Electronic Supplementary Information

Exploiting the Reversible Covalent Bonding of Boronic Acids for Self-Healing/Recycling of Main-Chain Polybenzoxazines

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CONTENTS:

Synthesis of *p*-cresol and benzylamine based benzoxazine (C-Bn)

In a round bottomed flask equipped with a stirrer *p*-cresol (10 g, 92.5 mmol), benzylamine (9.9 g, 92.5 mmol) and paraformaldehyde (5.6 g, 186 mmol) was dissolved in toluene:EtOH (2:1, v:v) (150 mL). The mixture was refluxed for 12 h. After cooling the content, the reaction solution was filtered with an ordinary filter paper. The solvent was removed by rotary evaporator and the remaining was dissolved in $CHCl_3$. The chloroform solution was washed with 1 M $NaOH_{(aq)}$ solution three times and deionized water with 2 times. Then, the chloroform solution was dried by using anhydrous Na_2SO_4 and the solid particles filtered. The remaining solution was evaporated. Crystallization from acetone/ethanol mixture gave the desired product. (Yield: ~80%)

Typical curing procedure of C-Bn with $PhB(OH)_2$ is as follows: C-Bn (99.1 mg, 0.41 mmol) and 10 % wt $PhB(OH)_2$ (11.01 mg, 0.09 mmol) were dissolved in 0.5 mL of $CHCl_3$ in a glass vial. The solvent was evaporated at room temperature for 1 day and in a vacuum for 1 days. After the solvent removal, mixture was exposed to thermal curing at 200 °C for 4 h in an open-air oven.

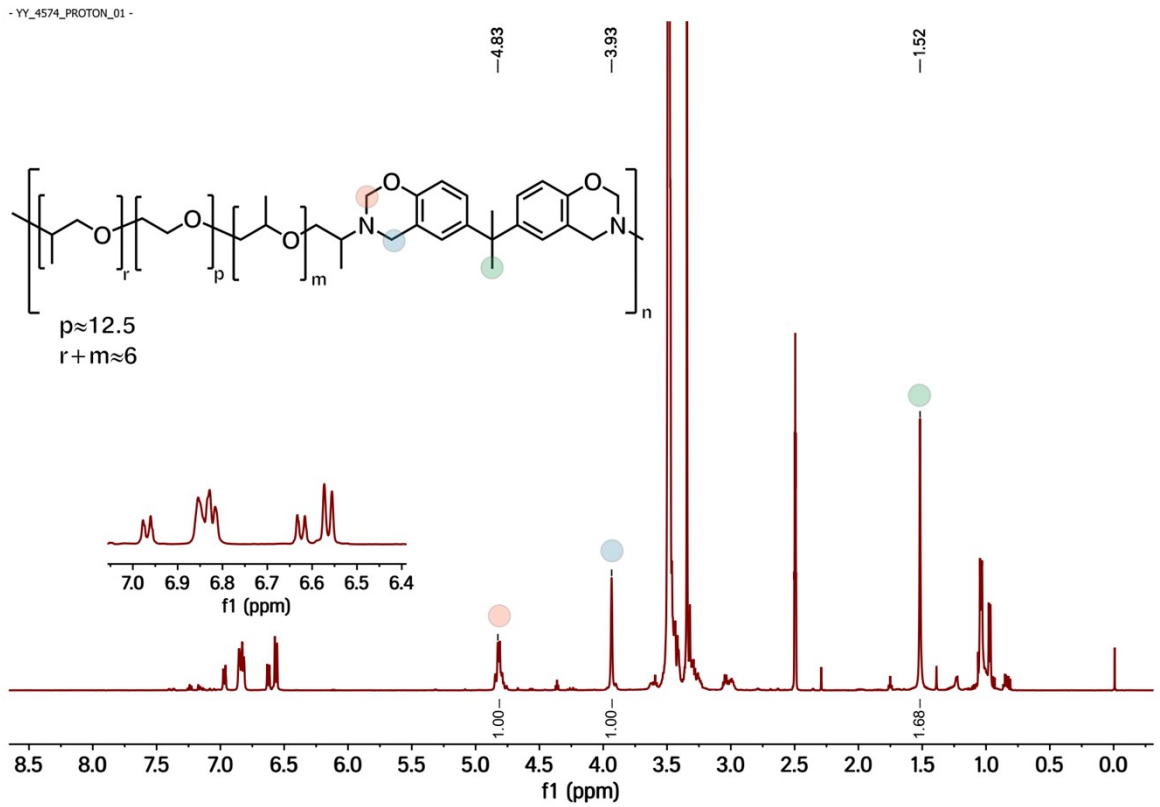


Figure S1: ^1H NMR spectrum of PPO_{900}-Bz. *Residue of DMSO and water.

