Supporting Information

Fabrication of Novel Porous Functional Nanonetwork-Structured Polymers with Enhanced Adsorption Performance from Well-Defined Molecular Brush Building Blocks

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EXPERIMENTAL SECTION

Materials

(2-Trimetylsiloxy)ethyl methacrylate (HEMA-TMS, Scientific Polymer Products), tertbutyl acrylate (tBA, 99%, Acros) and styrene (S, 99%, Aldrich) were purified by passing the monomer through a column filled with basic alumina to remove the inhibitor. Ethylene bis(2-bromoisobutvrate) (2f-BiB) was synthesized based on previously reported procedures^{1,2}. Ethyl 2-bromoisobutyrate (EBiB, 98%, Acros), copper(I) bromide (CuBr, 99.999%, Aldrich), copper(I) chloride (CuCl, ≥99.995%, Aldrich), copper(II) bromide (CuBr₂, 98%, Acros), copper(II) chloride (CuCl₂, ≥99.995%, Aldrich), 4,4'-dinonyl-2,2'bipyridyne (dNbpy, 97%, Aldrich), N,N,N',N", Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), tris(2-dimethylaminoethyl)amine (Me₆TREN, ≥99%, Alfa Aesar), potassium fluoride (KF, 99%, Aldrich), tetrahydrofuran (THF, HPLC, Aldrich), dimethyl formamide (DMF, HPLC, Aldrich), tetrabutylammonium fluoride (TBAF, 1.0 M in THF, Aldrich), α-bromoisobutyryl bromide (98%, Aldrich), 2,5-di-tert-butylphenol (DTBP, 99%), triethylamine (TEA, ≥99%, Aldrich), trifluoroacetic acid (TFA, ≥98%, Aldrich), anhydrous ferric chloride (FeCl₃, AR, Aladdin), dichloromethane (HPLC, Aladdin), formaldehyde dimethyl acetal (FDA, AR, Aladdin) and solvents were used as received without further purification.

Characterization

Apparent number-average molecular weights (M_n) and dispersity (D) were measured by gel permeation chromatography (GPC). The GPC was conducted with a Waters 515 pump and Waters 2414 differential refractometer using PSS columns (SDV 10⁵, 10³, 500

Å) with THF as eluent at 35 °C and at a flow rate of 1 mL min⁻¹. Linear poly(methyl methacrylate) (PMMA) and polystyrene (PS) standards were used for calibration. The conversion and composition of the polymers were measured via ¹H nuclear magnetic resonance (¹H NMR) spectroscopy using a Bruker Advance 300 MHz NMR spectrometer with CDCl₃ as a solvent. The nanostructures of the samples were investigated by a Hitachi S-4800 scanning electron microscope (SEM) and a FEI Tecnai G2 Spirit transmission electron microscope (TEM). Fourier transform infrared (FTIR) spectra were conducted at room temperature on a Bruker Equinox 55 Fourier transform infrared spectroscopy. N₂ adsorption measurements were carried out using a Micromeritics ASAP 2020 analyzer at 77 K. The BET surface area (SBET) was determined by Brunauer-Emmett-Teller (BET) theory. The pore size distribution was analyzed by original density functional theory (DFT) combined with non-negative regularization and medium smoothing. The concentration of methyl violet was detected by a Shimadzu UV-Vis-NIR Spectrophotometer. The thermal stability of the samples was monitored using a thermogravimetric analysis (TGA Q50) under nitrogen flow with a heating rate of 20 °C \min^{-1} .

Synthesis of poly(2-bromoisobutyryloxyethyl methacrylate) (PBiBEM)

The general procedure is described below for the synthesis of PB*i*BEM₁₈₆₀ (**Table S1**). A 25 mL Schlenk flask was charged with EBiB (1.3 μ L, 8.71 μ mol), HEMA-TMS (15.2 mL, 69.7 mmol), dNbpy (0.089 g, 0.218 mmol), CuCl₂ (0.6 mg, 0.004 mmol), and anisole (1.7 mL). The solution was degassed by three freeze–pump–thaw cycles. During the final cycle, the flask was filled with nitrogen, and CuCl (9.9 mg, 0.100 mmol) was

quickly added to the frozen reaction mixture. The flask was sealed, evacuated, and backfilled with nitrogen five times and then immersed in an oil bath at 40 °C. Polymerization was stopped when conversion reached 23.3% as determined by ¹H NMR spectroscopy. From the molar ratio of the reacted monomer to initiator, the degree of polymerization (DP) was calculated to be 1860. The reaction mixture was diluted with methylene chloride, passed through neutral alumina column to remove the catalyst, concentrated, and then used in the next step without further purification.

