Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

CO_2-switchable drying agents

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Contents

Experimental Methods

General Methods: 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Other chemicals were used as received from commercial sources. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance-400 spectrometer. Chloroform-*d* (D, 99.8%) was bought from Cambridge Isotope Laboratories, Inc. High resolution mass spectra were obtained using a Qstar XL QqTOF instrument with an ESI source. Thermogravimetic analysis (TGA) was performed using a TA Q-500 analyzer; the sample was heated in a nitrogen atmosphere. Particle size was determined using a Malvern Mastersizer 2000 (size range from 0.05 to 2000 μm) equipped with a Hydro2000S optical unit. A Philips XL-30 ESEM FEG instrument was operated at 2 kV to obtain the SEM images after the samples were coated by Au. The nitrogen sorption isotherm was run on a Quantachrome Autosorb-1C at 77 K after the particles had been degassed at 140 ˚C for at least 4 h. Water content was analyzed by a Perkin Elmer TCD detector on a Perkin Elmer Clarus 600 GC with a SLB-IL107 fused silica capillary column.

Synthesis of 1,4-bis(diethylamino)-2,3-butanediol:[1,2] KOH (8.75 g, 0.151 mol) was dissolved in deionized water at 0 ˚C and diethylamine (25 mL, 0.242 mol) was added. After 10 min, 2,3-dibromo-1,4-butanediol (15.1 g, 0.0605 mmol) was added into the aqueous solution. The reaction mixture was kept stirring for 18 h and then heated up to 50 ˚C. The reaction solution was kept at 50 ˚C overnight. When water and the excess of diethylamine were removed under reduced pressure, dimethyl carbonate (50 ml) was mixed with residue and the filtrate was collected. After removing dimethyl carbonate under reduced pressure, pure 1,4-bis(diethylamino)-2,3-butanediol was obtained (7.62 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$, see Figure S3): δ (ppm) = 3.77 (t, 12H, J = 5.7 Hz), 2.71-2.57 (m, 12H), 1.06 (t, 12H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 68.8, 56.4, 47.3, 11.6; HRMS (m/z): $[M]^+$ calcd. $C_{12}H_{28}N_2O_2$, 232.2151, found 232.2157.

Synthesis of crosslinkable monomer, 1: 1,4-Bis(diethylamino)-2,3-butanediol (6.9 g, 30 mmol) and triethylamine (20 mL) in anhydrous dimethylcarbonate (150 mL) were cooled down to 10 °C under a nitrogen atmosphere. Methacryloyl chloride (7.2 mL, 74 mmol) in dimethyl carbonate (50 mL) was added via a syringe. The reaction solution was stirred overnight. Once the byproduct salt was removed by filtration, the filtrate was washed with water twice to remove the excess of triethylamine, and filtered through a bed of basic aluminum oxide to produce the product (8.9 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, see Figure S4): δ (ppm) = 6.15-6.00 (m, 2H), 5.51-5.49 (m, 2H), 5.30-5.24 (m, 2H), 2.60-2.37 (m, 12H), 1.87 (brs, 6H), 0.92 (t, 12H, J = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 166.1, 136.2, 125.4, 70.8, 52.3, 47.8, 18.1, 11.9; HRMS (m/z): $[M]^+$ calc. $C_{20}H_{36}N_2O_4$, 368.2675; found 368.2668. Anal. Calc. for $C_{20}H_{36.5}N_2O_{4.25}$: C, 64.40%; H, 9.86%; N, 7.51%. Found: C, 64.60%; H, 9.90%; N, 7.23%.

Preparation of polymer particles via suspension polymerization: Monomer (2.73 g, 7.4 mmol) and AIBN (12 mg, 0.073 mmol) were dissolved in toluene (4 mL). Polyvinyl alcohol (87-89% hydrolyzed, average M_w 124,000-186,000, 0.4 g) and 40 mL water in a 250 mL flask were mechanically stirred at 300 RPM. Once the oil solution was added, the mixed solution was bubbled with nitrogen and heated up to 80 ^oC. After 4 h at that temperature, the mixture was cooled down and filtered. The porous polymer particles were washed with hot water three times and dried at 100 °C under vacuum. The yield was 70%.

Preparation of polymer grafted silica particles: Silica particles (SiliaFlash P60, 45-60 uM, 230-400 mesh) were subjected to a three part treatment in order to removed organic contaminants and promote a hydroxyl rich surface.[3] Firstly, the particles were stirred in an acid piranha solution, consisting of a $7:3$ (v/v) solution of sulfuric acid/hydrogen peroxide $(H_2SO_4/30\%\ H_2O_{2\,(aq)})$ for 1 h at $85\ ℃$, followed by rinsing three times with millipore water. Secondly, the particles were stirred in a base piranha solution, consisting of a $5:1:1$ $(v/v/v)$ solution of water/hydrogen peroxide/ammonium hydroxide $(H_2O_2/30\%\ H_2O_{2\,(aq)}/NH_4OH)$ for 20 min at $70\ ℃$, followed by rinsing three times with millipore water. Lastly, the particles were vacuum filtered and dried in an oven overnight at 110 ℃. The clean and hydroxyl-rich particles were stored in a sealed vessel until further use.

The clean and hydroxyl-rich particles were subjected to two different methods in order to graft the initiator to the surface.

Initiator grafting method 1: 5 g of clean and hydroxyl-rich silica was added to a 100 mL round bottom flask containing a mixture of potassium carbonate (4.6 mmol) in 50 mL of acetone. To that mixture the initiator, α-bromoisobutyryl bromide (BIBB, 18 mmol) was added dropwise at room temperature. The contents of the round bottom flask was heated at a continuous reflux for 12 h.

