

Supporting Information

for

Creation of Discrete Active Site Domains via Mesoporous Silica Poly(styrene) Composite Materials for Incompatible Acid-Base Cascade Reactions

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1. Materials

Copper (0) powder < 75 μm , 99% (Sigma Aldrich) was purified by agitation in concentrated HCl (37%, ACS, VWR) for 30 minutes at room temperature. Afterwards, it was filtered and rinsed with deionized (DI) water and dried before use. Both styrene ($\geq 99\%$, contains 4-tert-butylcatechol as stabilizer, Sigma Aldrich) and 4-vinylbenzyl chloride ($\geq 90\%$, contains 0.1% total stabilizer, Sigma Aldrich) were purified by filtering through a column of basic alumina (aluminum oxide activated, basic, Brockmann I, Sigma Aldrich) before use.

P123 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) average $M_n \sim 5,800$ 20:70:20 (EO:PO:EO)), tetraethyl orthosilicate (TEOS) ($\geq 99.0\%$, Sigma Aldrich), Hexadecyltrimethylammonium bromide (CTAB) ($\geq 98\%$, Sigma Aldrich), NH_4OH solution 28% ($\geq 99.99\%$ trace metals basis, Sigma Aldrich) were used as received.

The anhydrous solvents tetrahydrofuran (THF) ($\geq 99.9\%$, contains 250 ppm BHT as inhibitor, Sigma Aldrich), toluene (99.8%, Sigma Aldrich), acetonitrile (MeCN) (99.8%, Sigma Aldrich) were used as received.

The bulk solvents toluene ($\geq 99.5\%$ ACS, VWR Chemicals BDH), dichloromethane (DCM) ($\geq 99.5\%$ stabilized ACS, VWR Chemicals BDH), ethanol 200 proof (99.5%, Koptech/VWR) were used as received.

The reagents (3-mercaptopropyl) trimethoxysilane 95%, 5-hexen-1-ol 98%, α -bromoisobutyrylbromide 98%, pyridine anhydrous 99.8%, magnesium sulfate anhydrous $\geq 99.5\%$, sodium azide $\geq 99.5\%$, *N,N*-dimethylformamide anhydrous 99.8%, triphenylphosphine 99%, phthalic anhydride $\geq 99\%$, triethylamine $\geq 99.5\%$, *N,N,N',N'',N'''*-pentamethyldiethylenetriamine 99%, copper(II) bromide 99%, 2,2-dimethoxy-2-phenylacetophenone (DMPA) 99%, benzaldehyde dimethyl acetal 99%, benzaldehyde $\geq 99\%$, malononitrile $\geq 99\%$, decane $\geq 95\%$, hydrogen peroxide solution 30 % (w/w) in H_2O , contains stabilizer, hydrazine hydrate reagent grade, N_2H_4 50-60% were all purchased from Sigma Aldrich and used as received.

2. Analytical tools and instrumentation

Organic contents for all functionalized silica samples were measured via a Netzsch STA-409 Luxx – thermogravimetric analyzer – differential scanning calorimeter (TGA-DSC). The temperature program used was from 25 – 900 °C at 10 °C/min. Mass changes for thiol grafted samples were recorded in the 200 – 600 °C range. Mass changes for the brush functionalized samples were recorded in the 200 – 700 °C range. Loss from the bare supports in the same ranges were accounted for in all TGA loading calculations.

Polymer distributions and molecular weights were determined using a Tosoh EcoSEC gel permeation chromatograph (GPC). A refractive index detector was the primary source for the analysis and the synthesized copolymer poly(styrene) derivative samples were compared to narrow poly(styrene) standards.

Physical characterization of the mesoporous silicas was determined through applying the BET method with a Micromeritics tristar N₂ analyzer at 77 K. Prior to analysis, samples were activated overnight at 30 mTorr at 110 °C for 6 h. The isotherm data points were taken from $P/P_o = 0.01$ to 0.99. Pore volume measurements were calculated from the quantity of nitrogen adsorbed to the samples at $P/P_o = 1.0$. BET surface area, external surface area, and pore size distributions were obtained from the Microactive software package provided by Micromeritics.

A Shimadzu Prestige 21 Fourier Transform Infrared Spectrometer (FT-IR) was used with diffuse light scattering for all the samples analyzed in this work. Spectra were recorded from 600 – 4000 cm⁻¹ with a total number of 128 scans.

A combustion elemental analyses (EA) was performed for all functionalized silica samples. These samples were analyzed for carbon, hydrogen, nitrogen, and sulfur. Analyses were performed by Atlantic Microlab in Norcross, GA. 6180 Atlantic Blvd., Ste M, Norcross, GA 30071

Imaging was performed using a Hitachi HD-2700 dedicated scanning-transmission electron microscope (STEM) operated at 200 KeV. Regular scanning and transmission images were recorded for both the SBA-15 and MCM-41 samples and are shown below with their respective procedures.

All nuclear magnetic resonance (NMR) spectra were collected via a Bruker AV3 HD 700 MHz NMR spectrometer. For small molecules, only 16 scans were used for ^1H NMR spectra and 512 for ^{13}C . For polymer samples, D1 was increased to 5 seconds and 128 scans were recorded to allow for visible end groups and quantitative end group analyses.

Thiol-ene click chemistry experiments were performed in tall 40 mL vials inside of a Rayonet RMR-600 photochemical reactor on a magnetic stir plate with 8 ultraviolet lamps at 365 nm at room temperature. A fan was also used to prevent heat from accumulating inside of the chamber.

3. Molecular dynamics simulation summary

Table S1: Representative radii of gyration values for the copolymers studied in this work

Entry	copolymer	MW (g/mol)	R_g^a (nm)
1	-	3600	0.92
2	poly(<i>st-co-NPhth</i>)-1	6100	1.48
3	poly(<i>st-co-NPhth</i>)-2	16000	1.80
4	poly(<i>st-co-NPhth</i>)-3	46000	-

^aDetermined through the approach outlined in the experimental section in the full paper

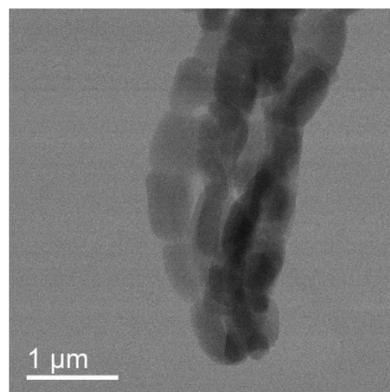
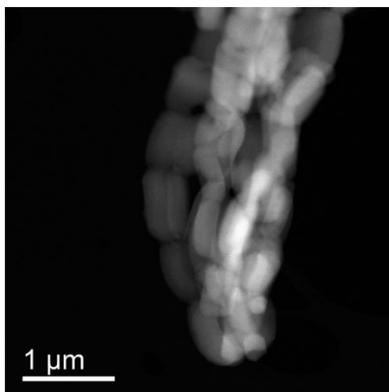
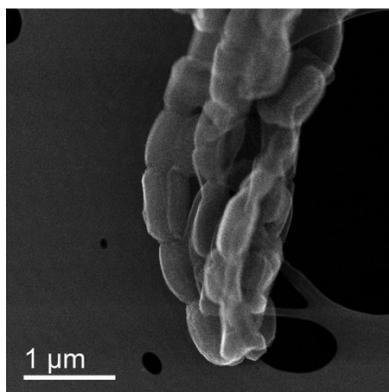
Polymer – MCM-41 pore confinement with representative 16,000 g/mol poly(*st-co-NPhth*)

To investigate the structures of the copolymers in the pores of MCM-41, we modeled a singular poly(*st-co-NPhth*) chain in the pores of MCM-41. For this purpose, first, we built MCM-41 as described by Ugliengo and co-workers,¹ with a diameter of ~ 30 Å with a wall thickness of ~ 10 Å as shown in Figure S1a. Next, we put an equilibrated poly(*st-co-NPhth*) chain with MW = 16,000 g/mol into the MCM-41 pore in the absence of solvent molecules and energy-minimized the structure using the Dreiding force field described in the models and simulation methods section. It

is demonstrated in Figures S1b and S1c that the poly(*st-co-NPhth*) chain is squeezed to fit into the pore, implying that the molecular transport through the pore would be blocked or significantly hindered. From this simulation, showing a very tight fit for the polymer chain under these conditions, it is expected that the dimension of the poly(*st-co-NPhth*) chain with MW = 16,000 g/mol would become more swollen and thus more hindered if we increase the temperature and introduce solvent due to the molecular thermal motion and solvation.