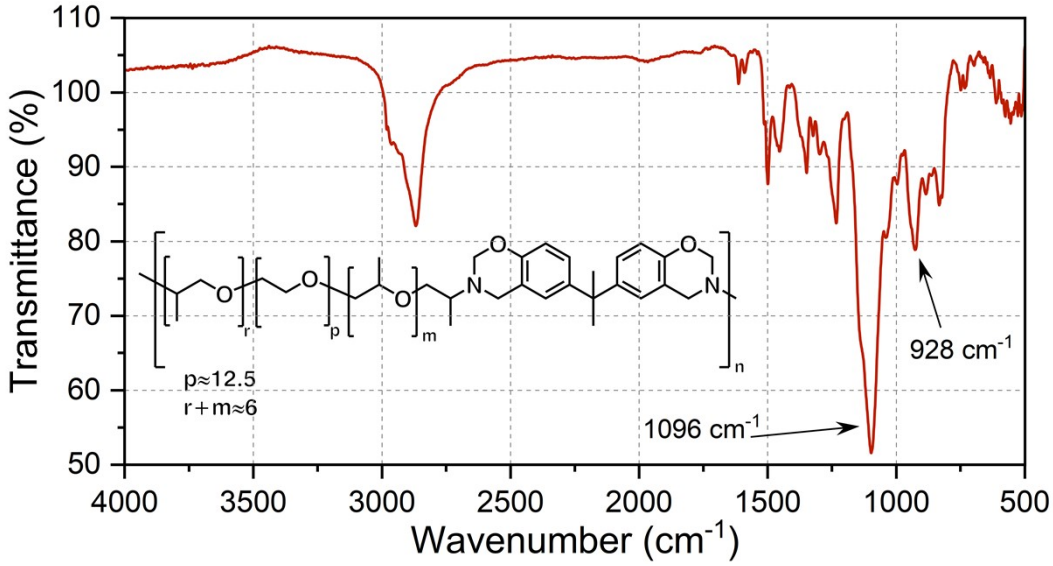


Figure S2: FTIR spectrum of PPO_{900}-Bz

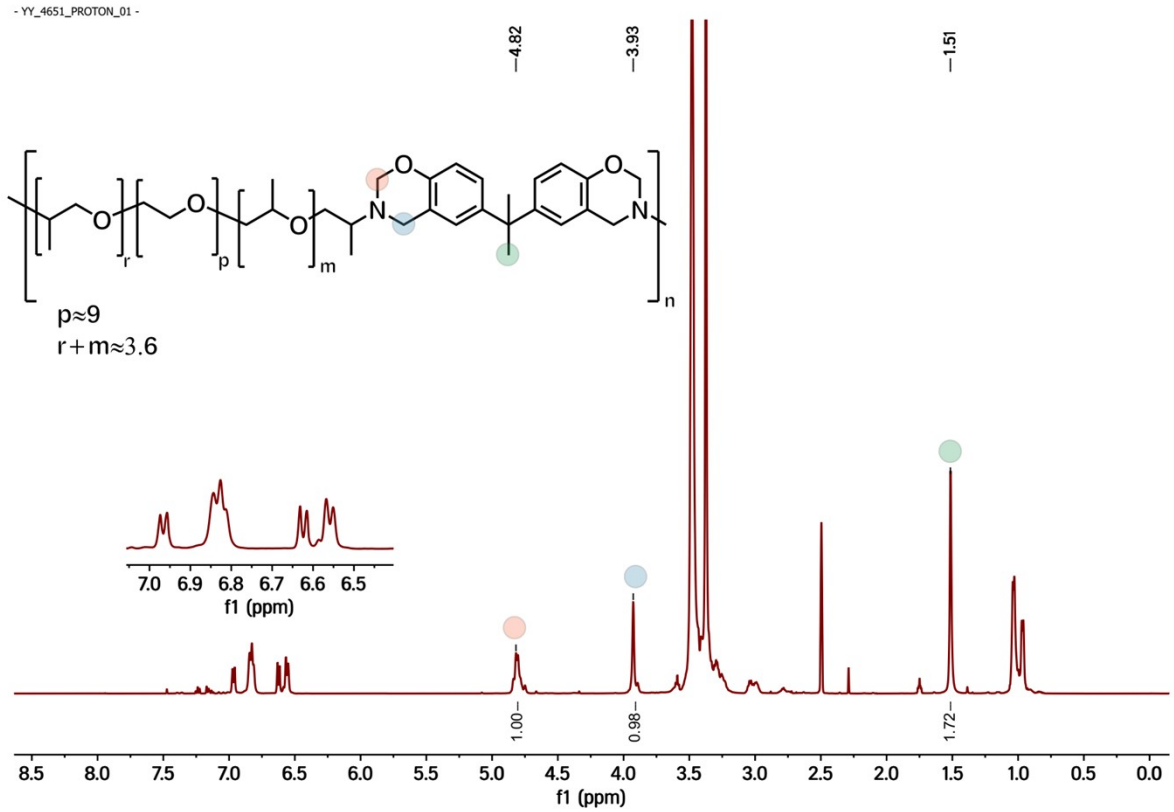