Initiator grafting method 2: 5 g of clean and hydroxyl-rich silica was added to a 100 mL round bottom flask containing a mixture of triethylamine (80.9 mmol) in 50 mL of tetrahydrofuran. The mixture was continuously stirred while being cooled to 0℃. After 1 h, a solution of the initiator, α-bromoisobutyryl bromide (BIBB, 18 mmol) in 10 mL tetrahydrofuran, was added dropwise to the cooled mixture. The solution was warmed to room temperature and allowed to react for 12 h. In both cases the silica was recovered by vacuum filtration and washed thoroughly with ethanol, followed by multiple washings with distilled water. The washed particles were dried at $110\ ℃$ for 20 min, then stored under $Ar_{(g)}$ until further use.

A comparison of the ^{13}C and ^{29}Si CP/MAS NMR spectra before and after grafting (Figures S5 and S6) confirm the attachment of BIBB to the surface, that the Si environment has not changed, and no new Si signals have appeared.

Surface-Initiated Atom Transfer Radical Polymerization: 2.5 g of the initiator functionalized silica was added to a 100 mL 3-neck round bottom flask containing 40 mL of anhydrous methanol. The mixture was degassed with $Ar_{(g)}$ for 1 h. The monomer, N-[3-(dimethylamino)propyl]methacrylamide (DMAPMAm 90 mmol, 10 eq.) was prepared by running it over a basic alumina column followed by degassing for 30 min. The catalyst was prepared by mixing copper(I) bromide (9 mmol, 1 eq.) with pentamethyldiethylenetriamine (PMDETA, 18 mmol, 2 eq.) in 10 mL anhydrous methanol. The mixture was degassed with $Ar_{(g)}$ for 1 h. The degassed components were added to the 3-neck flask under $Ar_{(g)}$ and heated to 45 ℃ overnight. The polymer-grafted silica was recovered via vacuum filtration and washed thoroughly with an aqueous solution of ethylenediaminetetraacetic acid (EDTA) followed by multiple washings with distilled water. The particles were dried at 110 ℃ overnight, then stored under $Ar_{(g)}$ until further use.

Titration Method:

Extra caution was used in order to prepare precise pH solutions. All containers/vessels were plastic, they were purchased brand new and rinsed thoroughly with Millipore water (18.2 $M\Omega \cdot cm$). The vessels were filled with Millipore water and the pH was measured. If the pH of the solution was > 6, the vessel was rinsed once more and a new pH reading was taken. This process was repeated until the pH was > 6. On the majority of occasions a pH of 7.5 ± 0.3 was achieved. In some instances it is hard to remove dissolved $CO_{2(g)}$, as a result of the dissolved $CO_{2(g)}$ the pH of the water was > 6 but < 7. Stock solutions of NaOH, 9.006 mM, and HCl 10.5 mM were prepared. In some instances the stock solutions were diluted to either 5.25 mM (HCl) or 0.9006 mM (NaOH) in order to achieve better accuracy. In a typical experiment ca. 10 mg of drying agent was added to 20 mL of Millipore (18.2 $M\Omega \cdot cm$) in a 50 mL centrifuge vial. 10.5 mM HCl was added in 0.1 mL aliquots, between each of which the vial was capped and vigorously shaken for 20-30 seconds. The pH was recorded after each addition and the titration was stopped ca. pH 4 or pH 2 depending on the nature of the titration. Acidified samples were then centrifuged for 30 min at 3000 rpm. 15 mL of the supernatant was removed and placed into a freshly washed centrifuge vial. The acidified supernatant was back-titrated with NaOH until neutral, ca. pH 7.

$$Moles\ of\ HCl\ added\ - Moles\ HCl\ left\ in\ supernatant = Moles\ of\ Accessible\ Amines$$

$$\frac{Moles\ of\ Accesible\ amines}{mg\ of\ sample\ used} * \frac{1000\ mmol}{1\ mol} * \frac{1000\ mg}{1\ g} = \frac{mmol}{g}$$

Sample Titration Calculation for PGS-1: "PGS-1 D"

$pH_i = 9.02$

$pH_A = 4.07$

$pH_B = 7.04$

$V_{H_2O} = 20\ mL$

$m_{PGS-1} = 9.37\ mg$

$V_{HCl} = 1\ mL$

$C_{HCl} = 5.25\ mM$

$V_{NaOH} = 1.8\ mL$

$C_{NaOH} = 0.9006\ mM$

$V_{supernatant} = V_{HCl} + V_{H_2O}$

$V_{supernatant} = 21\ mL$

$V_{supernatant\ extract} = 15\ mL$

n_{HCl} = 5.25E-6 mol

n_{NaOH} = 1.62108E-6 mol

$C_{supernatant}$ = 1.62108E-6 mol / 0.015 L

$C_{supernatant}$ =1.08072E-4 M

$n_{supernatant}$ = 1.08072E-4 M * 0.021 mL

$n_{supernatant}$ =2.26951E-6 mol

$n_{accesible\ amines} = n_{HCl} - n_{supernatant}$

$n_{accesible\ amines}$ = 2.98049E-6 mol

$$Accessible\ amines = \frac{n_{accessible\ amines}}{m_{PGS-1}}$$

$Accessible\ amines$ = 2.98049E-3 mmol / 0.00937 g

$Accessible\ amines = 0.31808\ mmol/g$

$Accessible\ amines = 0.3\ mmol/g$

Sample Calculation for "*Molar hydration value"*

Standard reaction conditions for the drying of isobutanol

Sample ID: DMA-S

Accessible amines = "aa"