4. Synthesis of prerequisite materials

SBA-15 was synthesized according to a previous report.² To a 4 L Erlenmeyer flask equipped with a long magnetic stir bar was added 24 g of P123 triblock copolymer. To this was added 636 g of deionized water and 120 mL of 37% aqueous HCl. Vigorous agitation was allowed for up to 1 h in order to adequately dissolve the polymer. Afterwards, 46.6 g of TEOS was added dropwise then the mixture was allowed to stir at room temperature for 20 h. Next, the stir bar was removed and the temperature was increased to 100 °C for an additional 24 h. After the reaction, the mixture was filtered and rinsed with several liters of water, stored overnight at 80 °C then calcined. The calcination program is as follows: ramp from room temperature to 200 °C at 1.2 °C/min and hold for 1 h. Next, ramp from 200 °C to 550 °C at the same rate followed by a 6 h hold.



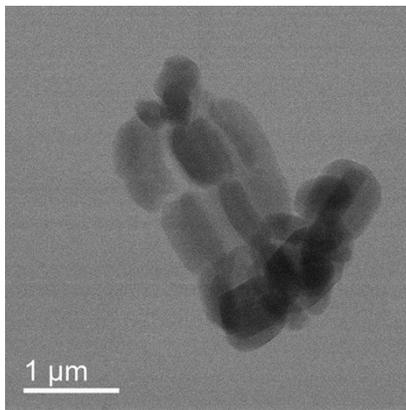
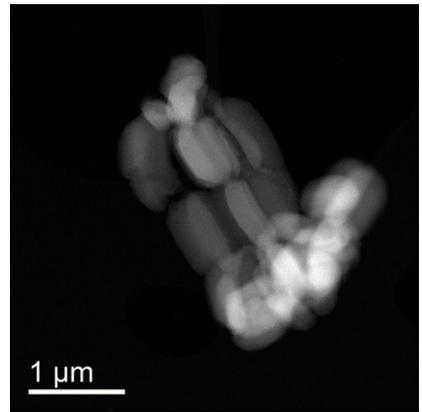
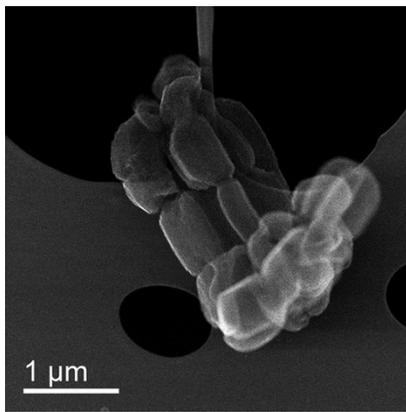
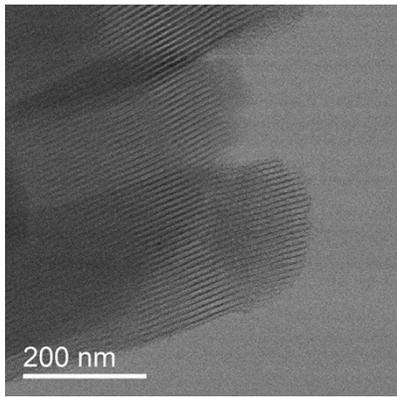
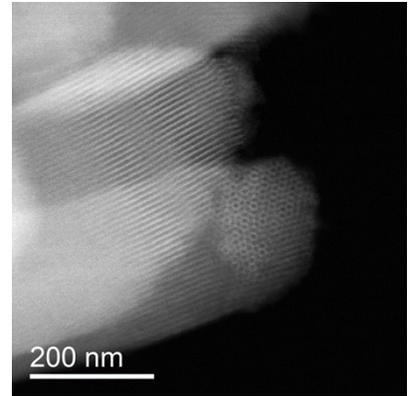
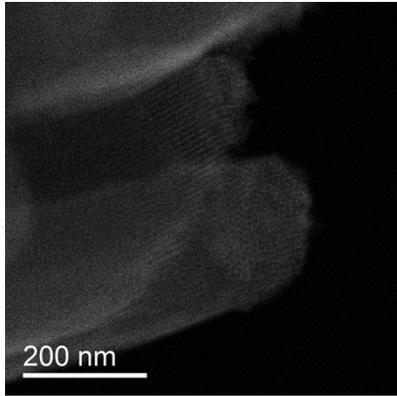
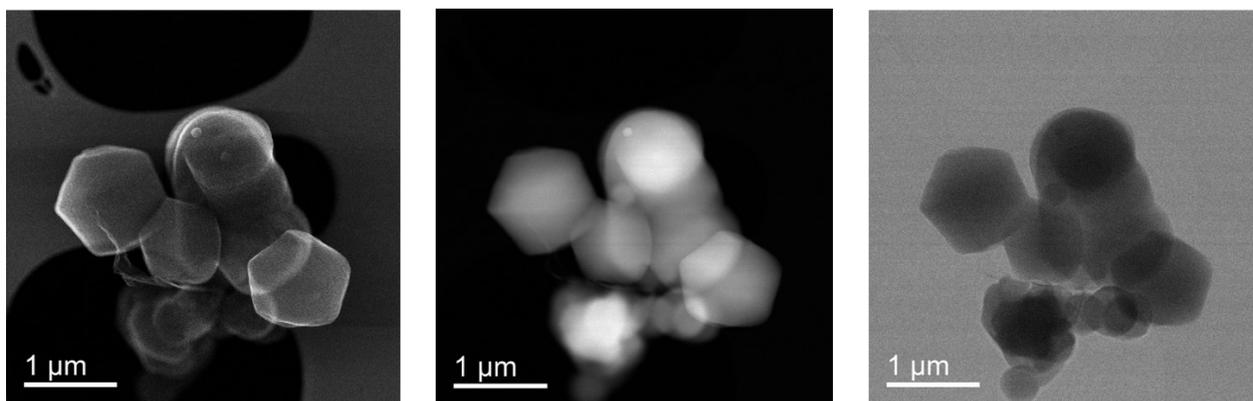


Figure S1: SEM and TEM images of the SBA-15 used in this study additional images provided (lower 6)

MCM-41 was synthesized according to a previous report.³ 1400 mg of cetyltrimethylammonium bromide was dissolved in 605 mL of deionized water in a 3 L round bottom flask equipped with a large football shaped magnetic stir bar. Next, 42.5 g of 28 wt% NH_4OH (aq) was added to the mixture followed by dropwise addition of 50 g of TEOS. The mixture was stirred vigorously at room temperature for 2 h followed by filtering and rinsing with several liters of deionized water. The collected MCM-41 sample was dried in an oven at 80 °C then calcined. The calcination program is as follows: ramp from room temperature to 200 °C at 1.2 °C/min and hold for 1 h. Next, ramp from 200 °C to 550 °C at the same rate followed by a 12 h hold.