Figure S3: ^{1}H NMR spectrum of PPO_{600}-Bz. *Residue of DMSO and water.

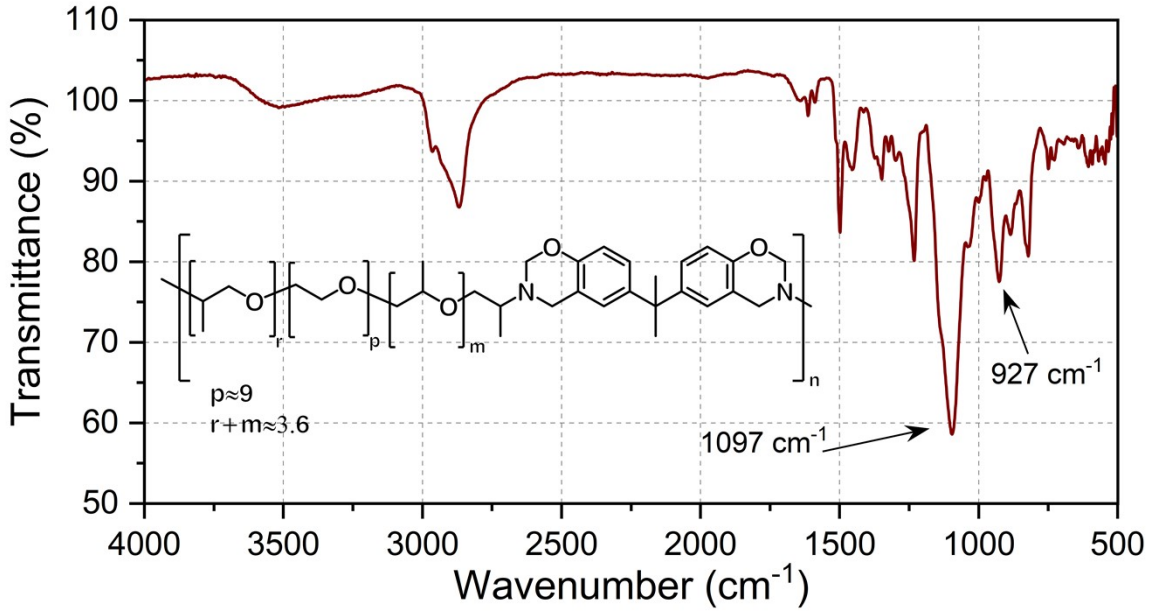


Figure S4: FTIR spectrum of PPO_{600}-Bz.