Drying agent = "da"

$$DMA - S_{aa} = 1.1\frac{mmol}{g}$$

DMA-S removed 180 $\frac{mg_{H_2O}}{g_{da}}$

$$\frac{180\frac{mg_{H_2O}}{g_{da}}}{18.02\frac{g_{H_2O}}{mol_{H_2O}}} = 10\frac{mg_{H_2O}}{g_{da}} * \frac{mol_{H_2O}}{g_{H_2O}}$$

$$10\frac{mg_{H_2O}}{g_{da}} * \frac{mol_{H_2O}}{g_{H_2O}} * \frac{1g}{1000mg} = 0.01\frac{mol_{H_2O}}{g_{da}}$$

$$0.01\frac{mol_{H_2O}}{g_{da}} * \frac{1000\ mmol}{1\ mol} = 10\frac{mmol_{H_2O}}{g_{da}}$$

$$\frac{10\frac{mmol_{H_2O}}{g_{da}}}{1.1\frac{mmol_{aa}}{g_{da}}} = 9.09\frac{mmol_{H_2O}}{g_{da}} * \frac{g_{da}}{mmol_{aa}}$$

$$= 9.09\frac{mmol_{H_2O}}{mmol_{aa}}$$

Therefore the Molar Hydration Value for DMA-S is 9.09 $\frac{mmol_{H_2O}}{mmol_{aa}}$

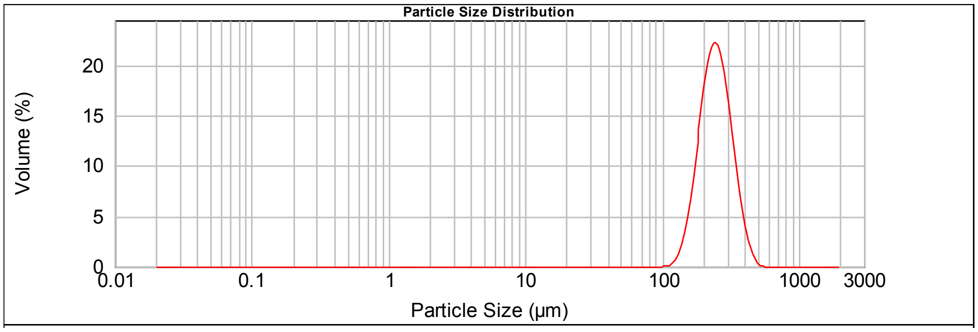


Figure S1. Light scattering analysis for the particle size of particles P-1.

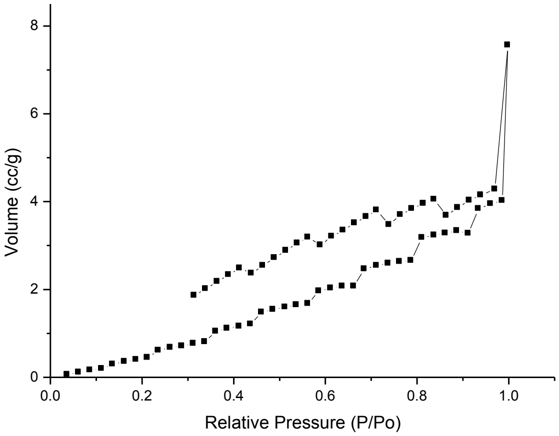


Figure S2. Isotherm for the adsorption of N_2 in porous polymer beads P-1 at 77 K.

