

Supporting Information for the manuscript entitled:

Cross-Linked Benzoxazine-Benzimidazole
Copolymer Electrolyte Membranes for Fuel Cells at
Elevated Temperature

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Characterization of 3-Phenyl-3,4-dihydro-6-tert-butyl-2H-1,3-benzoxazine (*p*BUa). The benzoxazine monomer, *p*BUa, was polymerized by stepwise heating to 220 °C. The resulting polymer, P(*p*BUa), was confirmed by ¹H NMR spectroscopy (Figure S1). ¹H NMR spectroscopy was also performed after additional heating to 180 °C and to 200 °C to observe the curing kinetics systematically. The signals at 5.3 and 4.6 ppm were attributed to protons in the oxazine ring of the *p*BUa. Increasing the thermal curing temperature decreased these signals (asterisk) and introduced new signals, attributable to neighbors of the Mannich bridge, at *ca.* 4.2 and 3.7 ppm (arrow). After curing at 220 °C, the signals at 4.2 ppm also disappeared, indicating the complete formation of symmetric Mannich bridges.^{S1}

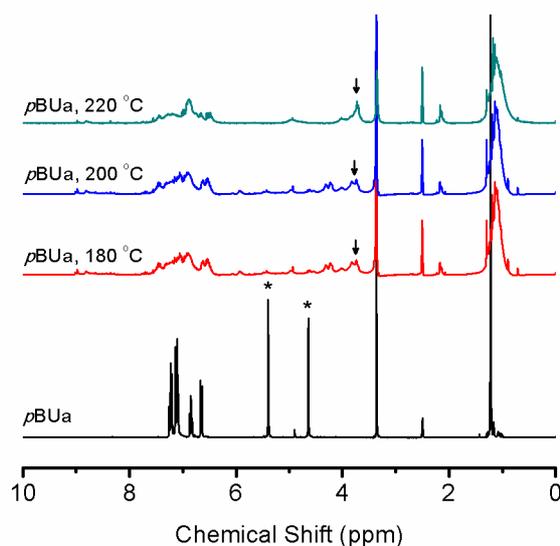


Figure S1. ¹H NMR spectroscopy of *p*BUa after each heat treatment including 180, 200, and 220 °C.

FT-IR spectra of dried membranes and powder samples were recorded in the attenuated total reflectance (ATR) mode in the frequency range of 4000-650 cm⁻¹ on a Nicolet 6700 instrument (Thermo Scientific, USA). The spectrum was recorded as the average of 32 scans with the resolution of 8 cm⁻¹. Each of samples was put in equal physical contact with the sampling plate of the spectrometer accessory to avoid differences caused by pressure and penetration depth.

The chemical structure of P(*p*BUa) and its monomer was further confirmed by FT-IR spectroscopy after each curing cycle (Figure S2). Ring-opening polymerization of the benzoxazine monomers was demonstrated by the disappearance of the oxazine ring peaks at around 1496 cm⁻¹ (tri-substituted benzene ring), 1480 cm⁻¹ (tetra-substituted benzene rings), 1234 cm⁻¹ (C-O-C asymmetric stretching mode), 1166 (C-N-C asymmetric stretching mode), and 944 cm⁻¹ (-C-O-C-cyclic acetal vibrational mode or a C-H out-of-plane deformation). Additionally, characteristic broad absorption bands assigned to -OH stretching vibrations appeared at 3700 ~ 3100 cm⁻¹. No absorption band at 3700 ~ 3100 cm⁻¹ was shown by the monomer or samples cured at up to 180 °C, indicating that ring-opening did not occur completely. Peak resolution also decreased, indicating the ring-opening of the oxazine rings and the polymerization of the monomer into oligomers and polymers.