A 50 ml round-bottom flask was charged with the product of the previous step (1.60 g, 7.92 mmol HEMA-TMS repeat unit), KF (0.55 g, 9.5 mmol), DTBP (163 mg, 0.792 mmol), and then dry THF (25 mL) was added under nitrogen. The reaction mixture was cooled down in an ice bath, followed by the injection of tetrabutylammonium fluoride (0.08 mL, 1.0 M in THF, 0.08 mmol) and subsequent dropwise addition of α -bromoisobutyryl bromide (1.18 mL, 9.5 mmol) over the course of 20 min. The reaction mixture was then allowed to reach room temperature and was stirred for another 24 h. Afterwards, the solids were filtered off and the mixture was precipitated by the addition of the filtered solution to methanol/water (70/30). The solids were then re-dissolved in methylene chloride (20 mL) and passed through the column filled with basic alumina. The product PB*i*BEM₁₈₆₀ was re-precipitated three times in hexanes and dried overnight under vacuum. Apparent molecular weight determined by THF GPC: $M_n = 342,000$, and $M_w/M_n = 1.43$.

 $PBiBEM_{1640}$ was also prepared according to the above procedure using the stoichiometric ratios shown in **Table S1**.

Entry	М	dNbpy	CuCl	CuCl ₂	Solvent	Conv. ^b	DP ^b	$M_{\rm n}{}^{\rm c}$	$M_{\rm w}/M_{\rm n}^{\rm c}$
PBiBEM ₁₈₆₀	8000	25	11.5	0.5	10%	23.3%	1860	342,000	1.43
$PBiBEM_{1640}^{d}$	8000	48	47	1	10%	20.5%	1640	293,000	1.28

Table S1. Experimental condition for the synthesis of PB*i*BEM^a

^a Numbers in the column of M, dNbpy, CuCl and CuCl₂ stand for molar ratios of initial monomer, ligand, CuCl and CuCl₂ to EBiB initiator. ^b The conversion measured by ¹H NMR and the degrees of polymerization (DP) of backbones calculated from the monomer conversion and the initial monomer to initiator ratio. ^c Determined by GPC using linear PMMA standards. ^d Equivalents scaled to one equivalent of a bifunctional initiator (2f-BiB).

Synthesis of poly(2-bromoisobutyryloxyethyl methacrylate)-*graft*-polystyrene) (P(BiBEM-g-PS))

The general procedure for the synthesis of the bottlebrush macromolecules is described below for the synthesis of P(B*i*BEM-*g*-PS₂₂₀)₁₈₆₀ (**Table S2**). The PB*i*BEM₁₈₆₀ (0.0182 g, 0.0652 mmol initiator centers), styrene (15.0 mL, 0.130 mol), PMDETA (45.2 mg, 0.26 mmol), CuBr₂ (1.2 mg, 0.0052 mmol), and anisole (1.7 mL) were added to a 50 mL Schlenk flask. The solution was degassed by three freeze–pump–thaw cycles. During the final cycle, the flask was filled with nitrogen, and CuBr (36.4 mg, 0.256 mmol) was quickly added to the frozen reaction mixture. The flask was sealed, evacuated, and backfilled with nitrogen five times and then immersed in an oil bath at 55 °C. Polymerization was stopped when conversion reached 11% as determined by ¹H NMR spectroscopy. The reaction mixture was diluted with methylene chloride, passed through a neutral alumina column to remove the catalyst, and concentrated, and the product was precipitated by addition to methanol and dried overnight under vacuum. Apparent molecular weight determined by THF GPC: $M_n = 1,350,000$, and $M_w/M_n = 1.33$.

Table 52. Experimental condition for the synthesis of P(BiBEM-g-PS)	Table S2	. Experimenta	l condition	for the s	ynthesis	of P(BiBEM-g-	PS)
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Entry	М	PMDETA	CuBr	CuBr ₂	Solvent	Conv. ^b	DP _{PS} ^b	$M_{\rm n}^{\rm c}$	$M_{\rm w}/M_{\rm n}^{\rm c}$
P(BiBEM-g-PS ₂₂₀) ₁₈₆₀	2000	4.0	3.9	0.08	10%	11%	220	1,350,000	1.33

^a Numbers in the column of M, PMDETA, CuBr and CuBr₂ stand for molar ratios of initial monomer, ligand, CuBr and CuBr₂ to initiating sites, respectively. ^b The conversion measured by ¹H NMR and the DP of PS side chain calculated from the monomer conversion and the initial monomer to initiator ratio. ^c Determined by GPC using linear PS standards.