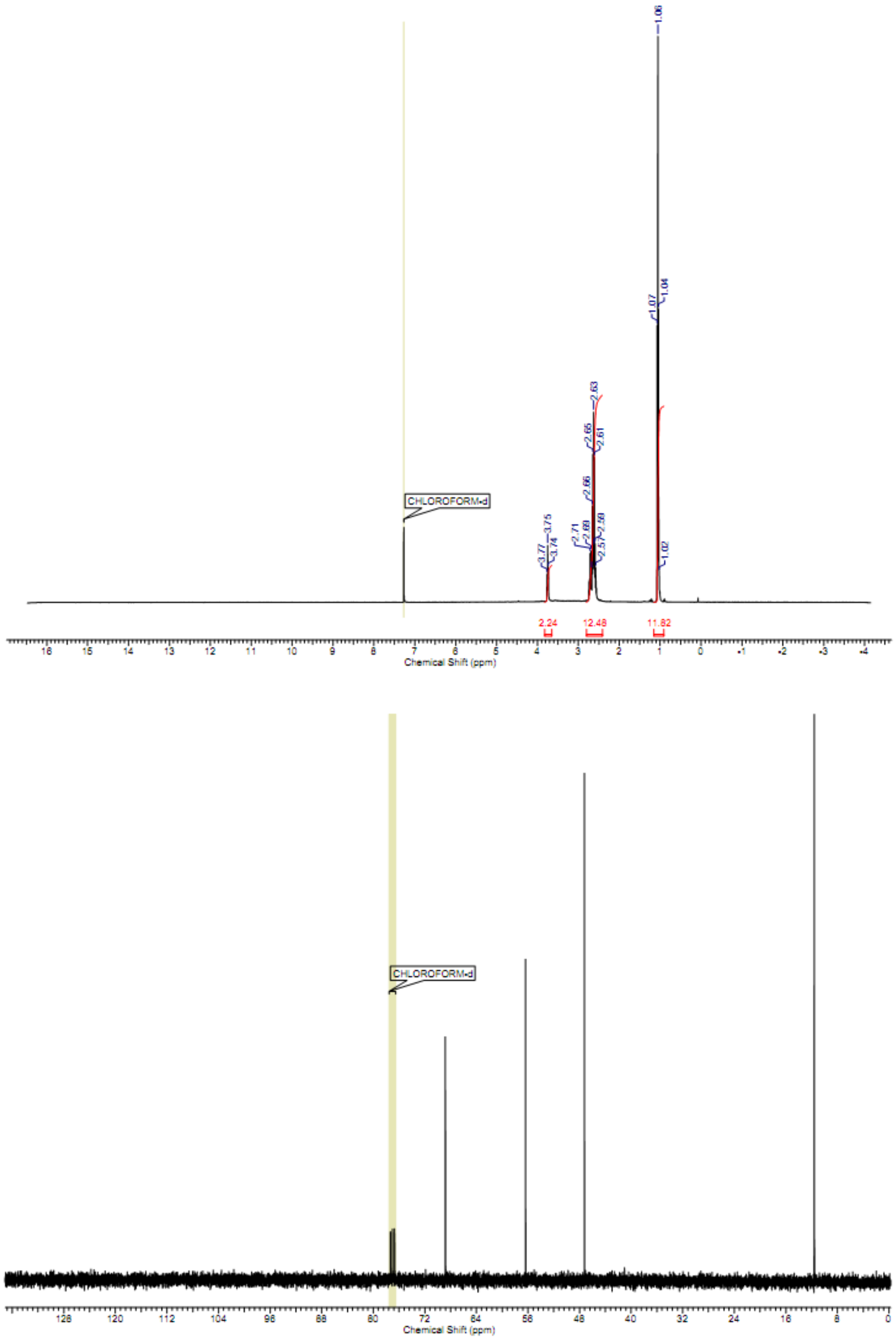


Figure S3. ^{1}H and ^{13}C{^{1}H} NMR spectra of 1,4-bis(diethylamino)-2,3-butanediol.

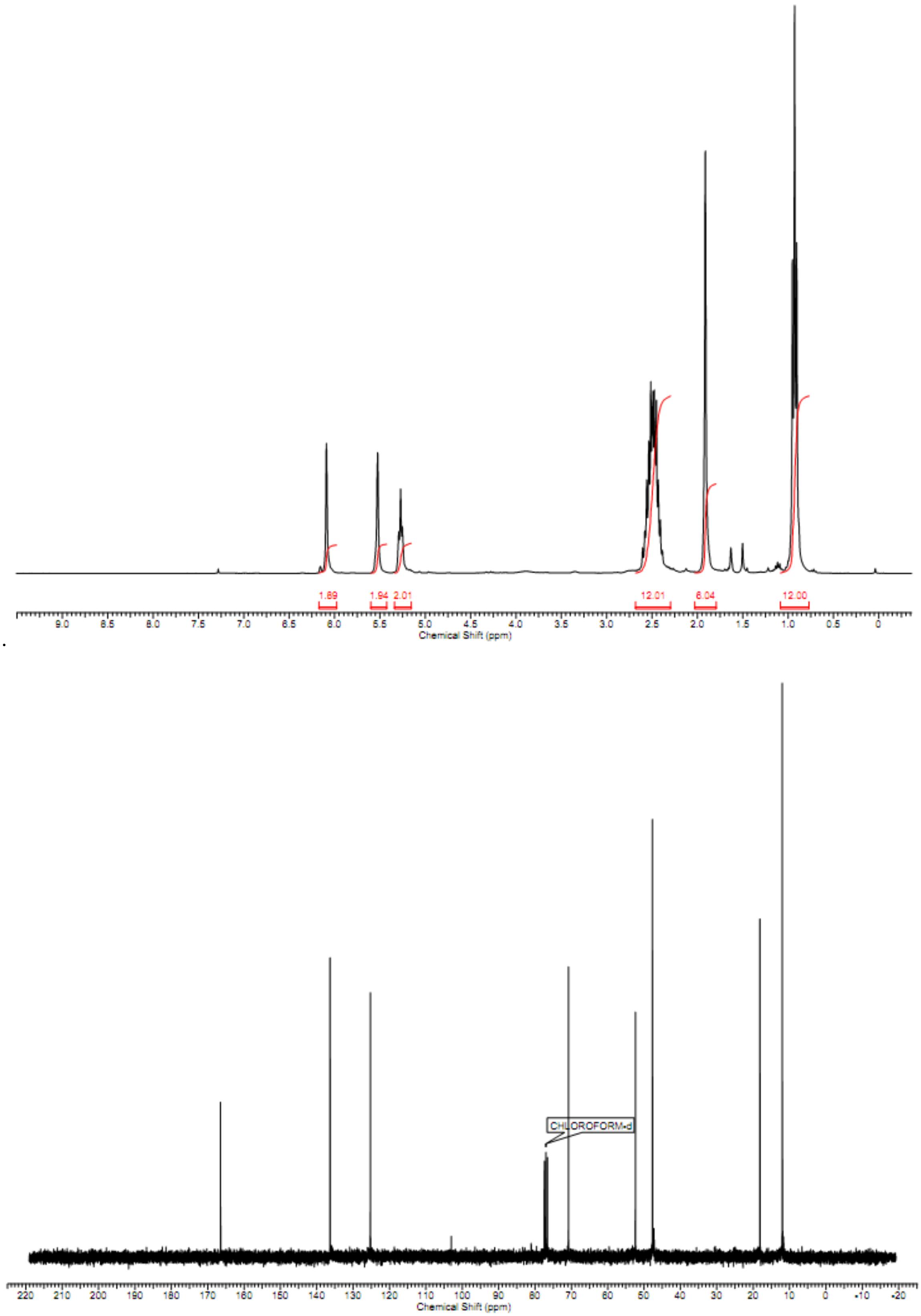
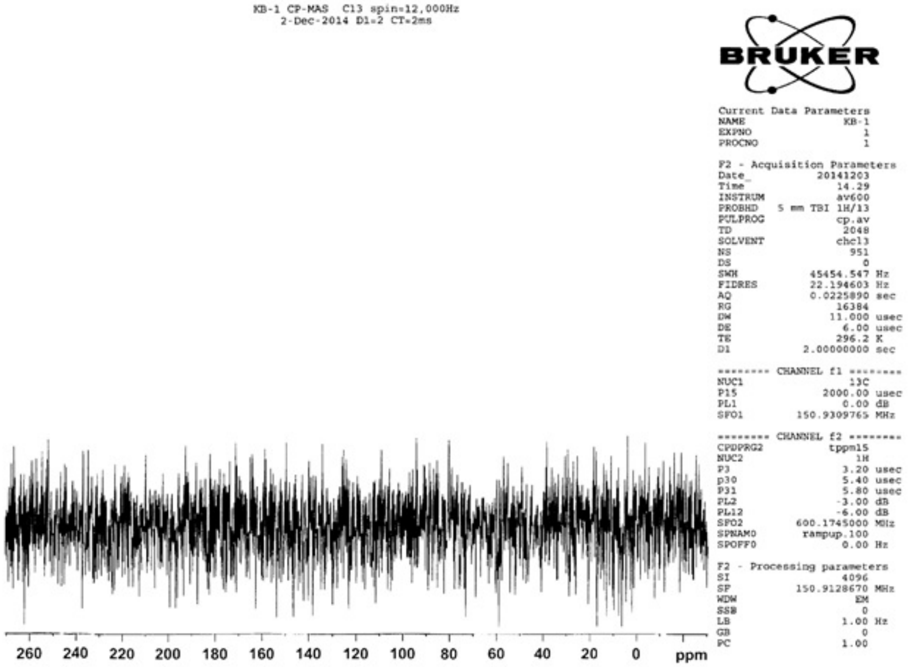