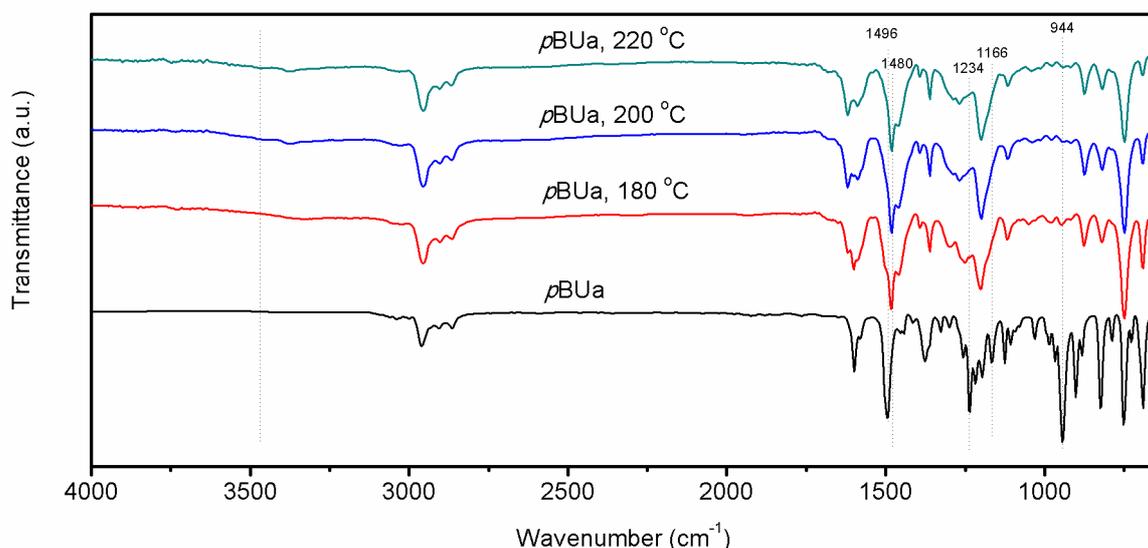


Figure S2. Infrared spectra of *p*BUa after each heat treatment including 180, 200, and 220 °C.

The curing behavior of *p*BUa was examined by DSC at a rate of 10 °C min⁻¹ (Figure S3). The sharp endothermic transition observed at *ca.* 74 °C was attributed to its melting (Figure S3a), and disappeared completely with heating at 220 °C (Figure S3b). Endothermic peak of *p*BUa were not

observed in 2nd DSC heating curves or the 1st DSC cooling curves. P(*p*BUa) showed a glass transition temperature (T_g) of 115 °C. Therefore, *p*BUa showed thermosetting characteristics, in agreement with previous work on polybenzoxazines,^{S2} and we believe that 220 °C is adequate for the cure of *p*BUa.

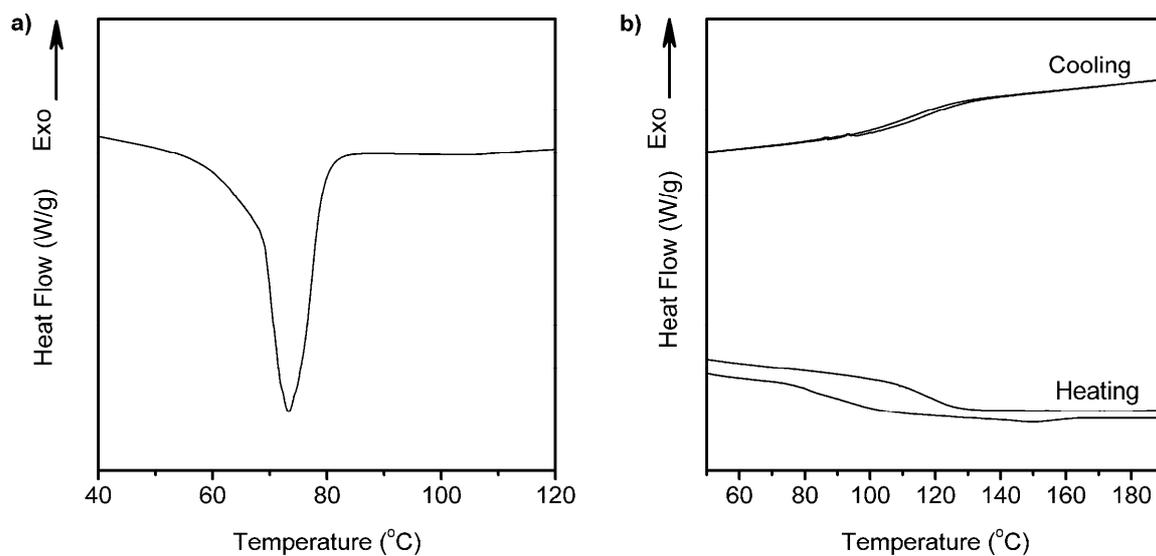


Figure S3. DSC a) 1st heating curves of *p*BUa and b) heating and cooling curves of P(*p*BUa).