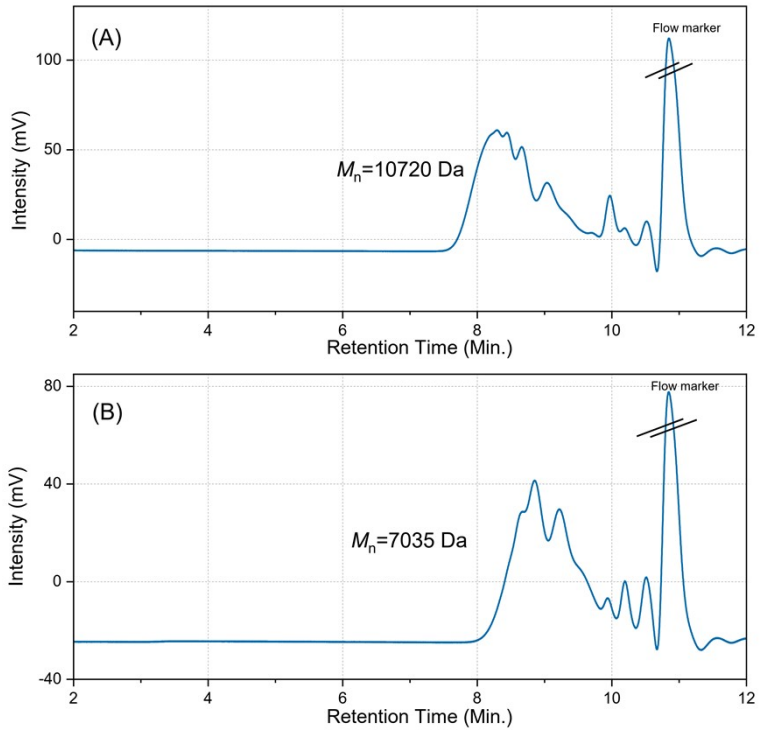


Figure S5: GPC chromatograms of PPO_{900}-Bz (A) and PPO_{600}-Bz (B)

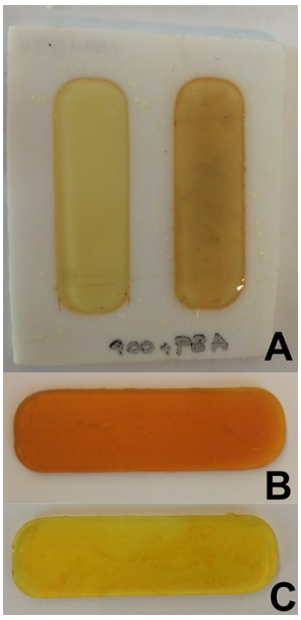


Figure S6: The PPO_{900}-Bz (right) and PPO_{900}-Bz-Bor (left) in molds before thermal treatment (A), cured PPO_{900}-Bz-Bor (B) and cured PPO_{900}-Bz (C)

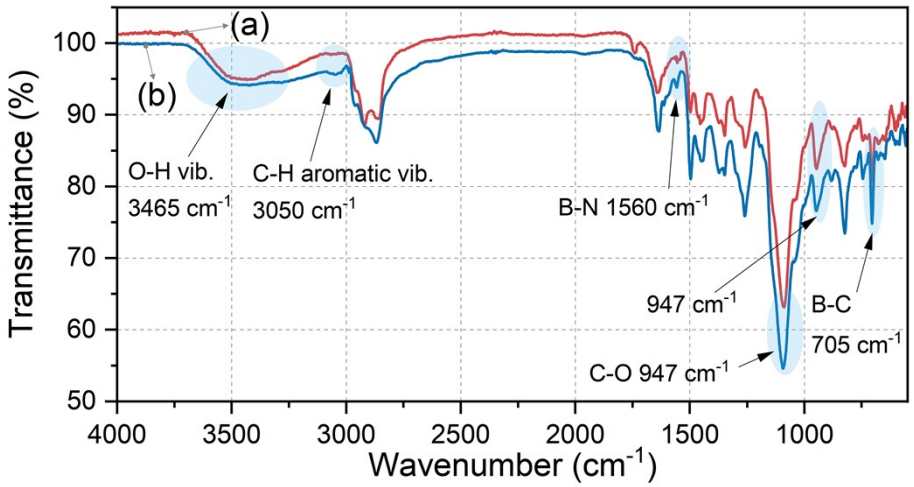


Figure S7: The overlaid FTIR spectra of cured PPO_{900}-Bz-Bor (a) and PPO_{600}-Bz-Bor (b)

