## From Flexible to Mesoporous Polybenzoxazine Resins Templated by Poly(ethylene oxide-*b*-ε-caprolactone) Copolymer through Reaction Induced Microphase Separation Mechanism

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Scheme S1: The possible different mesoporous polybenzoxazine by carefully controlling curing temperature and process.



Figure S1: <sup>1</sup>H NMR of PEO<sub>114</sub>-b-PCL<sub>88</sub> copolymer used in this study.



Figure S2: DSC thermogram of pure PA-OH by heating rate: 20 °C/min



Figure S3: TGA thermograms of polybenzoxazine/PEO-b-PCL blends of various compositions



Figure S4: (a) SAXS patterns and (b–e) TEM images of mesoporous polybenzoxazine templated by  $PEO_{114}$ -*b*-PCL<sub>168</sub> at weight fractions of (b) 40/60, (c) 50/50, (d) 60/40, and (e) 70/30



Figure S5: (a) SAXS patterns and (b–e) TEM images of mesoporous polybenzoxazine templated by PCL<sub>220</sub>-*b*-PEO<sub>2272</sub>-*b*-PCL<sub>220</sub> at weight fractions of (b) 40/60, (c) 50/50, (d) 60/40, and (e) 70/30



Figure S6: N<sub>2</sub> adsorption/desorption isotherms of templated by (a)  $PEO_{114}-b-PCL_{168}$  and (b)  $PCL_{220}-b-PEO_{2272}-b-PCL_{22}$ .