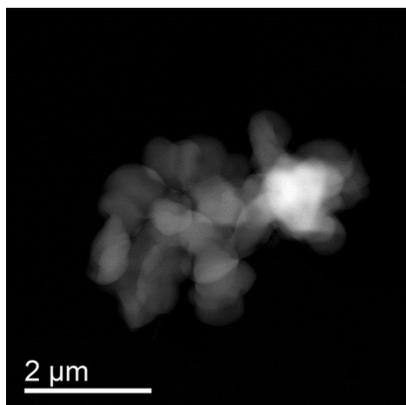
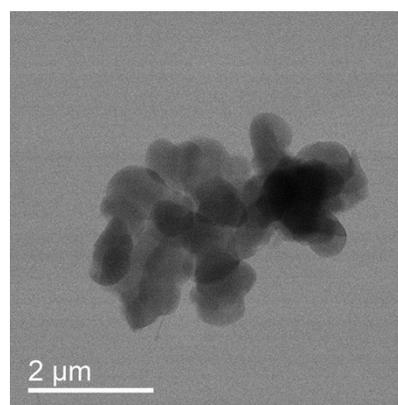
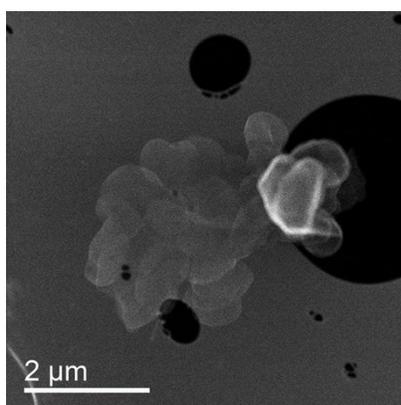
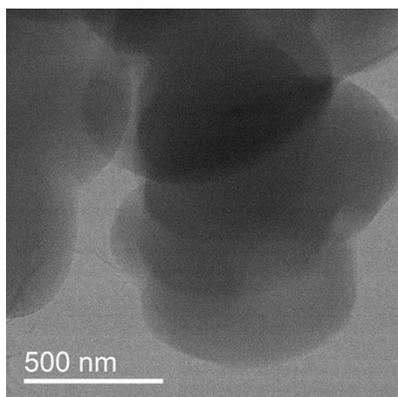
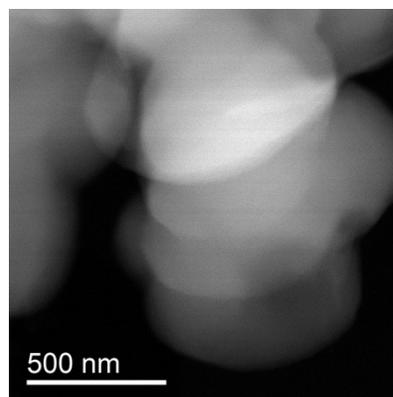
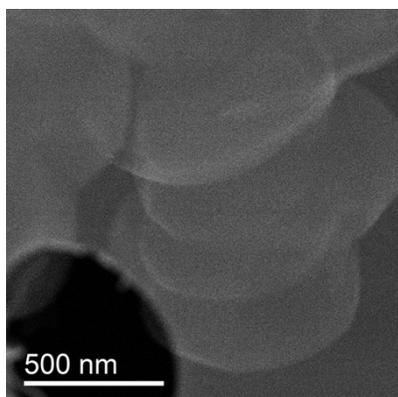
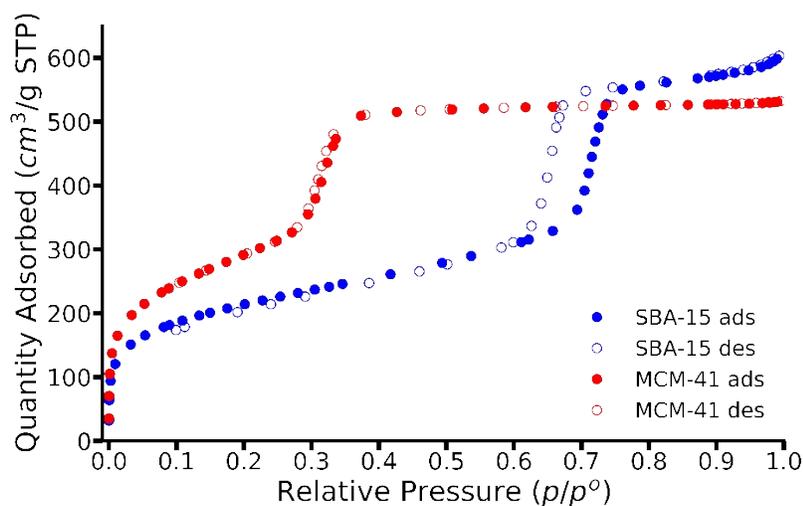


Figure S2: SEM and TEM images of the MCM-41 used in this study additional images provided (lower 6)



	SBA-15	MCM-41
BET surface area (m ² /g)	730	1220
Pore volume (cm ³ /g)	0.93	0.82
Micropore area (m ² /g)	119	53
Mesopore + external area (m ² /g)	610	1160
Total surface area (m ² /g)	729	1213
BJH ads. pore size (Å)	70	24

Figure S3: Isotherms and textural properties for the SBA-15 and MCM-41 used in this study

Monomer synthesis

The protected benzyl amine monomer (2-(4-vinylbenzyl)isoindoline-1,3-dione) was synthesized via a three step process through the same procedure as a previous report.⁴ First, 20 g of 4-vinylbenzyl chloride was purified via filtering through a plug of basic alumina and added to a 1 L round bottom flask with a magnetic stir bar. 262 mL of DMF was added along with 17 g of NaN₃. Vigorous agitation at room temperature was allowed for 24 h. Afterwards, the reaction mixture was transferred to a 2 L separatory funnel along with 500 mL of EtOAc. The mixture was washed 3 x 200 mL DI water and 1 x 200 mL brine. Dried over MgSO₄, filtered, concentrated, and dried. 18.4 g of 1-(azidomethyl)-4-vinylbenzene was isolated with an 88% yield.

First, 18.4 g of 1-(azidomethyl)-4-vinylbenzene was added to a 2 L round bottom flask equipped with a magnetic stir bar. 330 mL of THF and 55 mL of DI H₂O was added along with 60 g of PPh₃. Vigorous agitation was allowed for 48 h. Afterwards, THF was removed under reduced pressure followed by the addition of 400 mL of diethyl ether and 100 mL of H₂O. 1 M HCl was added until the pH was roughly 1. The mixture was washed 2 x 200 mL diethyl ether and the organic phase was removed. 400 mL of DCM was added to the acidic aqueous phase then the pH was adjusted to roughly 13 via a 1 M aqueous NaOH solution. The aqueous phase was washed 2 x 100 mL DCM. The final organics were collected, concentrated, and dried to produce 15.3 g of (4-vinylphenyl)methanamine at a 97% yield.

Next, 15.3 g of (4-vinylphenyl)methanamine was added to a 1 L round bottom flask with magnetic stir bar along with 400 mL of toluene. Then, 17.3 g of phthalic anhydride was added next as well as 1.6 mL of triethyl amine (TEA). The mixture was vigorously stirred at 110 °C for 24 h. After the reaction, the mixture was concentrated under reduced pressure and recrystallized twice from hot hexane to produce the desired monomer (2-(4-vinylbenzyl)isoindoline-1,3-dione). 25 g was isolated giving an 86% yield. The NMR spectra was matched with previous reports.

¹H NMR (700 MHz, CDCl₃): 7.84–7.70 (m, 4 H), 7.37 (m, 4 H), 6.71-6.63 (dd, 1 H), 5.71 (d, 1 H), 5.22 (d, 1 H), 4.84 (s, 2 H). ¹³C NMR (700 MHz, CDCl₃): 168.1, 137.3, 136.4, 135.9, 134.1, 132.2, 128.9, 126.5, 123.4, 114.2, 41.4.

ATRP initiator synthesis

The ene-functionalized ATRP initiator (hex-5-en-1-yl 2-bromo-2-methylpropanoate) was synthesized using similar procedure.⁵ 1.2 mL of 5-hexen-1-ol was added to an Ar-purged oven-dry round bottom flask equipped with a magnetic stir bar. 10 mL of anhydrous THF was subsequently added along with 1.28 mL of α -bromoisobutyrylbromide. 0.89 mL of anhydrous pyridine was then added dropwise, and the mixture was stirred at room temperature for 18 h. After the reaction, the crude mixture was filtered, rinsed with DCM, and concentrated under reduced pressure. The oil was then diluted with 50 mL DCM and the organic phase was washed 2 x 50 mL with 1 M aqueous HCl and 1 x 50 mL brine. Finally, the organics were dried over MgSO₄, filtered,

and concentrated under reduced pressure and dried. 2.45 g of hex-5-en-1-yl 2-bromo-2-methylpropanoate was isolated resulting in a 99% yield.