Figure S4. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of cross-linkable monomer **1**.



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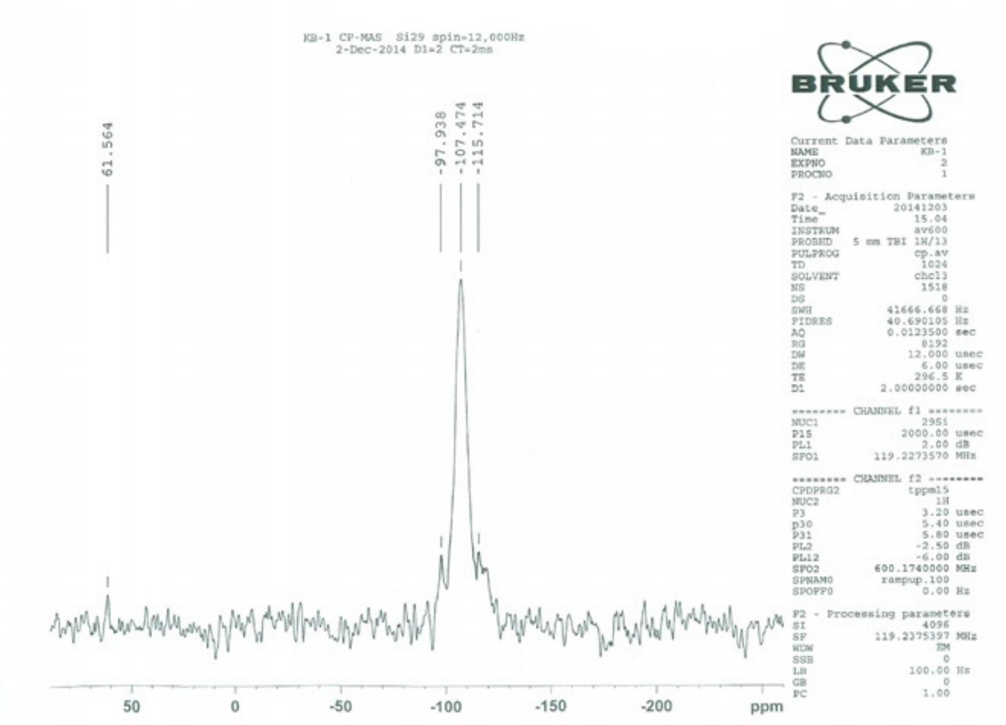

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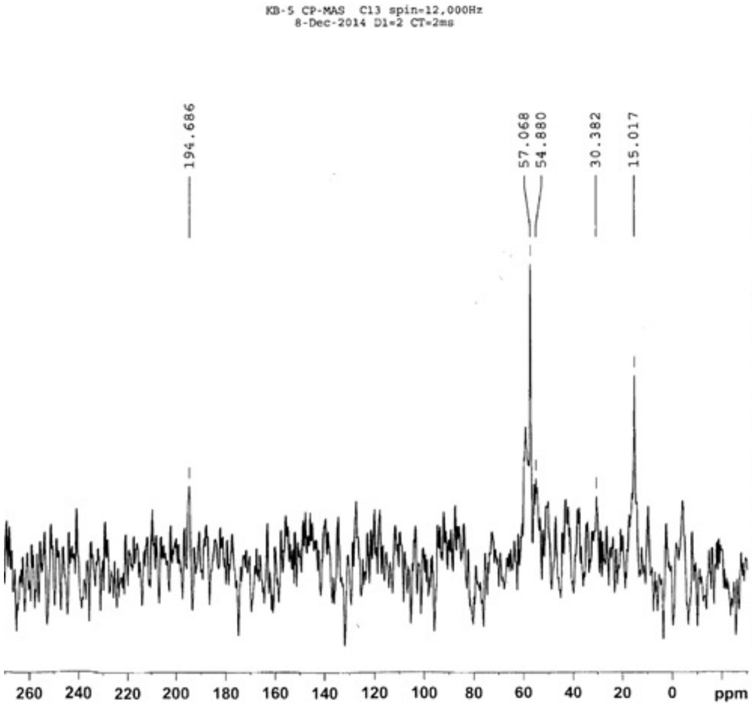
Figure S5. ^{13}C and ^{29}Si CP/MAS NMR spectra of bare silica.