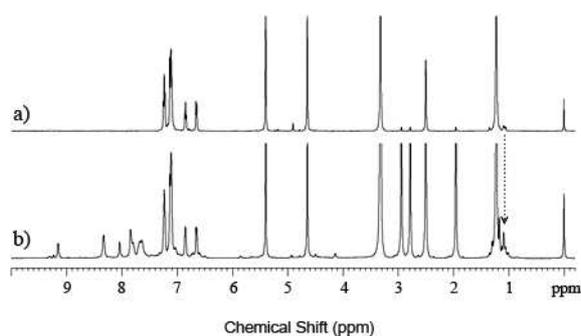


Figure S4. ¹H NMR spectroscopy of a) *p*BUa monomer and b) *p*BUa and PBI mixture (*p*BUa : PBI = 65 : 35 (wt%)) obtained at 140 °C for 30 min.

Chemical Stability. The extracts of P(*p*BUa-*co*-BI)-65 and P(*p*BUa-*co*-BI)-35 membranes after immersion in a 85 wt% PA solution at 160 °C for 5 h were neutralized and precipitated by K₂CO₃ aqueous solution. The precipitate was dried for 2 days in a vacuum oven and confirmed by ¹H NMR spectroscopy.

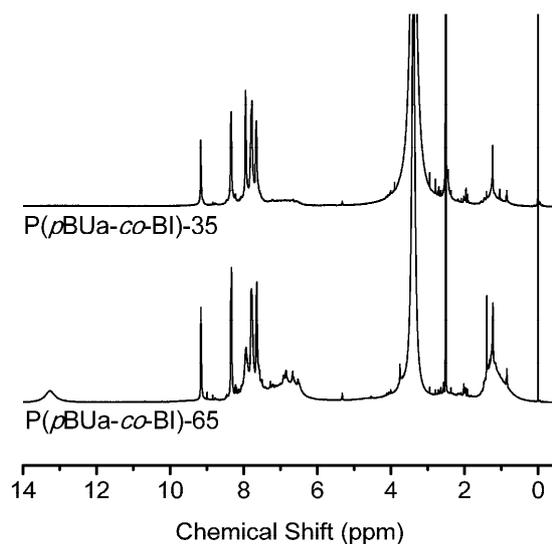


Figure S5. ¹H NMR spectroscopy of the extracts of P(*p*BUa-*co*-BI)-65 and P(*p*BUa-*co*-BI)-35 membranes after immersion in a 85 wt% PA solution at 160 °C for 5 h.

Thermal & Thermooxidative Stabilities. The thermal and thermooxidative behavior of the membranes with P(*p*BUa) were examined by TGA (TGA7, PerkinElmer Inc., USA) analysis in air atmosphere to determine the degradation temperature of the polymers up to 800 °C.

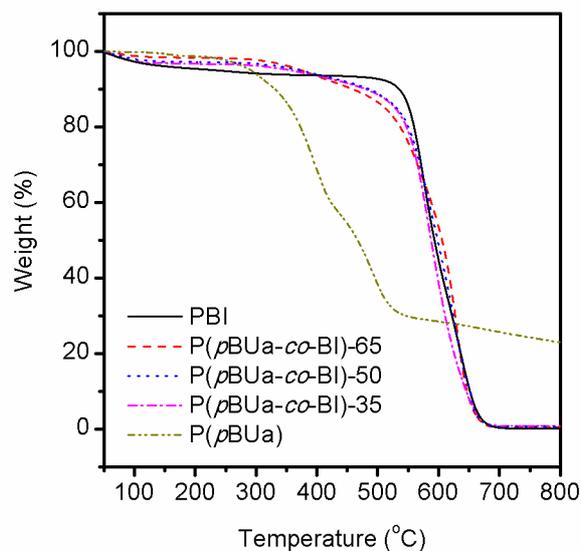


Figure S6. Thermal and thermooxidative stabilities of P(*p*BUa-*co*-BI)s under air atmosphere.

Dynamic Mechanical Thermal Analyzer (DMTA). The mechanical and thermal properties of undoped films were tested on a METTLER TOLEDO DMA/SDTA861[°] at the frequency of 1 Hz under a constant periodic stress. The specimens were measured at a force amplitude of 0.5 N and a heating rate of 3 °C min⁻¹.