^1H NMR (700 MHz, CDCl_3): 5.88–5.78 (m, 1H), 5.07–4.99 (dd, 2H), 4.20 (t, 2 H), 2.13 (q, 2 H), 1.96 (s, 6 H), 1.73 (quintet, 2 H), 1.52 (quintet, 2 H). ^{13}C NMR (700 MHz, CDCl_3): 171.7, 138.2, 115.1, 66.0, 56.1, 33.2, 30.8, 27.8, 25.1

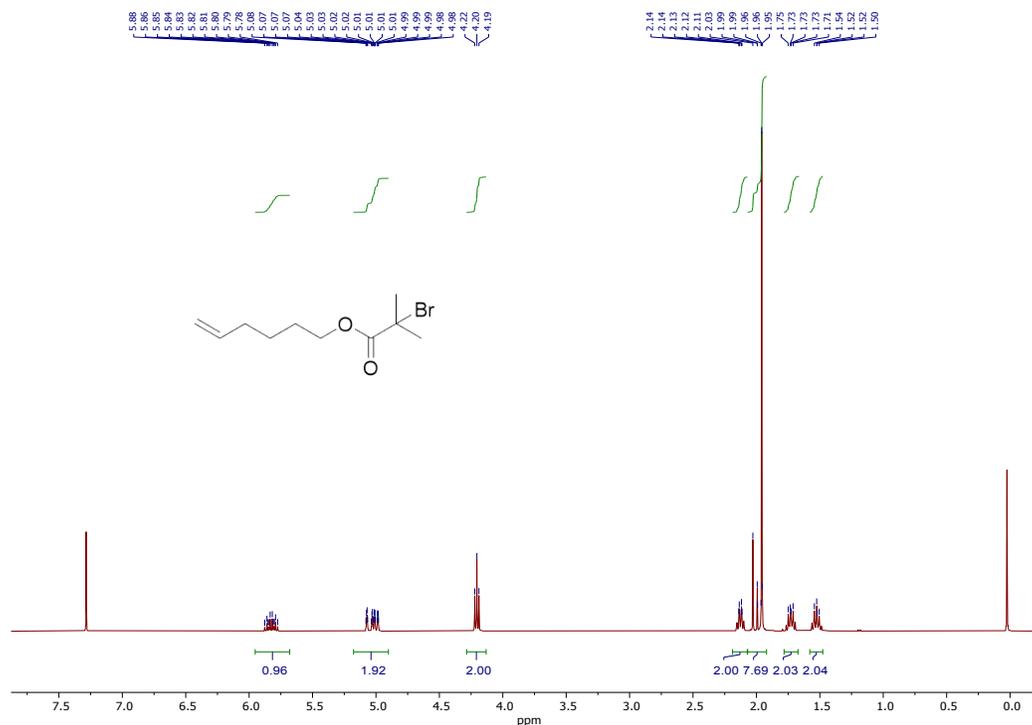


Figure S4: ^1H NMR spectrum of hex-5-en-1-yl 2-bromo-2-methylpropanoate (5-eneBMP) ATRP initiator

Polymer synthesis

Poly[styrene-*co*-(2-(4-vinylbenzyl)isoindoline-1,3-dione)] random copolymers were synthesized via supplemental activation and reducing agent – atom transfer radical polymerization. The method was adapted from a work focusing on homopolymers of just styrene.⁶ Stoichiometrically, all polymerizations were set-up using a 1:9 ratio of (2-(4-vinylbenzyl)isoindoline-1,3-dione) (NPhth) to styrene. Prior to all polymerizations, styrene was purified via filtering through a plug of basic alumina to remove the inhibitor (BHT).

A general procedure for all polymerizations is as follows. The phthalimide protected amine monomer, Cu(II)Br_2 , Cu(0) , and purified styrene are added to a vial. The ene-functionalized

initiator, PMDETA, and anhydrous toluene are added to a separate vial. Both vials are degassed via sparging with ultra-high purity argon (Airgas) at a flow rate of 2-3 bubbles/second for 25 minutes. Afterwards, the initiator/solvent mixture is injected into the first vial and heated at 90 °C under argon for the required time. After the polymerization, the solution is diluted with toluene and precipitated into a 10-fold excess of MeOH followed by filtering and drying.

Table S2: SARA-ATRP polymerization conditions used to synthesize the various MW polymers

[Styrene]	[NPhth]	Sty/tol (mL/mL)	Time (h)	$M_{n,NMR}$ (g/mol)	$M_{n,GPC}$ (g/mol)	\bar{D}
1040	46	1:2	72	50,000	46,000	1.33
225	25	1:1	20	16,600	16,000	1.15
90	10	1:2	15	6,300	6,100	1.16

For all polymerizations: [I]:[Cu(II)Br₂]:[Cu(0)]:[PMDETA] = [1]:[0.1]:[0.25]:[0.7]

NMR molecular weights were calculated by integrating the two terminal protons of the initiator, the two benzyl CH₂ protons on the NPhth units, and the whole aromatic proton section.

From ¹H NMR, the ratios of the two monomers in the polymer chain was equal for all 3 samples, indicating an equal incorporation of each monomer in the three polymers.

GPC molecular weights were calculated from and RI detector using narrow polystyrene standards

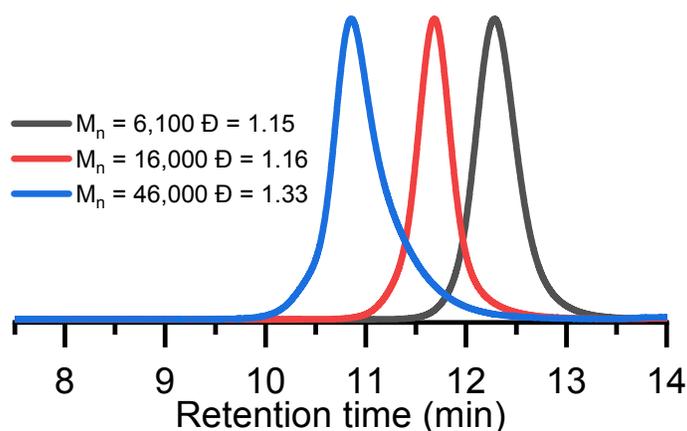


Figure S5: GPC traces for the poly(styrene-co-NPhth) structures used in this study

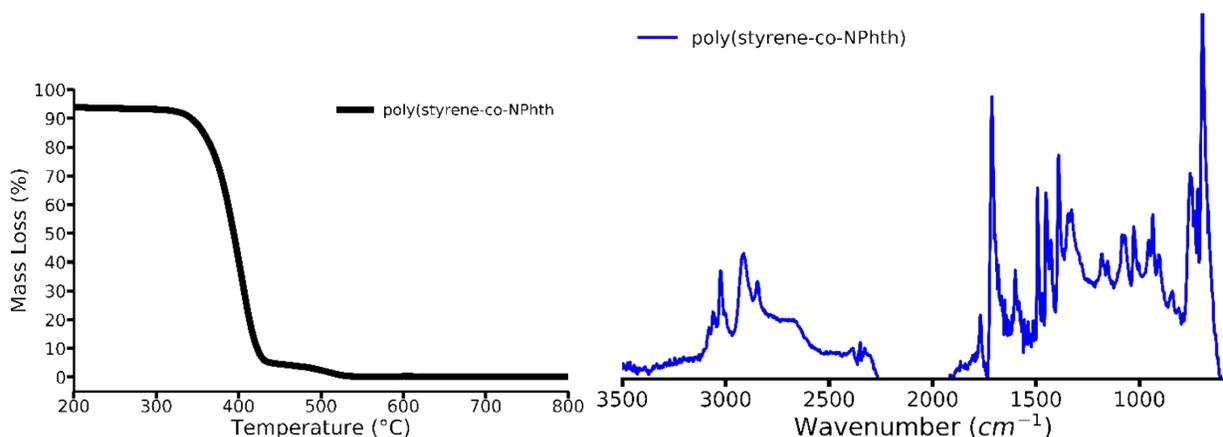


Figure S6: TGA curve and IR spectrum for the copolymer used in this study

5. Catalyst synthesis, activation, and testing

(3-mercaptopropyl) trimethoxysilane was grafted to the surfaces of both MCM-41 and SBA-15 in various loadings. For the catalysts synthesized in this work, an example procedure is described for the grafting to both mesoporous silicas. Before grafting, silica samples were dried overnight at 10 mtorr and 110 °C.