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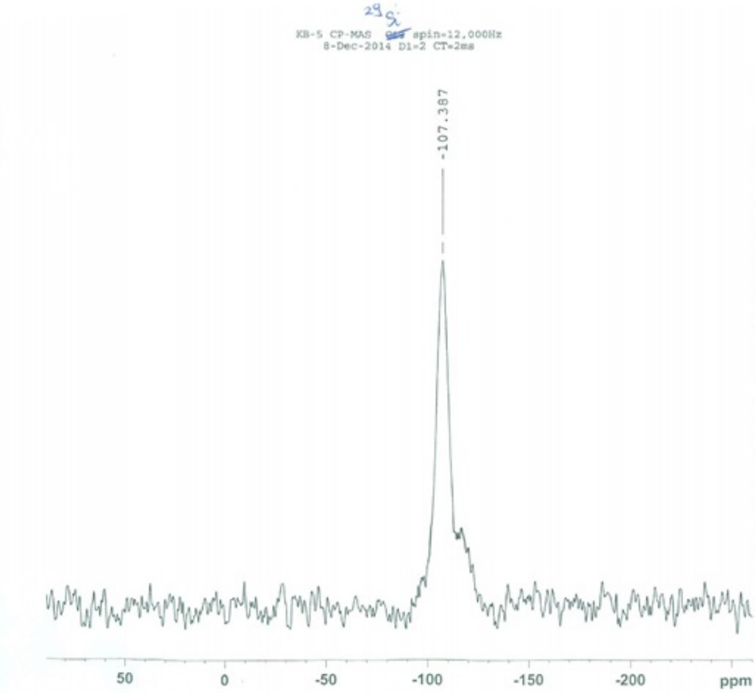

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D1             2.00000000 sec

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P15               2000.00 usec
PL1                  2.00 dB
SFO1          119.2273570 MHz

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p30                  5.40 usec
P31                  5.80 usec
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Figure S6. ^{13}C and ^{29}Si CP/MAS NMR spectra of BIBB functionalized silica.

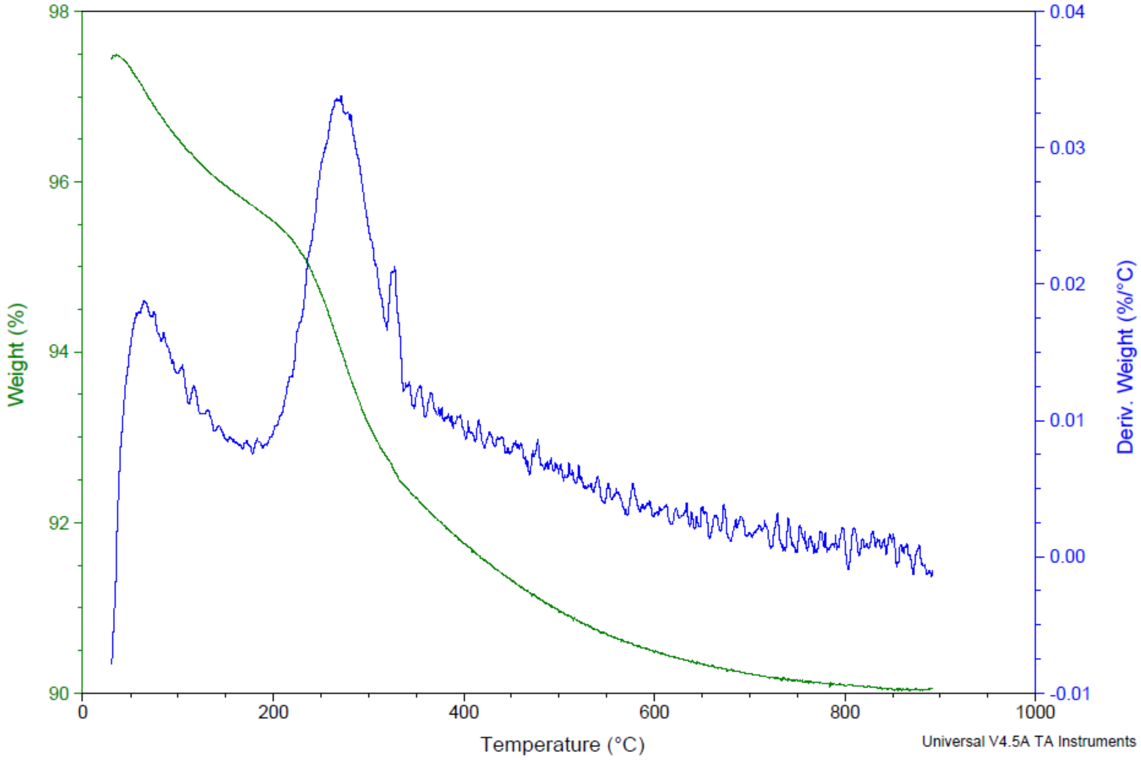

Figure S7. TGA of dried PGS-1 heated at a rate of 10 ^{o}C/min to 900 ^{o}C.