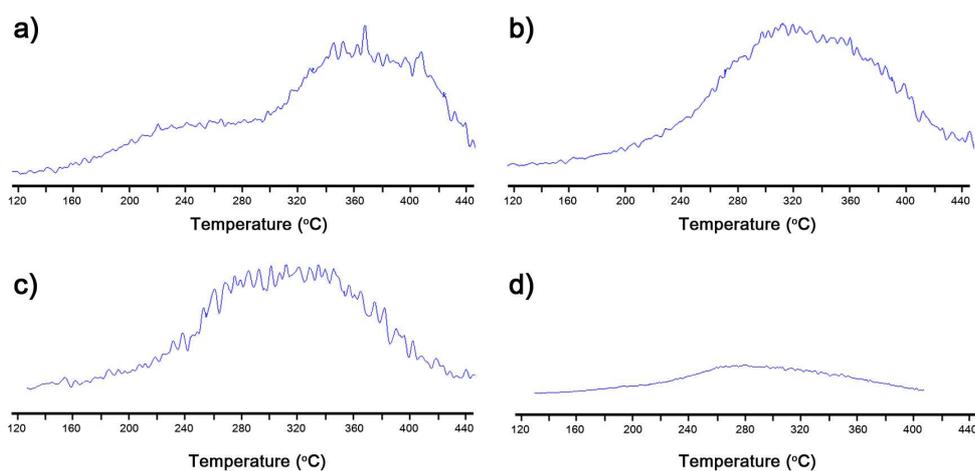


Figure S7. DMTA results of tangent delta for a) PBI, b) P(*p*BUa-*co*-BI)-35, c) P(*p*BUa-*co*-BI)-50, and P(*p*BUa-*co*-BI)-65

Mechanical Strength. While increasing PA content ensuring good proton conductivity, it also degrades mechanical properties.^{S3} Membranes' tensile strengths decrease with increasing P(*p*BUa) content at similar PA contents (Table S1). Still it is obvious that P(*p*BUa-*co*-BI) membranes could absorb a larger amount of PA and maintain the mechanical strength requiring for free-standing films. Considering that polybenzoxazine normally exhibit elongations at break of a few percent, this novel material appears quite different from ordinary thermosetting polymers. Its high ductility and high thermal resistance are unusual and attractive considering the high thermosetting resin content of these membranes.

Table S1. Mechanical properties of the membranes.

Membranes	PA content (wt%)	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
P(<i>p</i> BUa- <i>co</i> -BI)-65	88.5	2.19 ± 0.229	72.3 ± 5.93	5.70 ± 1.65
P(<i>p</i> BUa- <i>co</i> -BI)-50	83.9	2.69 ± 0.506	54.8 ± 18.5	14.5 ± 7.31
P(<i>p</i> BUa- <i>co</i> -BI)-35	83.0	4.25 ± 0.371	38.1 ± 3.65	41.4 ± 5.40
PBI ^a	81.2	5.34 ± 0.486	47.6 ± 7.73	43.2 ± 6.55

^acast from solution casting.

The mechanical properties were measured using a universal testing machine (Lloyd LR-10K). The dumbbell specimens were prepared using the ASTM standard D638 (Type V specimens dog-bone shaped samples). The tensile properties of the PA-doped membrane samples were measured in air at 23 °C under a 45% relative humidity (RH) with a gauge length and cross head speed of 15 mm and 10 mm min⁻¹, respectively.

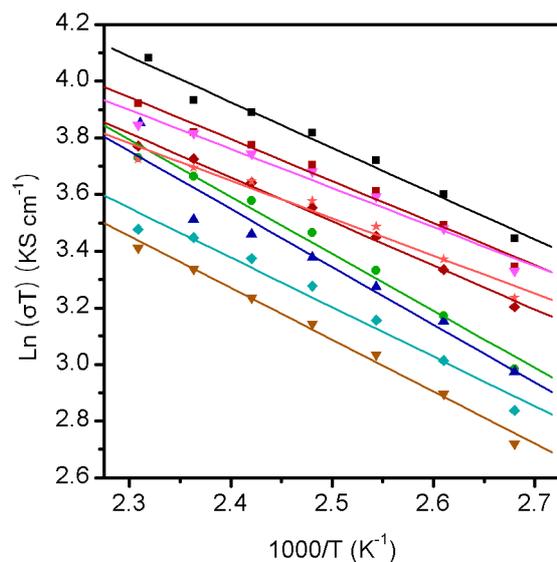


Figure S8. Proton conductivities of P(*p*BUa-*co*-BI)-65 (square), -50 (circle), -35 (triangle), -20 (reverse triangle), -10 (diamond), and PBI (star) membranes as a function of temperature (100 – 160 °C) under anhydrous condition.