2.0 g of dried SBA-15 OR MCM-41 is added to an oven dried round bottom flask with magnetic stir bar. 50 mL of anhydrous toluene is added, and the suspension is sonicated and agitated until there are no larger clumps and a fine suspension remains. Next, 0.44 mL of (3-mercaptopropyl) trimethoxysilane is added and the mixture is stirred for 1 h at room temperature. Afterwards, the flask is lowered into the oil bath and the temperature is ramped from room temperature to 80 °C for 22 h. After the allotted time, the reaction mixture is transferred to centrifuge tubes and washed via centrifuging, decanting, and redispersion in toluene. To re-disperse the thiol functionalized SBA-15/MCM-41, ultrasonication was performed for up-to 5 minutes. This cycle is repeated at a minimum of four times. The solid is then dried overnight at 80 °C and 50 mtorr.

After drying, the samples are submitted TGA and EA and the loadings of the grafted silane are acquired. With TGA, the loadings obtained are 0.44 and 0.35 mmol/g for SBA-15 and MCM-41 respectively. With EA, the loadings obtained are 0.42 and 0.40 mmol/g for SBA-15 and MCM-41 respectively. For all stoichiometric calculations regarding the thiol functionalized silicas, the

elemental analysis loadings were always used. FT-IR was not used to characterize due to the inability to see S-H stretching, even in the case over 1.0 mmol/g thiol loading.

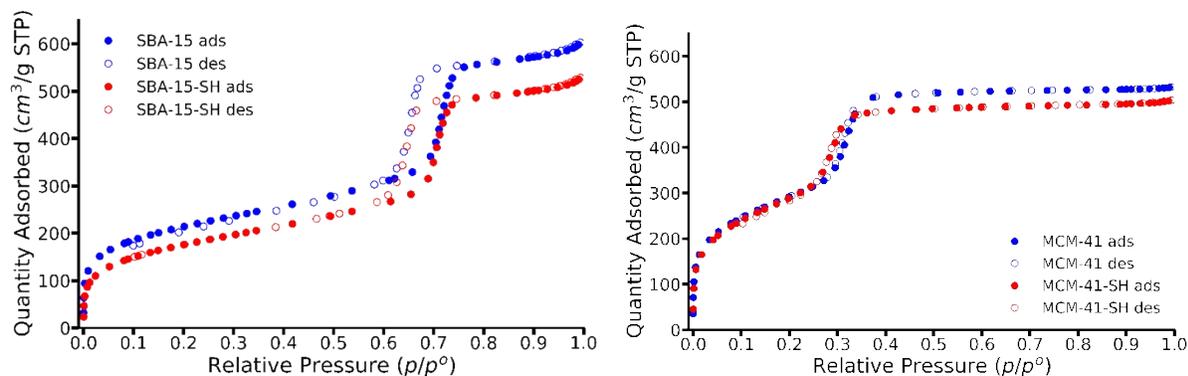


Figure S7: Bare and thiol functionalized isotherms for both MCM-41 and SBA-15

The thiol-ene click procedure between the -ene functionalized polymer and the grafted thiols are adapted from another report.⁵ 300 mg of the thiol functionalized SBA-15/MCM-41 is added to a vial with a magnetic stir bar. 5 mol% (relative to the SH content) photoinitiator (DMPA) is added along with 10 mL of DCM and the appropriate amount of polymer. The amount of polymer added is determined based on the thiol loading. For all thiol-ene experiments, the acid and base content was attempted to be made roughly equal. Therefore, the target N loading was made to be at least 0.42 times the thiol loading (see thiol oxidation conversion procedure). After all the reagents were added, the vial sonicated for 5 minutes then was sealed and sparged with UHP Ar for 25 minutes at a bubble rate of 2-3 bubbles/second. The vials were then placed inside the UV reactor on a magnetic stir plate and irradiated with 365 nm light for 24 h. After the reaction, the samples were transferred to centrifuge tubes and washed via centrifuging, decanting, and redispersion in DCM. To re-disperse functionalized SBA-15/MCM-41, ultrasonication was performed for up-to 5 minutes. This cycle is repeated at a minimum of four times. The solid is then dried overnight at 80 °C and 50 mtorr.