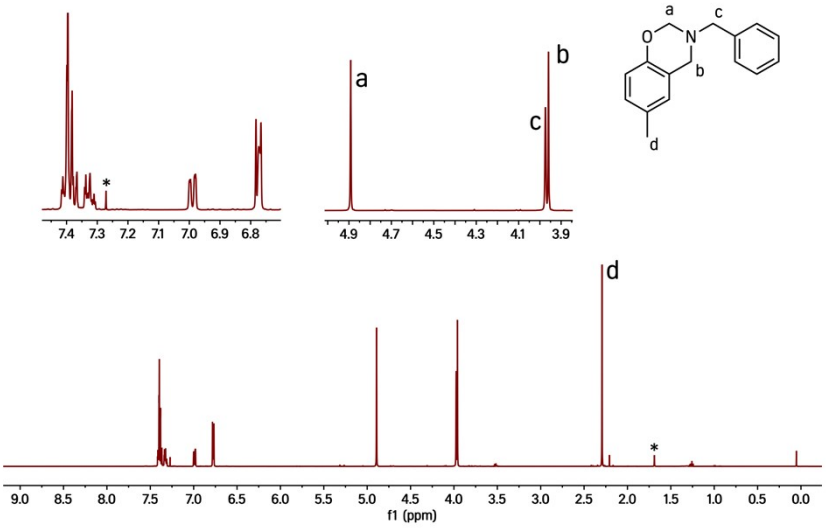
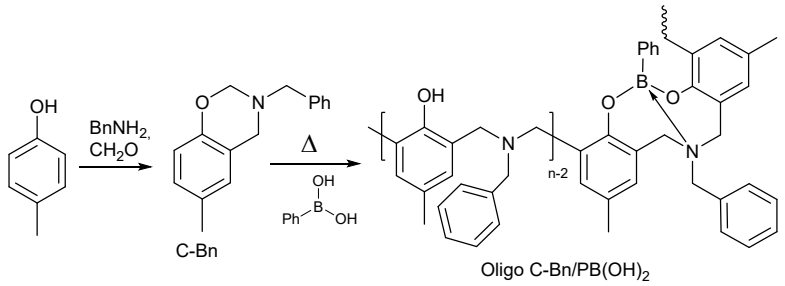


Figure S8: ^{1}H NMR spectrum of C-Bn. *$CHCl_3$ and H_2O



Scheme S1: Synthesis, oligomerization of C-Bn monomer and reaction between oligo C-Bn and $PhB(OH)_2$

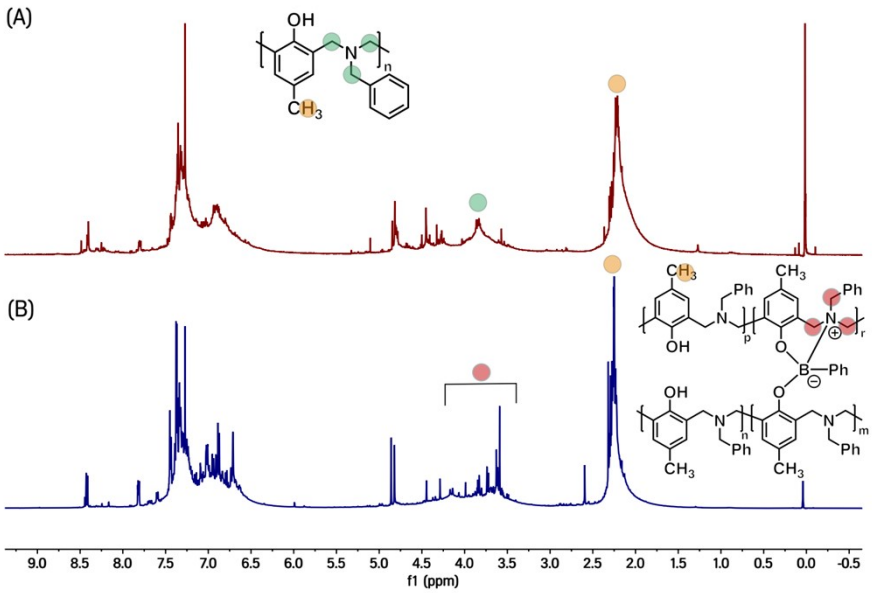


Figure S9: 1H NMR spectra of oligo C-Bn (a) and boron modified oligo C-Bn (b)

