-defined rod-coil graft copolymer comprising hydrophobic rigid main chains and hydrophilic flexible graft chains for AEMs, and special designs lie in adjusting the graft chain length and density. For this design, we have given careful considerations to the following points. The micro-phase separation morphology is generally controlled by factors including the chain length of each segment and their volume ratio<sup>22</sup>. Accordingly, the graft chains should be long enough to achieve preferable micro-phase aggregated morphology, for example, a bi-continuous structure. On the other hand, the quaternary ammonium groups are far away from the polymer main chains and thus will not alter the nature of the backbones, resulting in the improvement of alkaline stability<sup>23,24</sup>. The low graft density is required to reduce the adverse influence of the functionalized graft chains on the backbone.

## Results and discussion

**Polymer synthesis.** In this study, the PPO is chosen as polymer backbones, while poly(quaternary 4-vinylbenzyl chloride) (QVBC) as graft chains (Figure 1). The synthesis of poly(phenylene oxide)-g-quaternary 4-vinylbenzyl chloride (PPO-g-QVBC) copolymers via a “grafting from” macroinitiator approach involves an atom transfer radical polymerization (ATRP) process. The ATRP macroinitiators were readily obtained by bromination of the methyl-groups of commercially available PPO (Supplementary Figure 1), as confirmed by <sup>1</sup>H NMR spectroscopy (Supplementary Figure 2). The

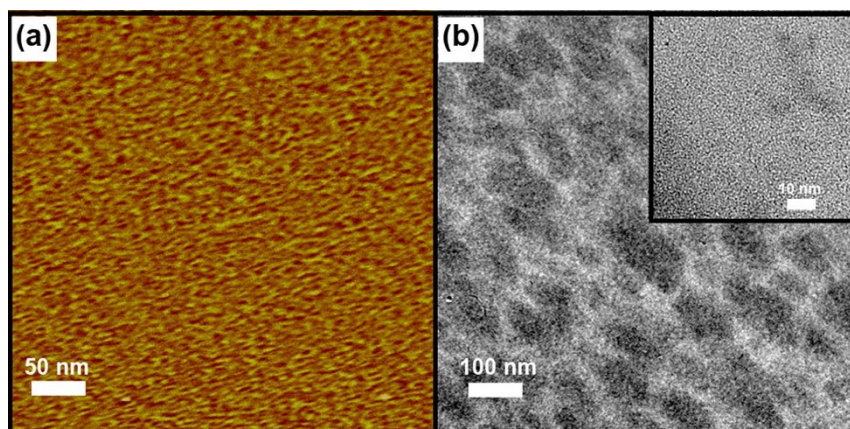
brominated degree of PPO was carefully projected considering the combination of the membrane forming capacity with the subsequently required graft polymerization reaction. Ultimately, the PPO with a 0.09 degree of substitution was selected for the subsequent synthesis of graft copolymers.

The coil graft chains were introduced onto brominated PPO through the successful ATRP graft polymerization of QVBC monomers (Supplementary Figure 3). By optimizing the added amounts of the catalysts (CuBr<sub>2</sub> and 2,2'-bipyridyl (bpy)), the resulting PPO-g-QVBC copolymers can maintain a uniform graft density (0.04). Consequently, the lengths of graft chains can be easily adjusted by varying the added amounts of monomers. The experimental numbers of graft chain repeat units (*m*) were determined from <sup>1</sup>H NMR spectra (Supplementary Figure S4) ranging from 6 to 12. Then, a series of rod-coil graft copolymers (R4-C<sub>m</sub>) with controlled graft density and varied graft lengths were obtained for investigating the effect of microscopic graft chain lengths on the membranes' macroscopic properties. Further information about experimental details and polymer characterizations are provided in the Supplementary Information.