Synthesis of poly[2-(2-bromoisobutyryloxy)ethyl methacrylate-*graft*-(*tert*-butyl acrylate)-*block*-styrene] (P[B*i*BEM-*g*-(P*t*BA-*b*-PS)])

The general procedure for the synthesis of the bottlebrush macromolecules is described below for the synthesis of P[B*i*BEM-*g*-(P*t*BA₄₂-*b*-PS₅₂)]₁₈₆₀ (**Table S3** and **Table S4**). A 100 mL Schlenk flask was charged with PB*i*BEM₁₈₆₀ (0.350 g, 1.25 mmol initiator centers), *t*BA (18.2 mL, 0.125 mol), Me₆TREN (72.3 mg, 0.314 mmol), CuBr₂ (14.0 mg, 0.0627 mmol), DMF (14.6 mL) and anisole (58.2 mL). The solution was degassed by three freeze–pump–thaw cycles. During the final cycle, the flask was filled with nitrogen, and CuBr (35.9 mg, 0.251 mmol) was quickly added to the frozen reaction mixture. The flask was sealed, evacuated, and backfilled with nitrogen five times and then immersed in an oil bath at 25 °C. Polymerization was stopped when conversion reached 42% as determined by ¹H NMR spectroscopy. From the monomer conversion and the initial ratio of initiator to monomer, the DP of P*t*BA side chains was calculated to be 42 (assuming 100% initiation efficiency from the multifunctional macroinitiator). Unreacted monomer was removed by ultrafiltration in methanol/THF (50/50, vol%) solution using an ultrafiltration membrane (Biotech, Regenerated Cellulose, MWCO: 3,500). The P*t*BA brush was dried under vacuum to a constant mass.

The P*t*BA brush (1.21g, 0.225 mmol chain end, assuming 100% initiation efficiency in last step), styrene (30.00 mL, 261 mmol), PMDETA (0.052 mL, 0.248 mmol), CuBr₂ (2.5 mg, 0.011 mmol), and anisole (3.3 mL) were added to a 50 mL Schlenk flask. The solution was degassed by three freeze–pump–thaw cycles. During the final cycle, the flask was filled with nitrogen, and CuBr (30.6 mg, 0.214 mmol) was quickly added to the frozen reaction mixture. The flask was sealed, evacuated, and backfilled with nitrogen five times and then immersed in an oil bath at 50 °C. Polymerization was stopped when conversion reached 4.5% as determined by ¹H NMR spectroscopy. The reaction mixture was diluted with methylene chloride, passed through a neutral alumina column to remove the catalyst, and concentrated, and the product P[B*i*BEM-*g*-(P*t*BA₄₂-*b*-PS₅₂)]₁₈₆₀ was precipitated by addition to methanol and dried overnight under vacuum. Apparent molecular weight determined by THF GPC: $M_{n,GPC} = 1,680,000$, and $M_w/M_n = 1.33$.

 $P[BiBEM-g-(PtBA_{50}-b-PS_{172})]_{1640}$ was also prepared according to the above procedure using the stoichiometric ratios shown in **Table S3** and **Table S4**.

Fable S3. Experimenta	l condition for	the synthesis	of P(B <i>i</i> BEM- <i>g</i> -P <i>t</i> BA) ^a
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Entry	М	Me ₆ TREN	CuBr	CuBr ₂	DMF	Anisole	Conv. ^b	DP _{PtBA} ^b	$M_{\rm n}^{\rm c}$	$M_{\rm w}/M_{\rm n}^{\rm c}$
P(B <i>i</i> BEM- <i>g</i> -P <i>t</i> BA ₄₂) ₁₈₆₀	100	0.25	0.20	0.05	16%	64%	42%	42	1,580,000	1.27
P(B <i>i</i> BEM- <i>g</i> -P <i>t</i> BA ₅₀) ₁₆₄₀	100	0.25	0.20	0.05	16%	64%	50%	50	2,160,000	1.21

^a Numbers in the column of M, Me_6TREN , CuBr and $CuBr_2$ stand for relative ratios of initial monomer, ligand, CuBr and $CuBr_2$ to initiating sites, respectively. ^b The conversion measured by ¹H NMR and the DP of PtBA side chain calculated from the monomer conversion based on the monomer to initiator ratio. ^c Determined by GPC using linear PS standards.