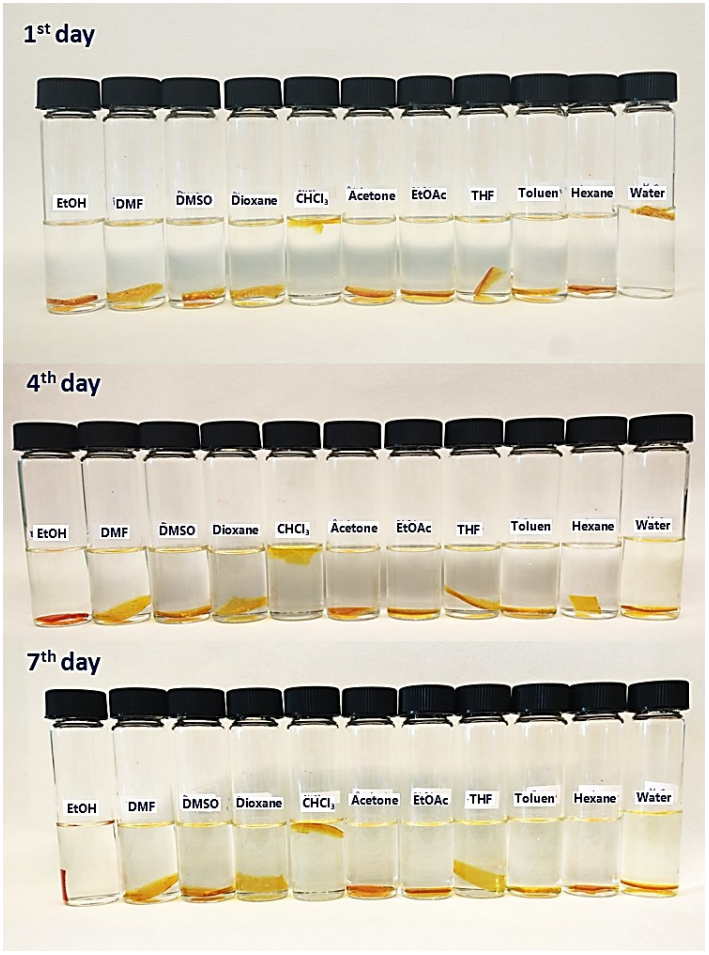


Figure S10: Images of solubility tests for cured PPO_{900}-Bz-Bor in different solvents

Table S1. Solvent fractions of PPO_{900}-Bz-Bor in different solvents at 30 °C.

Solvent	Gel fraction (%-wt)
EtOH	91
DMF	91
DMSO	94
1,4-Dioxane	93
$CHCl_3$	90
Acetone	93
EtOAc	94
THF	93
Toluene	99
Hexane	99
Water	88

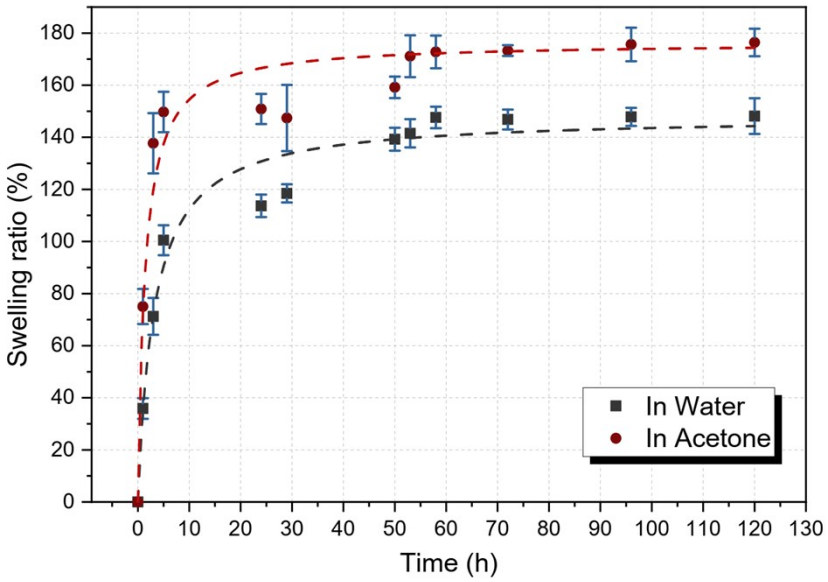


Figure S11: Swelling ratio vs time graphs for cured PPO900-Bz-Bor film in acetone and water. Curve fitting added as dashed lines.

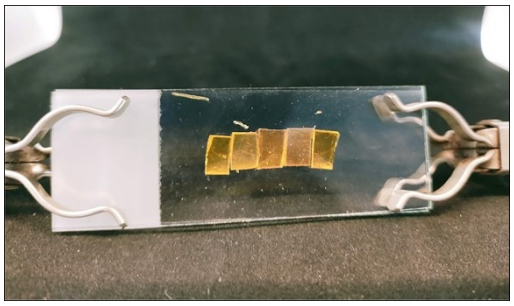


Figure S12: Image of a representative set-up for self-healing experiments

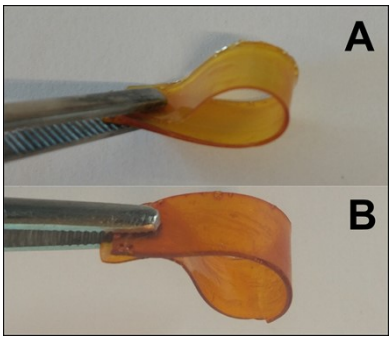


Figure S13: Images of cured PPO_{600}-Bz-Bor (A) and recycled (2 times) (B)

