

Supplementary Information for:

Bottle Brush Star Block Copolymer Nanoreactor for Efficient Photooxidation Catalysts: Effects of Chain Softness

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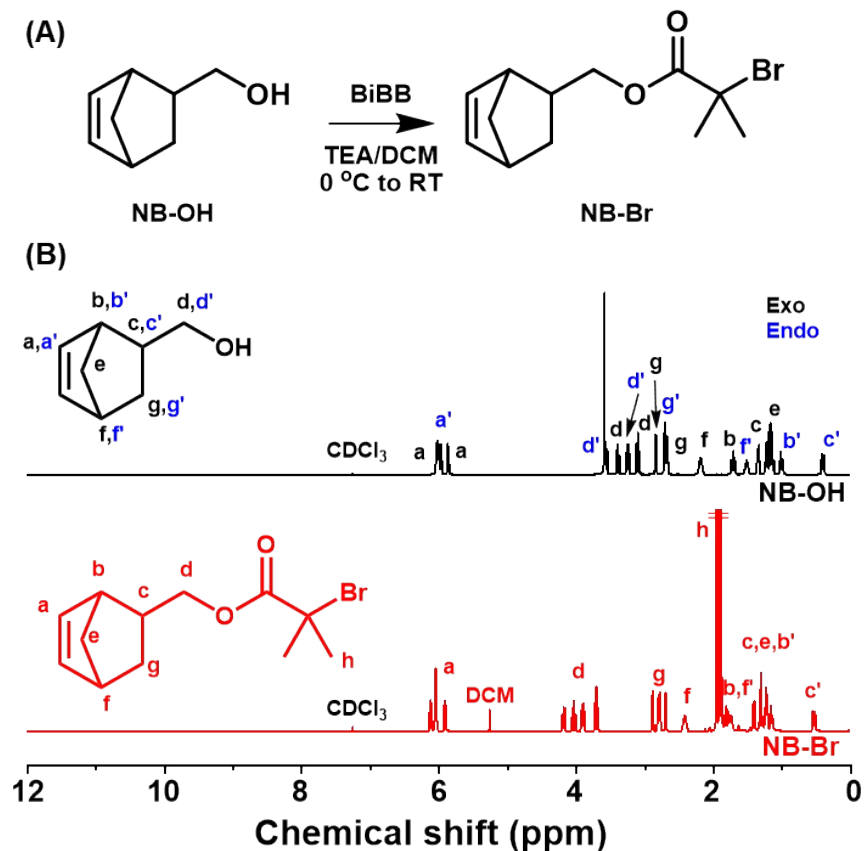


Figure S1. (A) Synthesis scheme of NB-Br and (B) ^1H NMR spectra of NB-OH and NB-Br.

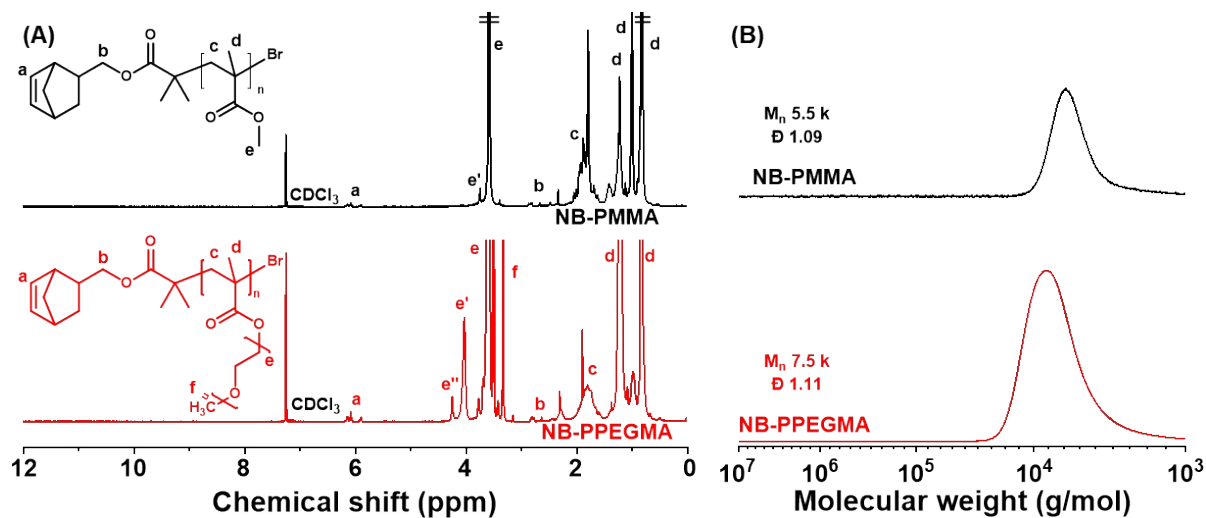


Figure S2. (A) ^1H NMR spectra and (B) GPC spectra of NB-PMMA and NB-PPEGMA.