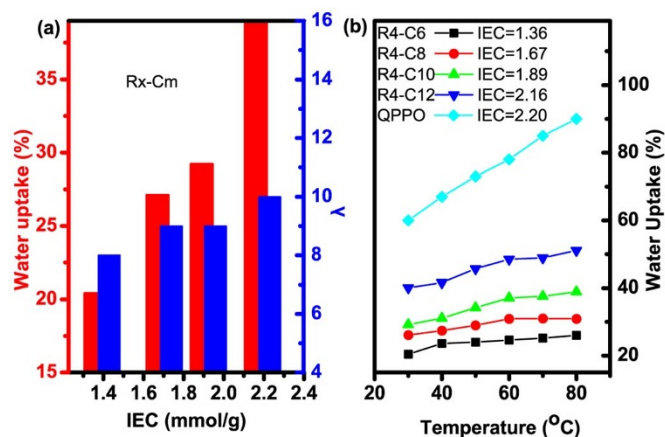
**Morphology analysis.** It is well-established that the formation of nanoscale domains enriched in the ion exchange membranes is critical for the resulting macroscopic hydroxide ion conductivity. Herein, the microphase separation occurs between the stiff hydrophobic main chains and the soft hydrophilic graft chains of PPO-g-QVBC, due to their enthalpy dissimilarities. As an example, the nanoscale morphology of the R4-C10 membrane was observed by tapping mode atomic force microscopy (AFM) and transmission electron microscopy (TEM). As shown in Figure 2(a), the hydrophilic domains appear darker, and the hydrophobic domains appear brighter. The AFM image displays well-defined micro-phase separation with the ionic nanochannels of 3–5 nm in size.

The microphase-separated morphology of the R4-C10 membrane stained with tungstate ions was further confirmed by TEM observation. Similar to the AFM image, the developed hydrophilic/hydrophobic phase separation with ionic clusters was clearly seen throughout the field of view (Figure 2(b)). Consequently, high hydroxide ion conductivity can be expected from the locally increased concentration of hydroxide ions within the ion aggregated domains.

The phase separation behaviors and nanoscale channels were also investigated by mesoscale simulation (Supplementary Figure S5 and simulation details in the Supplementary Information). All the PPO-g-QVBC membranes present well-defined nanoscale morphologies (Supplementary Figure S6). As increasing graft lengths, the ion conduction pathways become more interconnected and less tortuous, suggesting the formation of more efficient anion conduction channels.



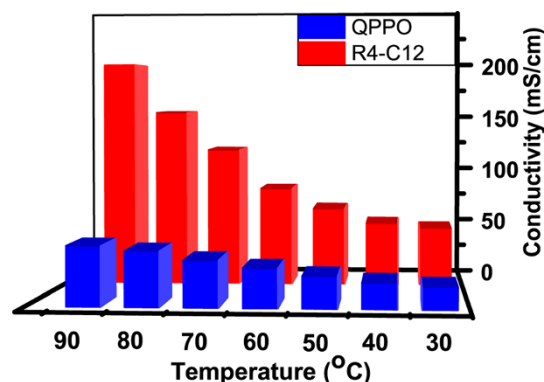
**Figure 2** | (a) AFM tapping phase image of surface, and (b) TEM image of R4-C10 membrane.



**Figure 3** | (a) The WU and  $\lambda$  values of PPO-*g*-QVBC membranes, and (b) the WU dependence of temperature.

**Water Uptake.** As shown in Figure 3(a), higher IEC membranes absorb more water due to the increased hydrophilic groups. Almost the same number of absorbed water molecules per quaternary ammonium group (designated as  $\lambda$ ) was observed. It indicates that the rod-coil graft copolymers always have the abilities to form equally inter-connected hydroxide ion channels, independent of IEC values. Meanwhile, the quaternized PPO (QPPO) with functional groups distributed backbones was chosen as the benchmark, and prepared according to previous reports<sup>25</sup> (QPPO, IEC = 2.20 mmol/g). When comparing the water uptake (WU) of R4-Cm membranes with that of QPPO membrane, the former shows lower WU (Table 1). Figure 3(b) displays the temperature dependence of the WU for all membranes, and it can be observed that the WU of R4-Cm membranes is less temperature sensitive. The micro-morphology with well-connected hydroxide ion conduction channels is considered to be responsible for the lower water absorption. The formation of small ionic domains enhances the elastic forces in the matrix that opposes the increasing osmotic pressure induced by the increasing temperature<sup>26</sup>. In addition to low WU, the R4-Cm membranes also display highly dimensional stability, while exhibiting anisotropic swelling behavior (Supplementary Figure S7). Larger dimensional changes occur in the through-plane direction, that is of great significance for the membrane electrode assembly. These properties reflect the highly mechanical stress of R4-Cm AEMs in the fully hydrated state. As shown in Table 1, the R4-Cm AEMs present tensile stress in the range of 14.3–24.1 MPa, with the higher IEC values membrane having lower tensile stress.