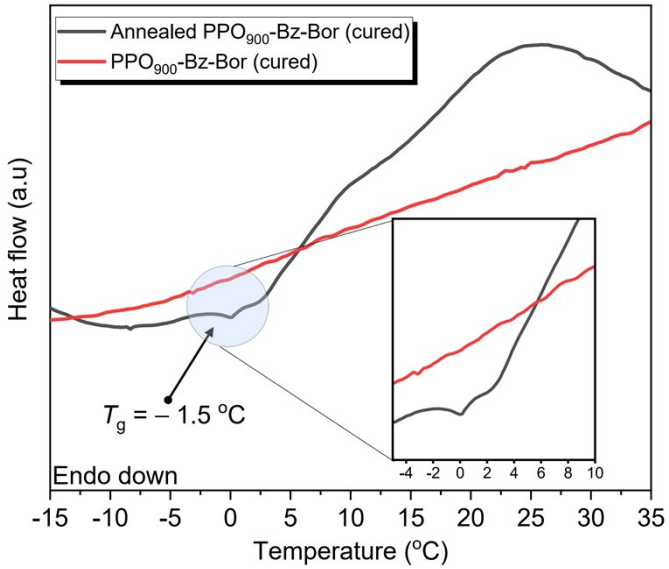
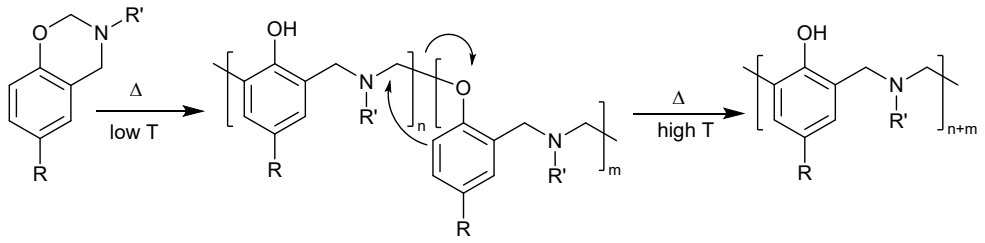


Figure S14: Overlaid DSC thermograms for cured PPO_{900}-Bz-Bor and annealed sample. Annealing was performed as follows: A piece of film was heated up to 100 °C and then immediately dropped in liquid nitrogen.



Scheme S2: Formation and subsequent rearrangement of phenoxymethyl type bridges

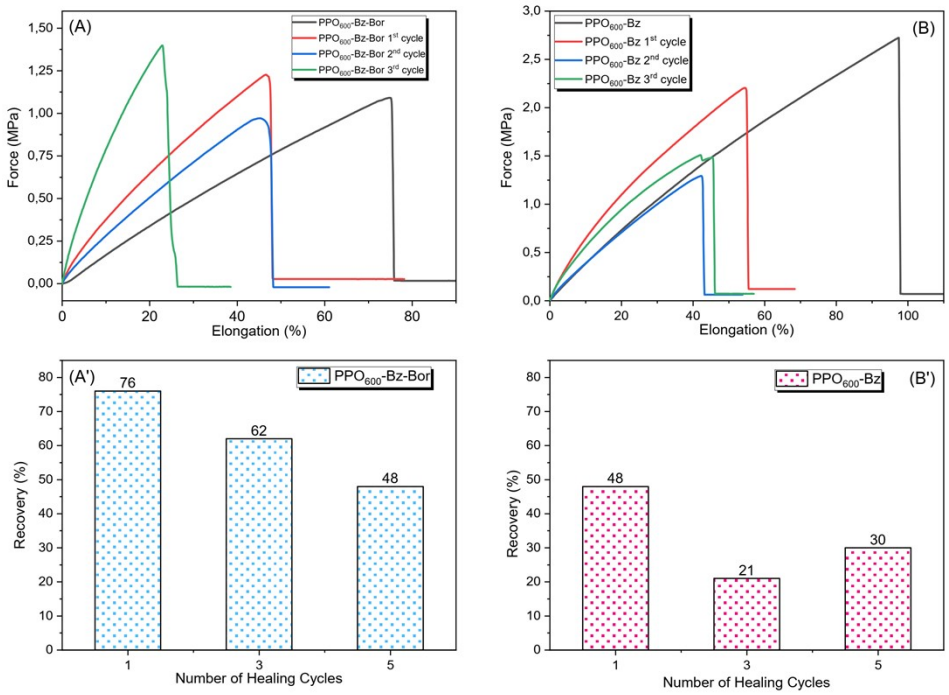


Figure S15: Stress-strain analysis of PPO_{600}-Bz-Bor (A), PPO_{600}-Bz (B) and healing efficiencies of PPO_{600}-Bz-Bor (A'), PPO_{600}-Bz (B')