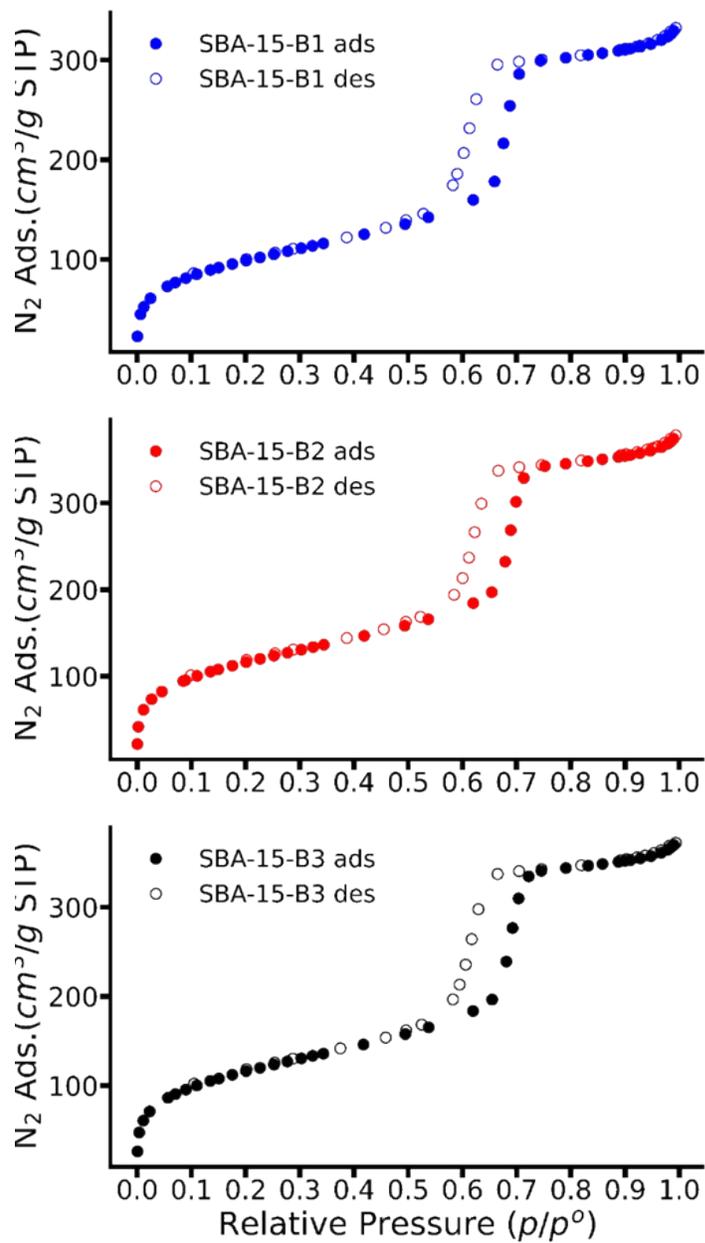


Figure S8: N_2 physisorption isotherms at 77 K for all SBA-15 brushes

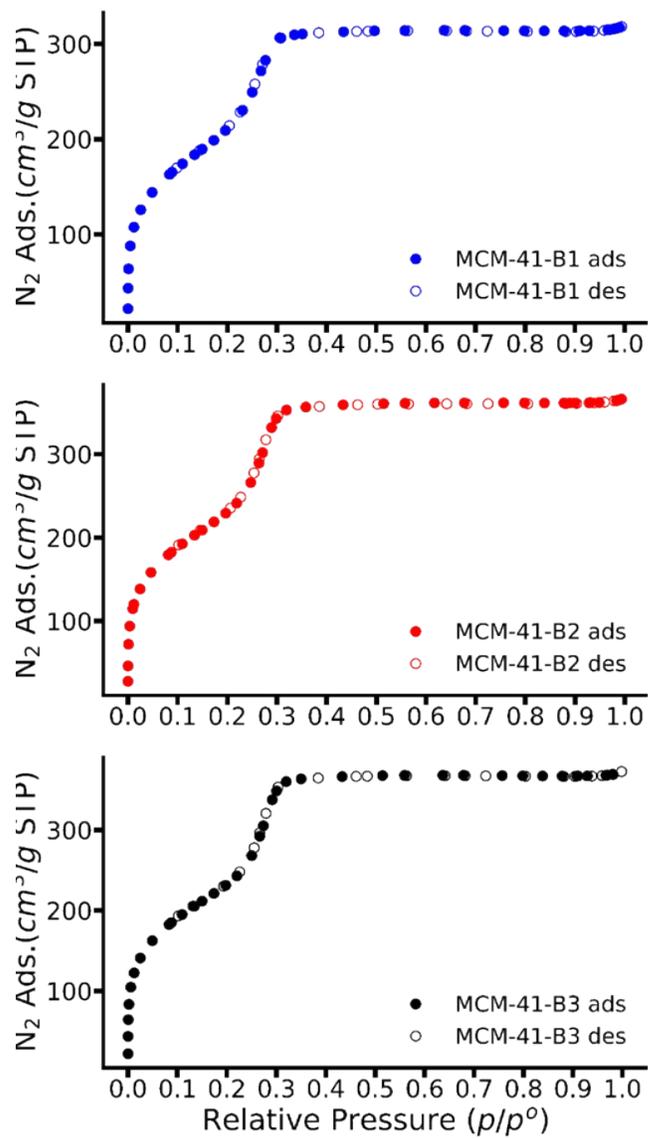


Figure S9: *N₂* physisorption isotherms at 77 K for all MCM-41 brushes

Table S3: All N_2 physisorption data for the functionalized silica samples (normalized and not normalized)

Entry	Sample	Support	Polymer M_n^a (g/mol)	Polymer wt%
1	SBA-15-poly(<i>st-co-NPhth</i>)-1	SBA-15	6100	16.4
2	SBA-15-poly(<i>st-co-NPhth</i>)-2	SBA-15	16000	13.6
3	SBA-15-poly(<i>st-co-NPhth</i>)-3	SBA-15	45000	13.2
4	MCM-41-poly(<i>st-co-NPhth</i>)-1	MCM-41	6100	11.9
5	MCM-41-poly(<i>st-co-NPhth</i>)-2	MCM-41	16000	7.5
6	MCM-41-poly(<i>st-co-NPhth</i>)-3	MCM-41	45000	6.8

Table S4: N_2 physisorption data for the functionalized silica samples (normalized per g silica and per g mate

rial)

Entry	Sample	BET surface area ^a (m ² /g)	Pore volume ^a (cm ³ /g)	Pore size ^a (Å)	BET surface area ^a (m ² /g _{SiO₂})	Pore volume ^a (cm ³ /g _{SiO₂})	f (g _{pore} /g _{total})
1	SBA-15	730	0.93	70	730	0.93	-
2	SBA-15-SH	610	0.77	67	623	0.84	-
3	SBA-15-B1	344	0.48	61	424	0.66	0.91
4	SBA-15-B2	404	0.55	63	481	0.70	0.86
5	SBA-15-B3	403	0.54	63	479	0.71	0.85
6	MCM-41	1220	0.82	24	1220	0.82	-
7	MCM-41-SH	1100	0.64	23	1155	0.68	-
8	MCM-41-B1	840	0.42	21	1025	0.59	0.83
9	MCM-41-B2	940	0.55	22	1047	0.65	0.70
10	MCM-41-B3	950	0.53	22	1050	0.66	0.70
11	SBA-15-SO ₃ H-PhCH ₂ NH ₂	440	0.623	66	483	0.68	

^aDetermined through N_2 physisorption analysis at 77 K.

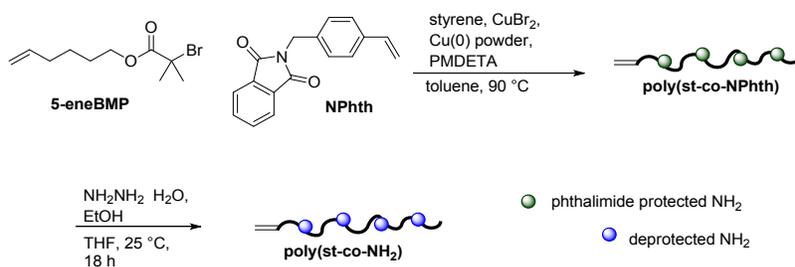


Figure S10: Synthesis route for the poly(st-co-NH₂)-1-3 copolymer catalysts

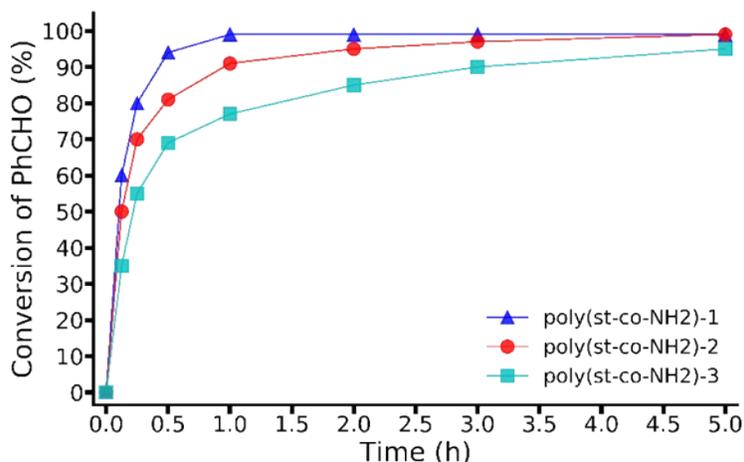


Figure S11: Kinetic data for the poly(st-co-NH₂)-1-3 copolymer catalysts in reaction B

Catalyst activation procedures

Deprotection of the phthalimide to prepare the Lewis base catalyst is accomplished through a similar procedure from another report.⁷ 200 mg of SBA-15/MCM-41-NPhth-SH was added to a vial with a magnetic stir bar. 2 mL of EtOH and 5 mL of THF is added followed by 0.2 mL of a hydrazine hydrate (N₂H₄) 50-60% aqueous solution. The mixture was allowed to stir for 18 h. Afterwards the reaction mixture is transferred to centrifuge tubes and washed via centrifuging, decanting, and redispersion in acetone. To re-disperse functionalized SBA-15/MCM-41, ultrasonication was performed for up-to 5 minutes. This cycle is repeated at a minimum of four times. The solid is then dried overnight at 80 °C and 50 mtorr.

The phthalimide deprotection was confirmed by TGA and IR. Disappearance of the C=O peak at 1700 cm⁻¹ indicates effective removal of the protection group via hydrazine. A reduction in mass

loss over the 200-700 °C indicates loss of organic matter, in this case, the large phthalimide functional group.