**Hydroxide conductivity.** Similar to WU variation, the hydroxide ion conductivity of PPO-*g*-QVBC membranes increases with increasing coil hydrophilic chain lengths, as shown in Table 1. It implies that the membrane's properties can be effectively controlled by adjusting the structure parameter -the graft chain length without altering the



**Figure 4** | Comparison of hydroxide conductivities R4-C12 and QPPO membranes as a function of temperature.

macromolecules' architecture, thereby guaranteeing the existence of well-defined morphologies. The R4-C12 membrane with IEC = 2.16 mmol/g shows the highest hydroxide ion conductivity 86 mS/cm at 60°C, that reveals the conduction of hydroxide ion is made as efficient as the proton conduction in Nafion.

The temperature dependence of the hydroxide ion conductivities of the R4-C12 and QPPO membranes in water is compared in Figure 4. Under the same conditions, the R4-Cm membrane displays much higher hydroxide ion conductivity than that of QPPO membrane (IEC = 2.20 mmol/g), particularly at elevated temperatures. The R4-C12 membrane shows the highest hydroxide ion conductivity value of 198 mS/cm at 90°C, which is ~4 times higher than that of QPPO membrane. The significant point is that the R4-Cm membrane absorbs less water molecules but exhibiting considerably higher hydroxide ion conductivity than the QPPO membrane. This fascinating conducting property further demonstrate that the inter-connected hydrophilic channel as presented in micro-morphology images is beneficial for transporting hydroxide ions. In addition, it should be noted that the conductivity gap between R4-Cm and QPPO membranes becomes larger with increasing temperature. This phenomenon is attributed to the larger amounts of water absorption for the QPPO membrane at high temperature, which limits the improvement of hydroxide ion conductivity due to hydroxide ion dilution. These results suggest that the rod-coil graft copolymer endowed with precise design is a promising material for AEMs to mitigate water swelling and improve hydroxide ion conductivity.

**Alkaline stability.** For AEMs, recently proposed strategies concentrate on the enhancements of hydroxide ion conductivity and water resistance, while leaving the issue of long-term alkaline durability out of consideration. The motivation of the present work is to solve the commonly existing challenges in AEMs by fine macromolecule structure design. To investigate the stability under alkaline conditions, the QPPO and R4-C10 membranes were exposed to a solution of 2 mol/L NaOH in water at 60°C. As shown in Figure 5(a), the IEC of R4-C10 remains at ~80% of the initial value after 550 h testing,

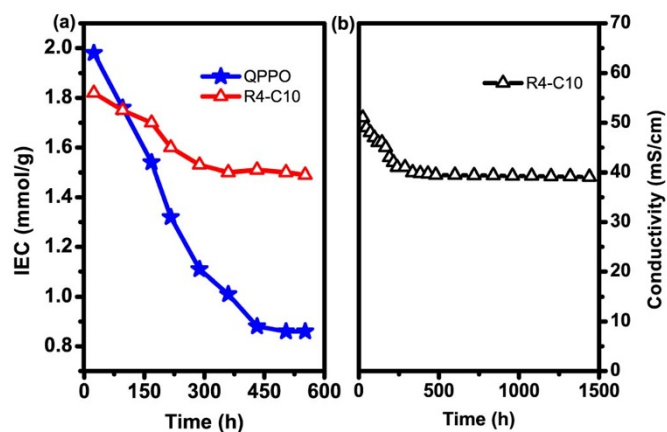
**Table 1** | Properties of PPO-*g*-QVBC membranes

Sample	IEC <sup>(a)</sup> (mmol/g)	IEC <sup>(b)</sup> (mmol/g)	WU (%)	$\lambda$	Conductivity 60°C (mS/cm)	Tensile <sup>(c)</sup> strength (MPa)
R4-C6	1.36	1.31	20.4	8	57	24.1
R4-C8	1.67	1.64	27.1	9	62	20.8
R4-C10	1.89	1.89	29.2	9	73	18.5
R4-C12	2.16	2.10	40.1	10	86	14.3
QPPO	2.20	-	60.0	15	32	-

<sup>(a)</sup>Calculated from titration.

<sup>(b)</sup>Calculated from <sup>1</sup>H NMR.

<sup>(c)</sup>Measurement in the fully hydrated state.