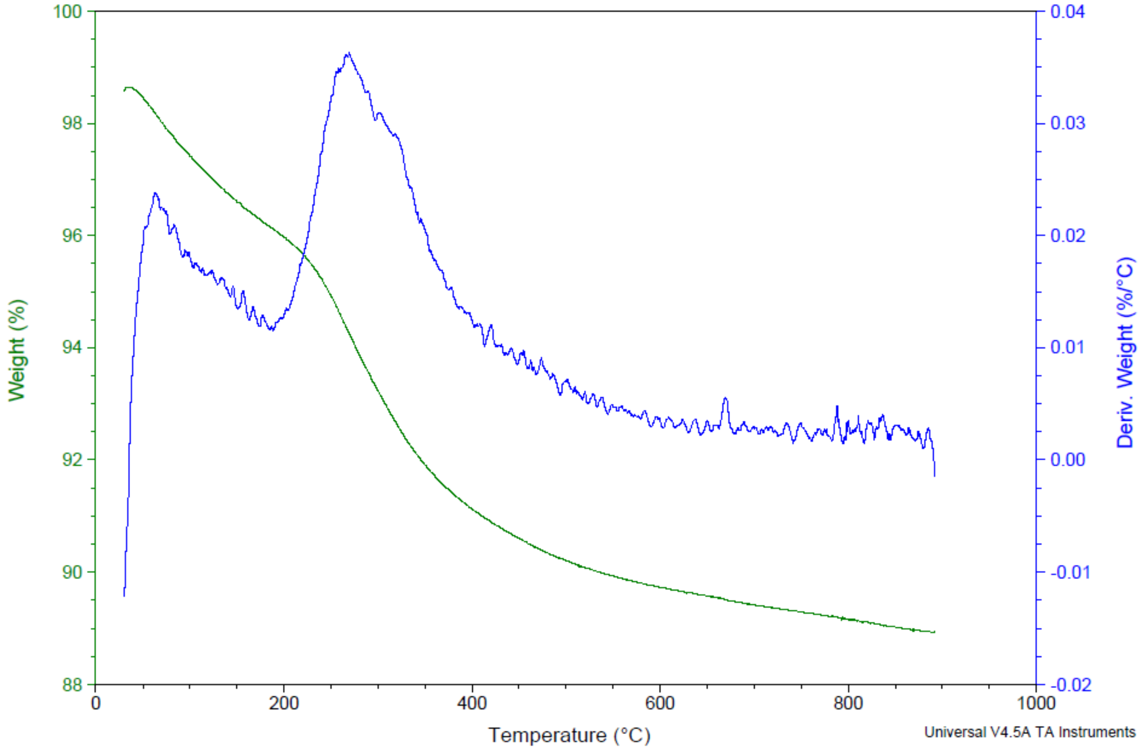

Figure S8. TGA of dried PGS-2 heated at a rate of 10 ^{o}C/min to 900 ^{o}C.

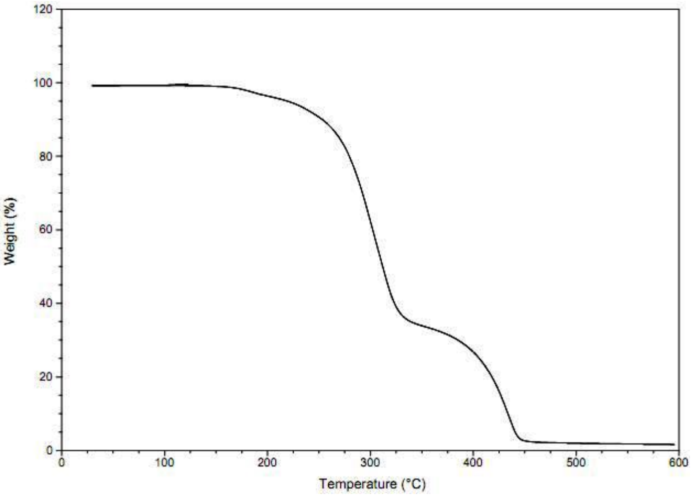

Figure S9. TGA of dried polymer particles heated at a rate of 10 ^{o}C/min to 600 ^{o}C.

Solvent retention:

Since the goal is to remove water, retention of the solvent would be undesirable, the amount of isobutanol retained by the polymer particles was examined. A known amount of used drying agent was added to D_2O and acidified with HCl. The acid is assumed to liberate any species necessarily associated with the nitrogen atoms through protonation. After the sample was stirred for 2 h, the amount of isobutanol present in solution was quantified by integrating the signals present in the ^{1}H-NMR spectrum against an internal standard (Figure S10). This experiment showed that the mass of water retained on the polymer particles is 1.3x greater than the amount of isobutanol, showing that the polymer particles preferentially bind water. Because the used drying agent particles were obviously physically wet with the solvent from which they were recovered, it is not surprising that isobutanol was detected.

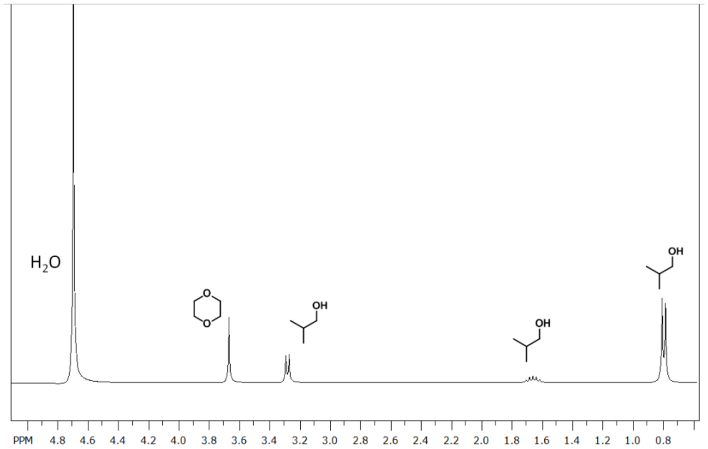

Figure S10. ^{1}H NMR spectrum showing residual isobutanol and internal standard (1,4-dioxane) present D_2O after an acidic extraction from the cross linked polymer particles.