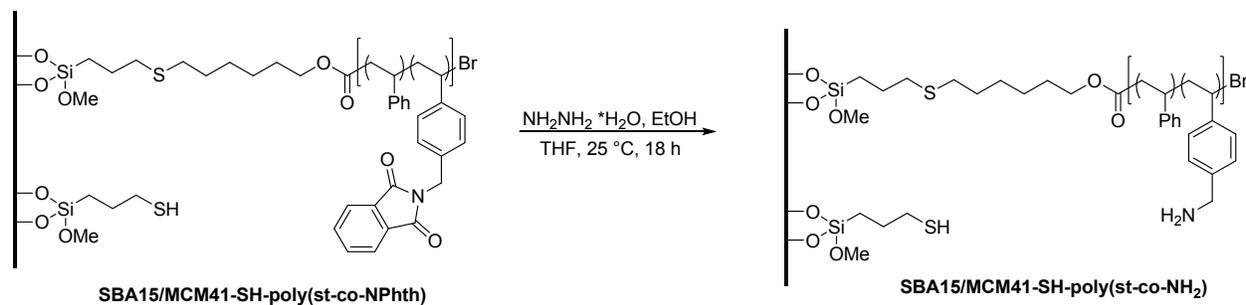


Figure S12: Phthalimide deprotection via aqueous hydrazine in EtOH and THF

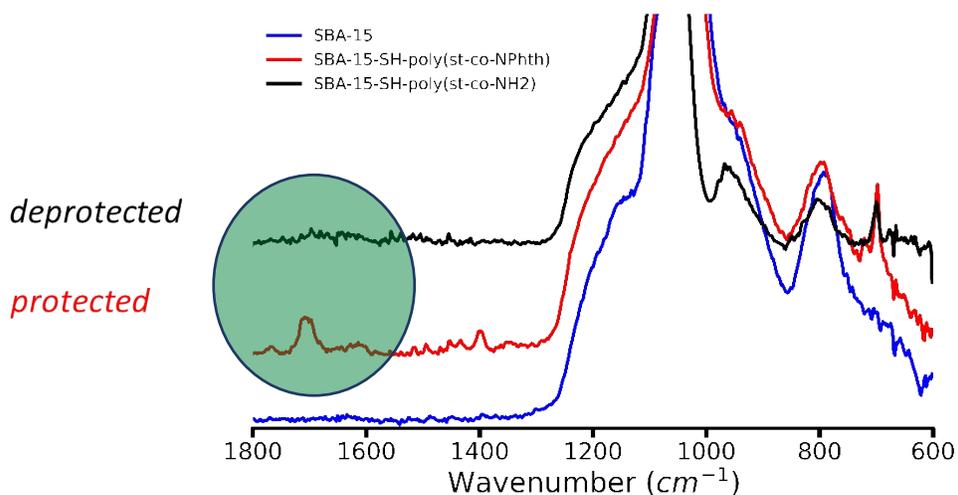
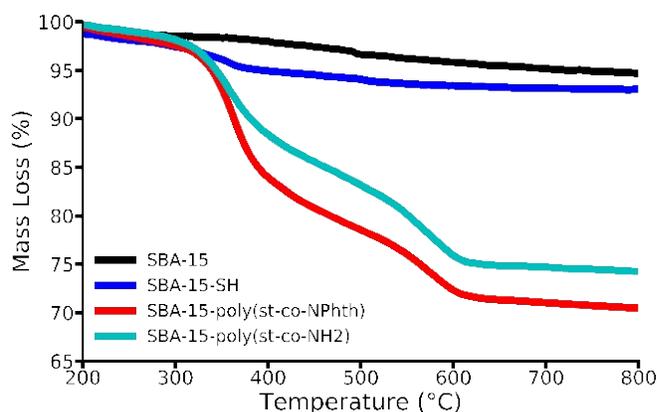


Figure S13: IR spectra of bare SBA-15, poly(styrene-co-NPhth) functionalized SBA-15, and poly(styrene-co-NH₂) functionalized SBA-15.



3.6 % mass difference between protected and deprotected between 200-700 °C, consistent with 100% deprotection

Figure S14: TGA curves for SBA-15, SBA-15-SH, SBA-15-NPhth, and SBA-15-NH₂

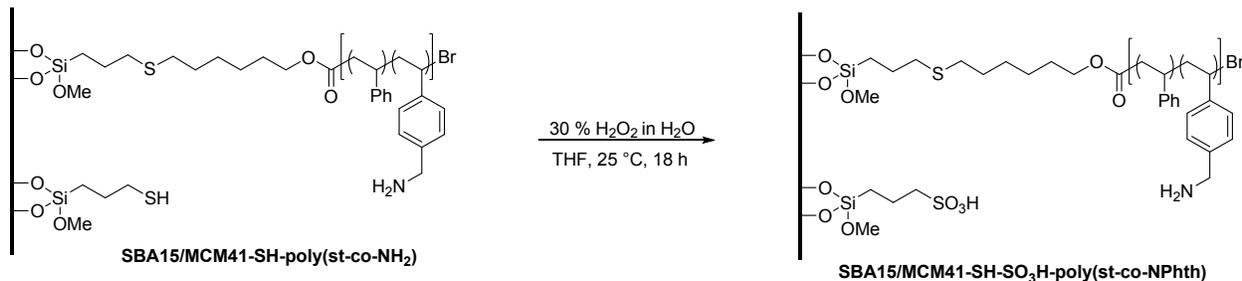


Figure S15: Thiol oxidation via aqueous hydrogen peroxide in THF

The sulfonic acid catalysts were produced via oxidation of residual surfaces grafted thiols post grafting-to brush formation. A typical thiol oxidation procedure is as follows. First, 200 mg of SBA-15/MCM-41-NH₂-SH is added to a vial with a magnetic stir bar. 5 mL of 30 wt% aqueous H₂O₂ and 5 mL of THF is also added. The mixture is sonicated for 5 minutes and allowed to stir for 16 h at room temperature. Afterwards the reaction mixture is transferred to centrifuge tubes and washed via centrifuging, decanting, and redispersion in acetone. To re-disperse functionalized SBA-15/MCM-41, ultrasonication was performed for up-to 5 minutes. This cycle is repeated at a minimum of four times. The solid is then dried overnight at 80 °C and 50 mtorr.

Acid content is determined after drying via back-titration via the following procedure. 50 mL of saturated solution of sodium chloride is added to 50 mg of the oxidized material (SBA-15/MCM-41-B1/2/3) and stirred for 3 hours. Afterwards, the solid is filtered dry and the filtrate is collected

into an Erlenmeyer flask and a magnetic stir bar is added along with several drops of phenolphthalein. This solution is titrated slowly with a 5 mM solution of NaOH until the color of the solution changes from clear to deep pink. Using the mass of sample, volume of aq. NaCl solution, and volume of 5 mM aq. NaOH an acid loading is calculated. Using the known thiol loading from EA, the oxidation conversion was determined from multiple runs to be 35%. This was then used as the method for calculating acid content in subsequent samples.

6. Control reactions

Table S5: Control experiments for reactions A and B

Entry	Reaction	Catalyst	Time (h)	Conversion of 1 or 2 (%)
1	A	none	6	10
2	B	none	6	6
3	A	SBA-15-SO ₃ H	1	99
4	A	SBA-15-SH	1	3
5	B	SBA-15-B1	5	99
6	B	SBA-15-B2	5	77
7	B	SBA-15-B3	5	35
8	B	MCM-41-B1	5	99
9	B	MCM-41-B2	5	9
10	B	MCM-41-B3	5	5
11	B	poly(<i>st-co-NH</i> ₂)-1	1	99
12	B	poly(<i>st-co-NH</i> ₂)-2	1	91
13	B	poly(<i>st-co-NH</i> ₂)-3	1	77

Table S6: Reaction C control experiments as well as cascade conversion data

Entry	Catalyst	Time (h)	Conversion of 1 (%)	Yield of 2 (%)	Yield of 3 (%)
1	SBA-15-SH-SO ₃ H-poly(<i>st-co-NPhth</i>)	6	99	99	0
2	SBA-15-SH-poly(<i>st-co-NH</i> ₂)	6	10	8	2
3	SBA-15-B1	7	99	1	99
4	MCM-41-B1	7	99	1	99
5	SBA-15-B1 1st recycle	7	98	1	97
6	SBA-15-B1 2nd recycle	7	95	5	90
7	SBA-15-B1 3rd recycle	7	90	10	80