**Figure 5** | (a) The changing trend in IEC values of QPPO and R4-C10 membrane, and (b) hydroxide ion conductivities of R4-C10 membrane after immersion in 2 mol/L NaOH at 60°C.

while the IEC of QPPO declines dramatically to  $\sim 40\%$  of the initial value under identical stability testing conditions. In fact, the QPPO membrane lost its flexibility, appearance and mechanical strength within only 100 h. The results demonstrate that the rod-coil AEMs bearing ionic graft chains are more tolerant to the alkaline environments than main-chain type AEMs. Further proof provided in Figure 5(b), the hydroxide ion conductivity of R4-C10 also keeps  $\sim 80\%$  of the initial value after 550 h measurement, and no further loss in conductivity is evident after up to 1440 h. The alkaline stability of R4-C10 membrane was also evaluated by recording the changes of mechanical properties. As listed in the Supplementary Table S3, R4-C10 keeps  $\sim 86\%$  of the original mechanical property after 552 h alkaline tolerance, demonstrating its elegant long-term alkaline stability.

The R4-Cm membranes are based on the typical quaternary ammonium groups, which have a tendency to disintegrate in alkaline solutions at high temperature due to the displacement of the ammonium group by  $\text{OH}^-$  via a direct nucleophilic substitution<sup>27</sup>. Consequently, the initial degradation of IEC and conductivity is inevitable. The greatly fascinating alkaline stability of R4-Cm AEMs is also reasonable. In the present study, the ammonium cations attached onto the graft chains, not on the backbones, can benefit the alkaline stability of AEMs. It has been well-documented that when quaternary ammonium cation is affixed to the benzyl position, the degradation of the backbone is triggered at the ether position<sup>23</sup>. In comparison, the well-designed structure separates the fixed cations from the backbones and protects the ether bonds from being attacked, and thus the rod-coil AEMs present more excellent alkaline stability (Supplementary Figure S8). This finding provides a novel strategy for improving the chemical stability of AEMs from the macromolecular architecture design perspective.

## Conclusion

The simultaneous enhancements of the hydroxide ion conductivity and alkaline stability as well as dimensional stability of AEMs can be achieved by the fine manipulation of the macromolecular architecture. The graft copolymers with rod backbones and coil graft ionic chains produce high hydroxide ion conductivity and excellent alkaline resistant AEMs. We have shown that the unique graft architecture combined the low graft density with appropriate graft length is the key considerations in obtaining high performance AEMs. A platform to prepare well-structured graft copolymers is provided, in which both the backbones and graft chains can be further optimized for the development of AEMs, to meet various electrochemical applications.

## Methods

**Synthesis of brominated poly(phenylene oxide).** Brominated poly(phenylene oxide) (Br-PPO) was prepared as previously reported. In summary, PPO was dissolved in chlorobenzene to form an 8% m/v solution and bromination reaction was conducted by adding bromine dissolved in chlorobenzene (33% v/v) at 130°C for 8 h. The Br-PPO was precipitated on addition of methanol, washed and dried at 80°C for at least 20 h. The degree of bromination was controlled by the amount of bromine added.

**Synthesis of PPO-g-QVBC.** Br-PPO (1.0 g) and a controlled amount of QVBC were dissolved in mixed solvents of NMP (30 mL) and chlorobenzene (10 mL) at room temperature in a dried 100 mL three-neck round bottom flask equipped with a magnetic stirring bar. After dissolving completely, the mixture was degassed by  $\text{N}_2$  bubbling for an hour. In a dried sealed tube,  $\text{CuBr}_2$  (0.0901 g), bpy (0.1254 g), and ascorbic acid (AsAc, 0.3538 g) were added, and then the mixture solution was added quickly into the sealed tube. Three freeze-pump-thaw cycles were performed to remove oxygen. After the tube was flame-sealed under vacuum, it was stirred in a 120°C pre-heated oil bath for 48 h. The polymerization reaction was stopped by cooling and exposure to air. The product solutions were firstly evaporated to remove chlorobenzene at 60°C. The final copolymers were obtained by deposition into diethyl ether anhydrous. The QVBC monomers were removed by washing thoroughly with ethanol. The resulting copolymers were dried under vacuum at 60°C for 24 h. The copolymer was denoted as PPO-g-QVBC.

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## Author contributions

J.R. and L.W. designed the project; J.R., B.W. and Y.C. carried out the experiments. J.R., L.W. and T.W. wrote the manuscript. All the authors discussed the results and commented on the manuscript.

## Additional information

**Supplementary information** accompanies this paper at <http://www.nature.com/scientificreports>

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