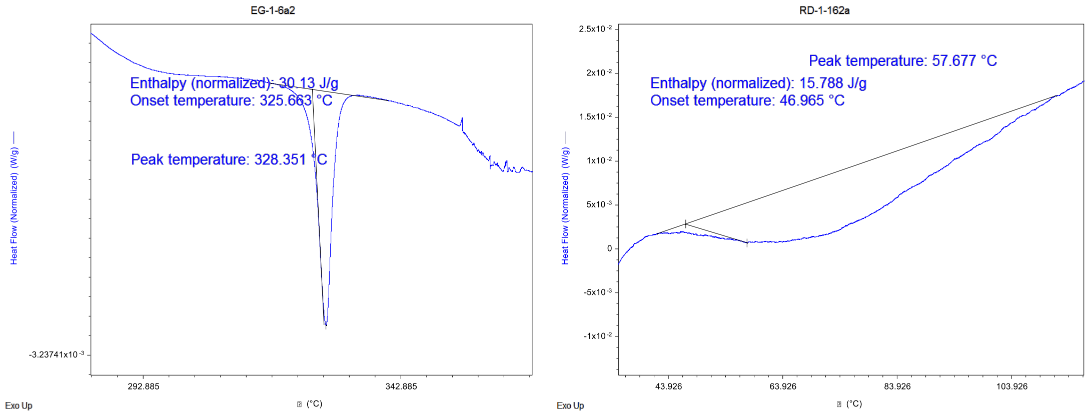

Figure S11. DSC curve for the regeneration of wet molecular sieves (left) and for the cross linked polymer particles (right). Values quoted are for water removed per gram of sample.

Calculation: Heat cost per gram of water removed from molecular sieves and polymer particles

Step 1: Calculate heat cost to regenerate drying agent per gram of sample

Heat cost per gram of sample = enthalpy to remove water + energy to heat up drying agent to temperature of water release

Integrating the peaks (Figure S11) provides the enthalpy for drying agent regeneration for mol. sieves at 30 J•g^{-1} and for polymer particles at 16 J•g^{-1}.

The heat capacity of fused silica[1] is 0.73 J•g^{-1}•°C^{-1} and for poly(methyl methacrylate)[2] is 1.42 J•g^{-1}•°C^{-1}. Note that the heat capacity for PMMA is used here as an approximate substitute for the unknown heat capacity of the new polymer.

The temperature of mol. sieves must be raised to 325 °C, increasing the temperature of the drying agent by 300 °C from RT to initiate water release.

The temperature of the polymer particles must be raised to 50 °C, an increase of 25 °C from RT to initiate water release.

∴ Heat cost to regenerate 'wet' mol. sieves = 30 J•g^{-1} + 0.73 J•g^{-1}•°C^{-1} × 300 °C = 249 J•g^{-1}

Heat cost to regenerate 'wet' pol particles = 16 J•g^{-1} + 1.42 J•g^{-1}•°C^{-1} × 25 °C = 52 J•g^{-1}

Step 2: convert energy cost per gram of sample to per gram of water removed using the drying agent

For molecular sieves, heat cost per gram of water = 249 J•g^{-1} ÷ 0.380 g of water removed per gram of drying agent

= 655 J•g^{-1}

For the polymer particles, heat cost per gram of water = 52 J•g^{-1} ÷ 0.380 g of water removed per gram of drying agent

= 137 J•g^{-1}

Toxicity:

The proposed drying agents are polymeric and pose little toxic threat due to the fact that polymers are not bioavailable. Given long term use and exposure to a variety of environmental factors the polymeric drying agents could release monomeric amines. The most likely degradation mechanism would be amide or ester hydrolysis given that the drying agent was exposed to either extreme of the pH scale. We have shown that the ester linkage the polymer-grafted silicas is stable at pH 2, however the lower and upper limit at which the material degrades is unknown at this time. Given enough time trace amounts of 3-dimethylaminopropylamine would be released as a result of degradation caused by hydrolysis. Depending on its concentration, DMAPA is strongly irritating or corrosive to the skin and mucous membranes. DMAPA is considered non-mutagenic and has been issued a no-observed-adverse-effect-level of 200 mg/kg/day to prevent reproductive and developmental toxicity.[6] DMAPA has a calculated half-life due to photochemical-oxidative degradation in the atmosphere by OH radicals of 3.2 hours.[6] Considering the low half-life, the presumably trace amounts of DMAPA should pose very little health hazard to industrial workers and the environment because they will never accumulate to a level at which toxic effects have been recorded.

Table 1. Specific acute toxicity measurements 3-dimethylaminopropylamine

Toxicity Measure	Comments
LC50 (daphnia magna, 48 h): 68.3 mg/L	Anything above 100 mg/L is not regulated – Cause for concern
LD50 (oral, rat): 1870 mg/kg	Above 2000 mg/kg is usually considered "generally safe for the majority of the population" – Not a cause for concern

References

1 W. F. Beech, *J. Chem. Soc.* 1951, 2483.
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3 K. Shirai et al, *J. Biomed. Mater. Res.* 2000, **53**, 204.
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