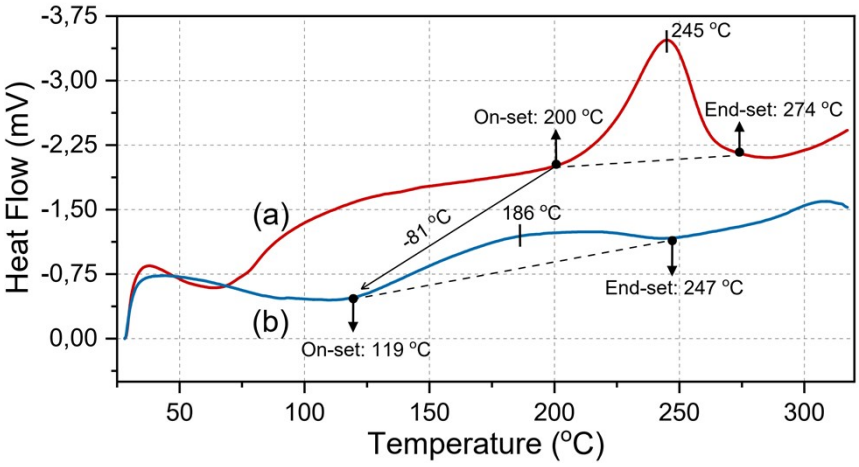


Figure S16: Overlaid DSC thermograms of PPO_{900}-Bz (a) and PPO_{900}-Bz/$PhB(OH)_2$ 10%wt mixture (b)

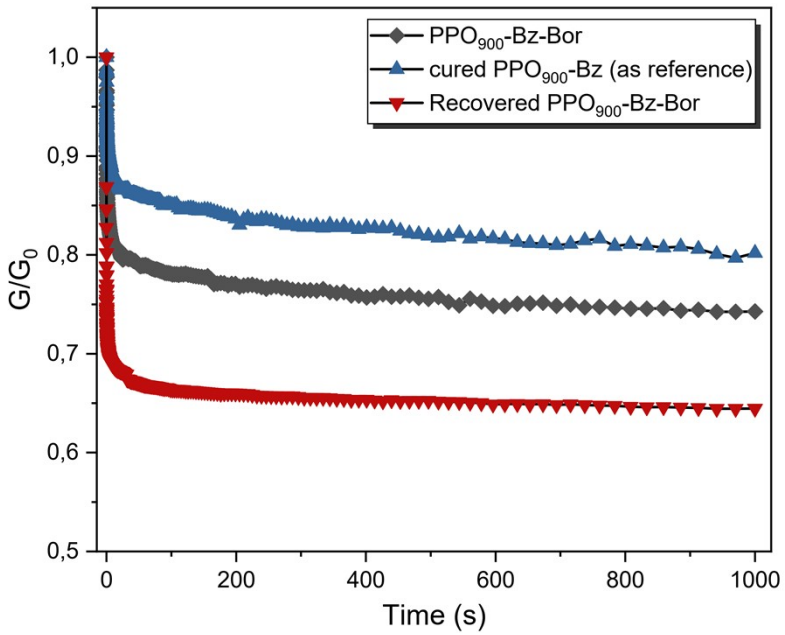


Figure S17: Normalized relaxation module (G) vs time graphs for PPO900-Bz-Bor, self-healed sample and PPO900-Bz as reference

Table S2: Thermal properties of the cured[a] PPO_{900}-Bz and PPO_{900}-Bz-Bor polymers.

Cured Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_c (%)	T_{max} (°C)
PPO_{900}-Bz	331	358	15	405
PPO_{900}-Bz-Bor	220	323	18	415
PPO_{900}-Bz-Bor 3rd recycle	277	339	22	416
PPO_{900}-Bz-Bor 5th recycle	314	352	25	416

[a] Curing of polymers was performed in an opne-air oven device at *ca.* 180 °C for 30 min. $T_{5\%}$: The temperature for which the weight loss is 5% by mass, $T_{10\%}$: The temperature for which the weight loss is 10% by mass, T_c: The char yield at 800 °C, T_{max}: The temperature for maximum weight loss that extracted from derivative TGA graph (Fig. 7).