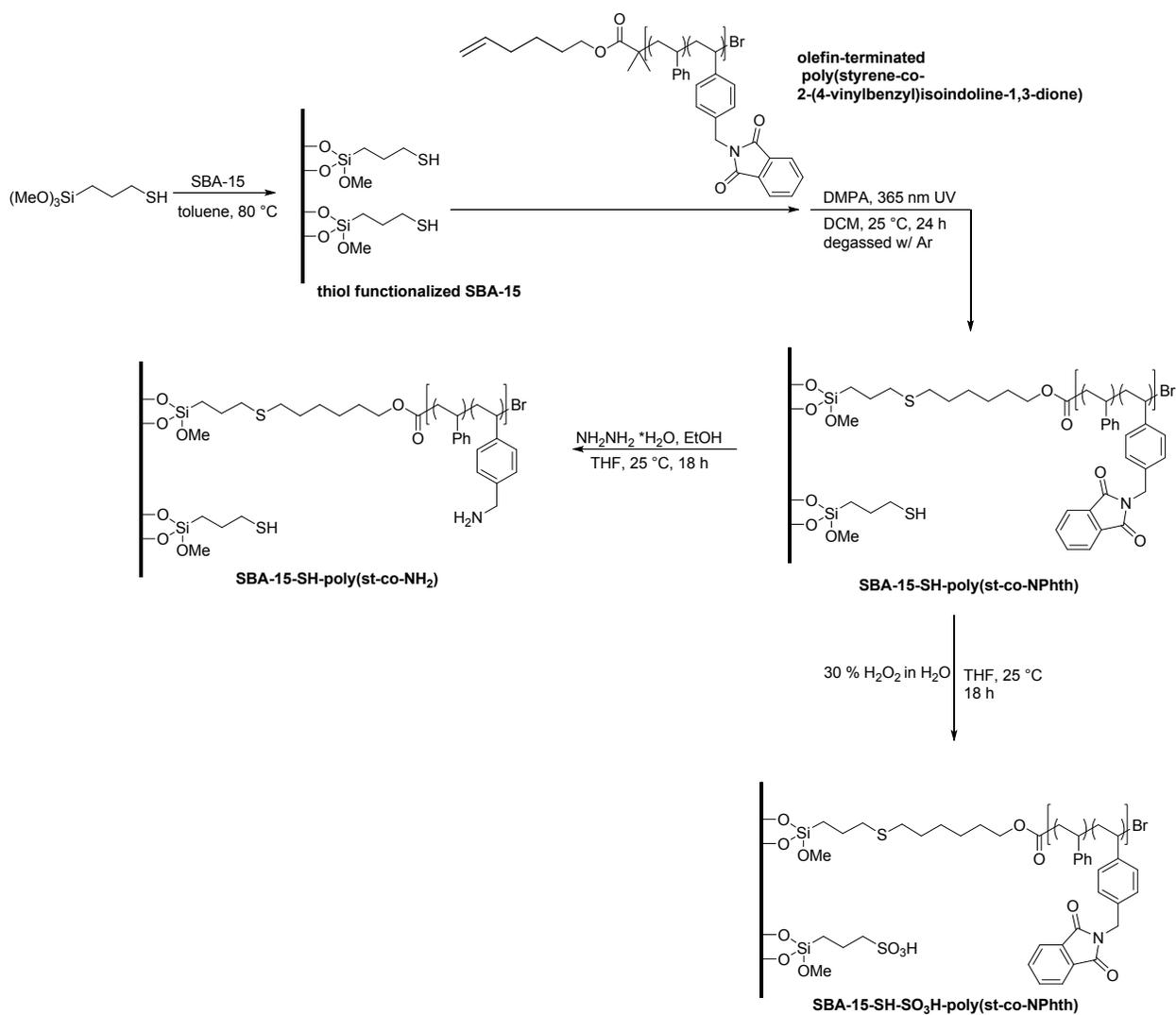


Figure S15: Synthesis route for *SBA-15-SH-poly(st-co-NH₂)* and *SBA-15-SO₃H-poly(st-co-NPhth)*

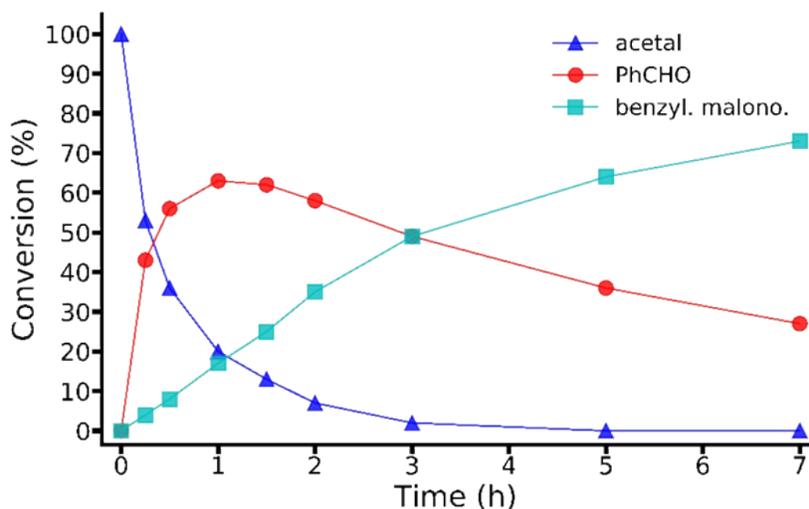
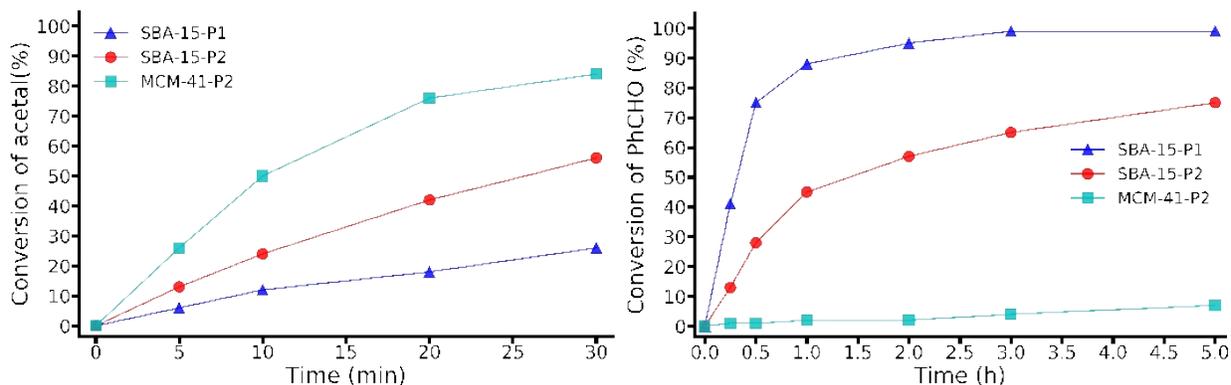


Figure S16: Cascade kinetics profile for reaction C performed with the polymer-free SBA-15-SO₃H-PhCH₂NH₂ bifunctional catalyst

7. Additional kinetic data



Entry	Sample	Reaction	Initial Rate (M/h) run 1	Initial Rate (M/h) run 2
1	SBA-15-P1	A	0.18	0.18
2	SBA-15-P2	A	0.42	0.39
3	MCM-41-P2	A	0.84	0.78
4	SBA-15-P1	B	0.43	0.41
5	SBA-15-P2	B	0.14	0.13
6	MCM-41-P2	B	0.01	0.01

Figure S17: Replicate kinetic data (of Fig 4) for reactions A (left) and B (right) using the SBA-15-P1, SBA-15-P2, and MCM-41-P2 composite catalysts. Results show good agreement with previous data indicating reproducibility between runs, as noted by tabulated rates.

8. Pore filling fraction calculation

Calculation of the polymer pore filling fraction for the mesoporous silica composites requires N₂ physisorption and TGA data for each sample. All values require proper normalization per g_{SiO₂} in order to obtain meaningful results.

f [unitless]: polymer pore filling fraction

P_{v,SH,SiO₂} [cm³/g_{SiO₂}]: Normalized (per g_{SiO₂}) pore volume for the thiol functionalized support

P_{v,P+SH,SiO₂} [cm³/g_{SiO₂}]: Normalized (per g_{SiO₂}) pore volume for the thiol + polymer 'clicked' functionalized support

ρ_P [g/cm³]: polymer density (1.05 g/cm³)

m_{P,SiO₂} [g/g_{SiO₂}]: Normalized (per g_{SiO₂}) polymer mass loss from 200-700 °C (from TGA)

$$(1) \quad f = \frac{\rho_P(P_{v,P+SH,SiO_2} - P_{v,SH,SiO_2})}{m_{P,SiO_2}}$$

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