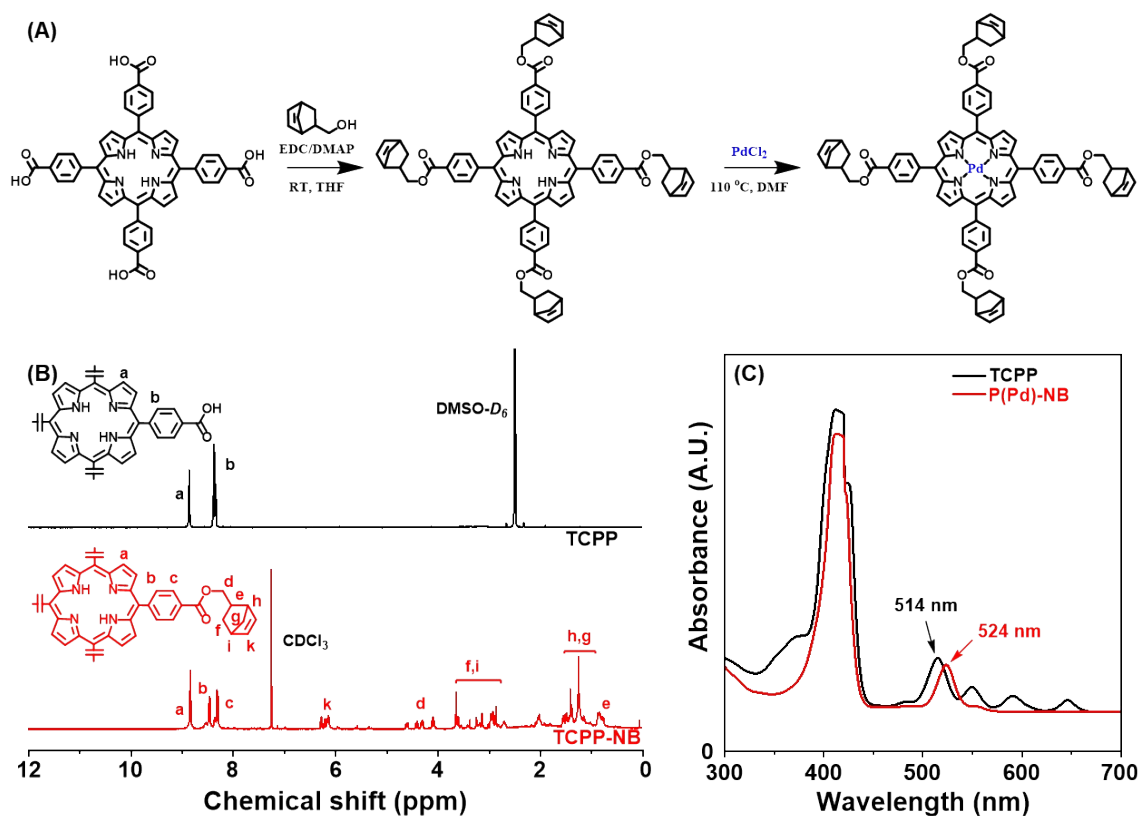


Figure S3. (A) Synthesis scheme of TCPP(Pd)-NB, (B) ¹H NMR spectra of TCPP and TCPP-NB, and (C) UV-Vis spectra of TCPP and P(Pd)-NB.