The extracts of P(*p*BUa-*co*-BI)-65 and P(*p*BUa-*co*-BI)-35 membranes after immersion in a 85 wt% PA solution at 80 °C for 4 h were neutralized and precipitated by K₂CO₃ aqueous solution. The precipitate was dried for 2 days in a vacuum oven and confirmed by ¹H NMR spectroscopy (Figure S9).

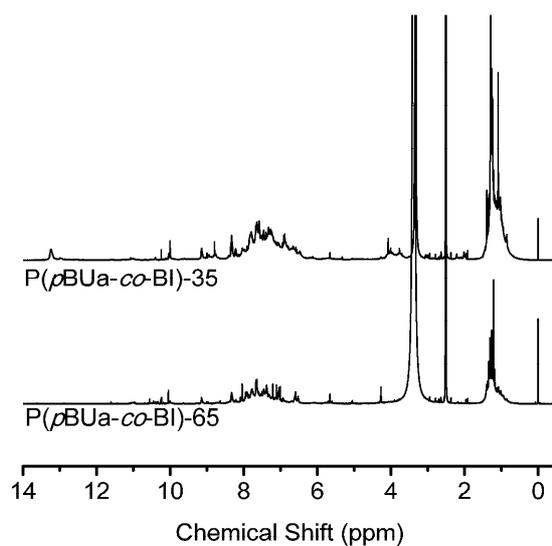


Figure S9. ^1H NMR spectroscopy of the extracts of P(*p*BUa-*co*-BI)-65 and P(*p*BUa-*co*-BI)-35 membranes after immersion in a 85 wt% PA solution at 80 °C for 4 h.

The films after immersion in a 85 wt% PA solution at 80 °C for 4 h were washed with distilled water several times. The films were dried for 2 days in a vacuum oven until constant weight and confirmed by ATR FT-IR spectra (Figure S10).

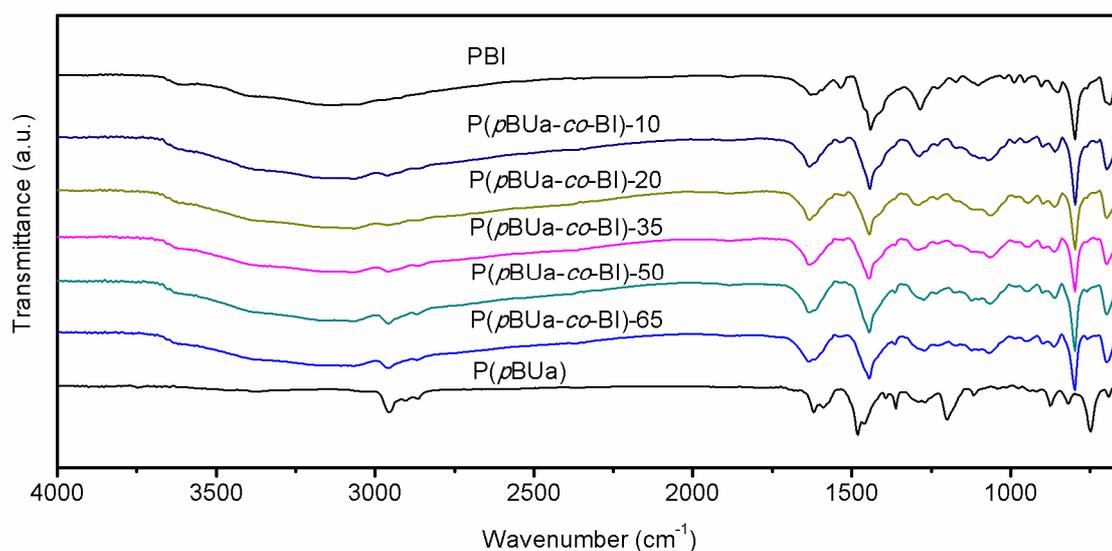


Figure S10. ATR FT-IR spectra of P(*p*BUa-*co*-BI) membranes along with PBI and P(*p*BUa) after immersion in a 85 wt% PA solution at 80 °C for 4 h.

References

- (S1) Ning, X.; Ishida, H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1121.
- (S2) Ghosh, N. N.; Kiskan, B.; Yagci, Y. *Prog. Polym. Sci.* **2007**, *32*, 1344.
- (S3) Li, Q.; He, R.; Jenson, J. O.; Bjerrum, N. J. *Fuel Cells* **2004**, *4*, 147.