Table S4. Experimental condition for the synthesis of P[B*i*BEM-g-(P*t*BA-*b*-PS)]^a

Entry	М	PMDETA	CuBr	CuBr ₂	Solvent	Conv. ^b	DP _{PS} ^b	M_n^{c}	$M_{\rm w}/M_{\rm n}^{\rm c}$
P[BiBEM-g-(PtBA ₄₂ -b-PS ₅₂)] ₁₈₆₀	1160	1.1	0.95	0.05	10%	4.5%	52	1,680,000	1.33
$P[BiBEM-g-(PtBA_{50}-b-PS_{172})]_{1640}$	2500	8.0	3.8	0.2	10%	6.9%	172	2,640,000	1.28

^a Numbers in the column of M, PMDETA, CuBr and CuBr₂ stand for relative ratios of initial monomer, ligand, CuBr and CuBr₂ to chain end, respectively. ^b The conversion measured by ¹H NMR and the DP of PS side chain calculated from the monomer conversion based on the monomer to initiator ratio. ^c Determined by GPC using linear PS standards.

Synthesis of functional nanonetwork-structured polymers (FNSPs)

70 mg of P[B*i*BEM-*g*-(P*t*BA-*b*-PS)] was dissolved in 20 mL of 1,2-dichloroethane under N₂ in a flask with a reflux condenser. Then, formaldehyde dimethyl acetal (200 μ L, 2.3 mmol) and FeCl₃ (400 mg, 2.5 mmol) were added. The flask was heated at 80 °C for 12 h with magnetic stirring. The as-prepared products were washed with acetone, 1 M HCl solution and water several times. FNSPs were collected via freeze-drying. The preparation process of nanonetwork-structured polymer (NSP) was the same as that of FNSPs, except using P(B*i*BEM-*g*-PS) as building block.

Adsorption experiments toward methyl violet

Methyl violet adsorption experiments were performed as follows. FNSPs (20 mg) was immersed in a solution (water/ethanol=24/1) of methyl violet (80 mL, 200 mg L⁻¹), and stirred in a water bath at 25 °C. At predetermined time intervals, 0.3 ml of solution was taken and diluted for UV-Vis test. The adsorption capacity was calculated by measuring methyl violet concentration before and after adsorbed by FNSPs. NSP was subjected to the same adsorption procedure described above and used as a control.



Figure S1. Syntheses of molecular bottlebrush poly[2-(2-bromoisobutyryloxy)ethyl methacrylate-*graft*-(*tert*-butyl acrylate)-*block*-styrene] (P[B*i*BEM-*g*-(P*t*BA-*b*-PS)]) as a building block.



Figure S2. ¹H NMR spectrum of P[B*i*BEM-*g*-(P*t*BA₅₀-*b*-PS₁₇₂)]₁₆₄₀ (solvent: CDCl₃).



Figure S3. GPC traces of $PBiBEM_{1640}$ (gray), $P(BiBEM-g-PtBA_{50})_{1640}$ (blue), and $P[BiBEM-g-(PtBA_{50}-b-PS_{172})]_{1640}$ (red).



Figure S4. SEM image of P[B*i*BEM-*g*-(P*t*BA₅₀-*b*-PS₁₇₂)]₁₆₄₀.



Figure S5. Friedel-Crafts hypercrosslinking reaction scheme for FNSPs. In presence of a Lewis acid, $CH_3OCH_2^+$ carbocations can react with the phenyl rings and form $-CH_2OCH_3$ groups, and then generate $-CH_2$ - crosslinking bridges between neighboring phenyl rings as the reaction progresses.



Figure S6. TGA curves of P[BiBEM-g-(PtBA₅₀-b-PS₁₇₂)]₁₆₄₀ and FNSP-PS_L.



Figure S7. FTIR spectra of $FNSP-PS_L$ and $P[BiBEM-g-(PtBA_{50}-b-PS_{172})]_{1640}$.



Figure S8. TEM image of FNSP-PS_s.

Sample	Adsorption capacity (mg g ⁻¹)	Reference
FNSP-PS _L	767	This work
FNNSP-PAA ₈₁ -b-PS ₁₂₁₈	339	[3]
ASPAL	232	[4]
h-XG/SiO ₂ -2 nanocomposite	378.8	[5]
РААС	500	[6]
CSM	99.3	[7]
GMC	202.8	[8]
Modified baker's yeast	60.8	[9]
GAC	95	[10]
Crosslinked amphoteric starch	333.3	[11]

Table S5. Summary of adsorption capacities toward methyl violet for reported adsorbents.

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