Table S1. Summarized profiles for synthesis of P(Pd)-P(NB-PMMA) by ROMP

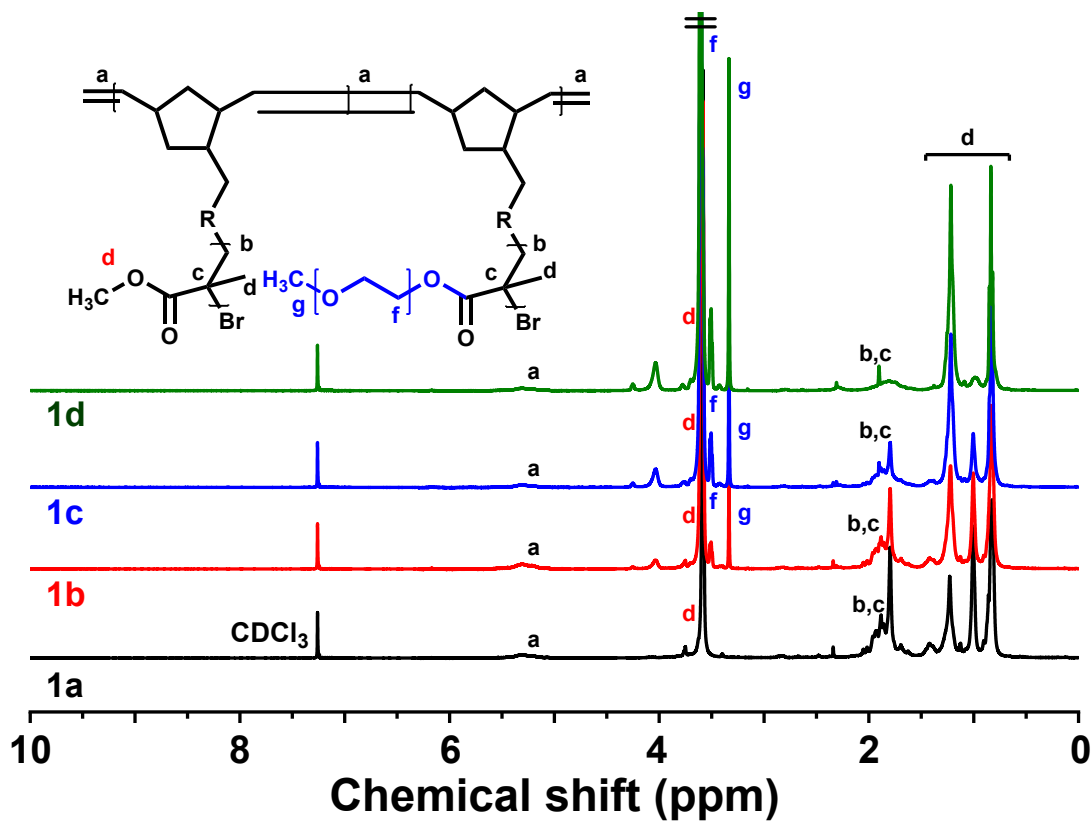
Time (min)	Conversion (%)	ln([M] ₀ /[M] _t)	M _n ^a (g/mol)	Đ ^a
1	39.3	0.499	44k	1.09
2	48.7	0.667	51 k	1.09
3	55.8	0.816	55 k	1.10
5	65.3	1.058	58 k	1.12
10	75.6	1.410	63 k	1.13
12	81	1.660	66 k	1.14
15	100	-	72 k	1.15

^a Molecular weight and Đ index of star polymers were characterized by SEC using PMMA standard.

Table S2. Summarized profiles for amphiphilic bottle brush star block copolymers

Entry	Sample name	$M_1 : M_2^a$	$M_{n,RI} / \bar{D}^b$
		(wt%)	(g/mol)
1	1a	100 : 0	72 k / 1.15
2	1b	63.1 : 36.9	68 k / 1.26
3	1c	27.8 : 72.2	70 k / 1.35
4	1d	0 : 100	61 k / 1.23

^a The relative ratios between M1 and M2 are calculated by ¹H NMR, ^b Molecular weight and $\bar{D}$ index of star polymers were characterized by SEC using PMMA standard.

**Figure S4.** ¹H NMR spectra of 1a, 1b, 1c, and 1d.

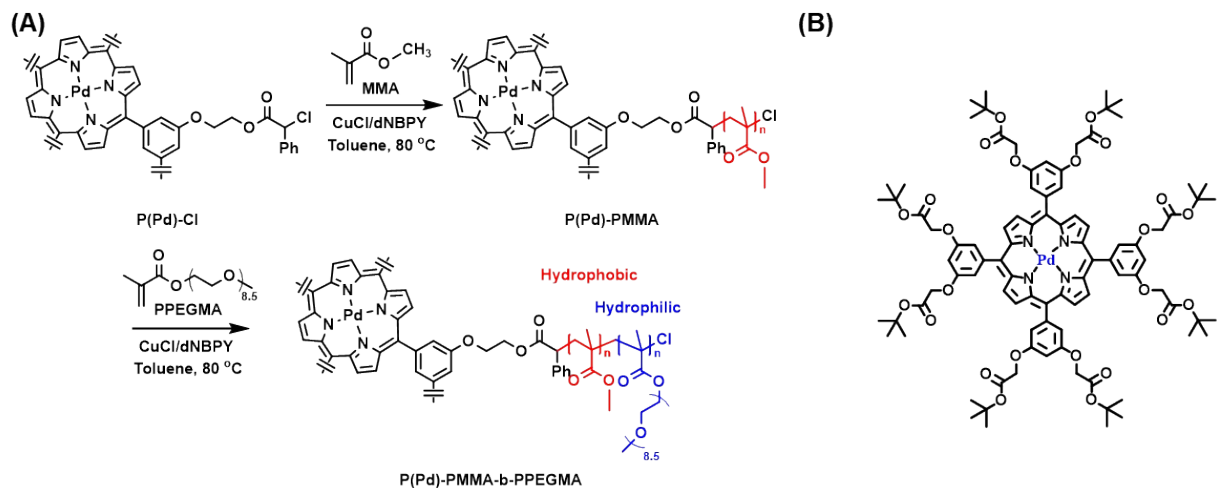


Figure S5. (A) Synthesis scheme of P(Pd)-PMMA-b-PPEGMA by ATRP, (B) Chemical structure of P(Pd) for photocatalytic reaction.

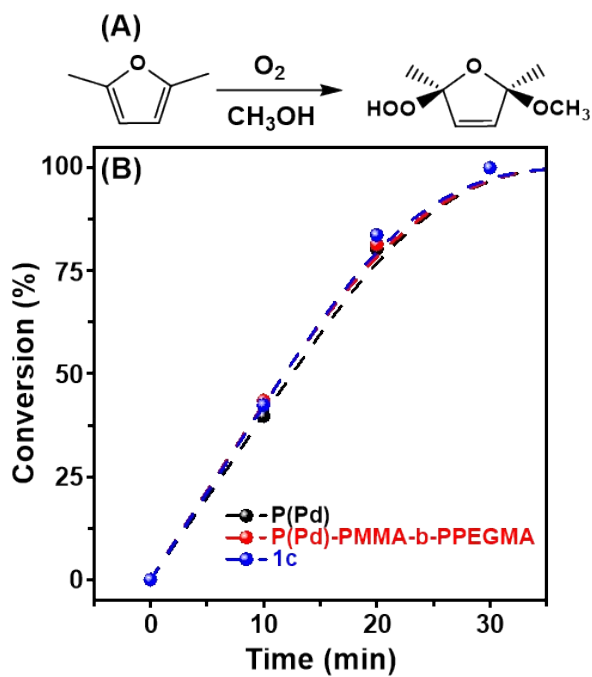
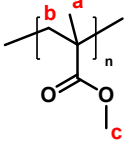


Figure S6. (A) 2,5-dimethyl furan oxidation scheme, (B) Oxidation kinetics of 2,5-dimethyl furfural using various catalysts

Table S3. Spin-Lattice relaxation (T_1) measurements for the PMMA polymer with linear or star structure

Entry	Structure	Architecture	T_1^a (ms)	T_1^b (ms)	T_1^c (ms)
1		Star	137.0	46.4	46.6
2		Bottle brush star	103.1	35.1	35.2

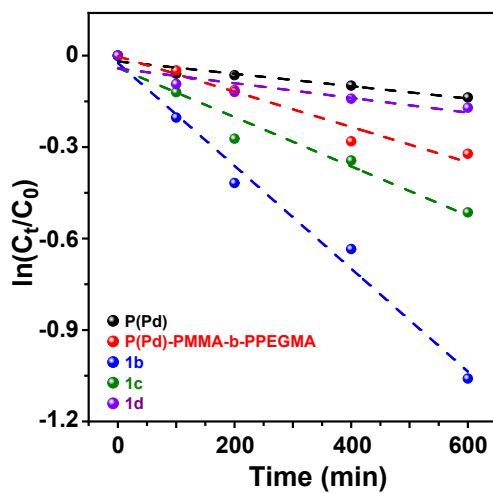


Figure S7. Linear plots ($\ln(C_t/C_0)$ vs., time) of the furfural oxidation using catalysts.