Supporting information

Halhalli et al. “An improved grafting technique for producing…”

Apparatus and methods

HPLC: The HPLC measurements were carried out on Hewlett-Packard HP 1050 instruments (Agilent Technologie, Waldbronn, Germany).

Elemental analysis: Carbon, nitrogen and sulphur contents were determined by elemental analysis at the Department of Organic Chemistry, Johannes Guttenberg Universität Mainz using a Heraeus CHN-rapid analyser (Hanau, Germany).

FT-IR spectroscopy: This was performed using a NEXUS FT-IR spectrometer (Thermo Electron Corporation, Dreieich, Germany).

SEM: The particle morphology, size and size distribution were determined using a scanning electron microscope 1550 “Gemini” Electronic Microscope (Carl Zeiss, Oberkochen, Germany) at the MPI für Kolloid-und Grenzflächenforschung, Golm (I_I and A_I series) or a Hitachi H-S4500 FEG Microscope in secondary electron mode with an acceleration voltage of 1 kV at the Department of Biochemical and Chemical Engineering, TU Dortmund. The samples were deposited on holders with a carbon foil without gold sputtering.

TEM: The transmission electron micrographs were recorded using a energy filter transmission electron microscope Omega 912 (Carl Zeiss, Germany) at the MPI für Kolloid-und Grenzflächenforschung, Golm. The samples were suspended in a liquid embedding medium (L. R. White Arylic Resin, London Resin Company Ltd.). The resin was allowed to solidify at 60°C for 3 days and the embedded particles were cut with a diamond knife of the ultramicrotome (Leica Ultracut UCT).

TGA: Thermogravimetric analysis was carried out using a TGAQ50 (TA instruments, Eschborn, Germany). The sample (10-15mg) was placed in a platinum pan, which is suspended in a sensitive balance together with the reference pan. The sample was then heated in a furnace with at a heating rate of 20 ^{0}C/min, under N_2 atmosphere.

Nitrogen sorption: Nitrogen sorption measurements were performed on a Quantachrome Autosorb 6B (Quantachrome Corporation, Boynton Beach, FL) automatic adsorption instrument. Prior to measurements, 100-150 mg of the samples were heated at 40-60ºC under high vacuum (10^{-5} Pa) for at least 12 hours. The specific surface areas (S) were evaluated using the BET method, the specific pore volumes (V_p) following the Gurvitch method and the average pore diameter (D_p) using the BJH theory applied to the desorption branch of the isotherm.

Azo-initiator immobilization (Table S1)

The silica supports were modified with azoinitiator in two steps as previously reported.[1] Silanization of rehydroxylated silica with APS was followed by condensation of the initiator ACPA with the surface amino groups to give the initiator modified supports listed in Table S1. In 250 mL three-necked round-bottom flasks equipped with a condenser, an overhead stirrer and a dropping funnel, 6g batches of rehydroxylated silica were suspended in 80 mL dry toluene. The whole system was flushed with N_2. According to the number of silanol groups on the silica surface (8 μmol/m^2) the appropriate amounts of APS was added to the mixture and refluxed overnight at 110°C. The products were filtered through glass funnels and washed with 2x 50 mL of toluene and 2x 50 mL of MeOH. The products were dried in a vacuum oven at 40°C for 24h. The products were characterised using elemental microanalysis, FT-IR spectroscopy and TGA and the amount of coupled ligands was estimated.

The silica gel used for this experiment had a 2.9 µmol/m^2 surface coverage of amino groups, meaning that ~ 30 % of the initial silanol groups had been converted into amino groups. The amino groups were reacted with the diacid azo-initiator (ACPA) in order to obtain one material with a high initiator coverage, used for the RAFT polymerisation, and another one with lower initiator coverage, useful for the conventional grafting in order to minimise solution polymerisation. Based on our previous experience, 100% conversion of the amino groups into initiator groups (2.9 µmol/m2) will lead to a complete pore blockage in the resulting composites and a low efficiency in HPLC. Therefore, the reaction conditions were designed to favour a maximum 50% conversion of the existing amino groups for the highest initiator coverage. Thus, for the high density ACPA-Si (1.5 µmol/m^2), to a 500 mL three-necked round bottom flask, equipped with a dropping funnel, on overhead stirrer and a ethanol thermometer, were introduced 250 mL dry THF. The mixture was then cooled at -78°C using a liquid-nitrogen-ethanol bath. Under continuous N_2 flow, 5.04 g (18 mmol) azo-initiator (ACPA), 1.95 g (18 mmol) ethylchloroformate and 1.82g (18 mmol) triethylamine were added. After stirring for 30 min at -78°C, 25 g of amino-modified silica were added to the mixture and the suspension was stirred for 3h at -78°C and then for 4 h at -10°C. The product was filtered, washed with THF and MeOH and dried under vacuum at room temperature.

Iniferter immobilization (Table S1)

The silica supports were modified with iniferter groups in two steps similar to the previously reported procedure.[2] In a three-necked 250 mL round bottom flask equipped with an overhead stirrer, a condenser and a dropping funnel, 15 g of previously rehydroxylated silica was suspended in 150 mL dry THF and the flask was connected to a N_2 stream. Then, 10.5 g (45 mmol) of p-(chloromethyl phenyl trimethoxysilane) (CPS) was drop-wise added and the mixture was refluxed with stirring over night. The modified silica was filtered, washed with 100 mL THF and 100 mL MeOH and dried in a vacuum oven at 60°C. Elemental analysis: %C=5.57; %H=0.69 (D_s=1.80 µmol/m^2). The modified silica (14g) was suspended in 150 mL dry THF. To this mixture, 8.8 g (40 mmol) sodium *N,N*-diethyldithiocarbamate trihydrate dissolved in 10 mL THF was added drop-wise under stirring. The suspension was stirred for another 12h at room temperature, filtered, washed with 100 mL THF and 100 mL MeOH and dried at room temperature under vacuum.

Elemental microanalysis: %C= 5.96; %H=1.67; %N=0.32; %S=1,70 (D_s=0.74 µmol/m^2)

Immobilization of RAFT agent (Table S2)

In a three-necked round bottom flask (250 mL), equipped with a dropping funnel, an overhead stirrer and an ethanol thermometer, was introduced 200 mL dry THF and the flask purged with nitrogen. For Si100-APS: 1.60g (5.74 mmol) 4-cyanopentanoic acid dithiobenzoate, 0.62g (5.75 mmol) ethylchloroformate and 0.58g(5.75 mmol) triethylamine and for Si500-APS: 1.395g 4-cyanopentanoic acid dithiobenzoate, 543mg ethylchloroformate and 506 mg triethylamine were consecutively added. The mixture was then cooled at -78°C using a liquid-nitrogen-ethanol bath. After stirring for 30 min, aminomodified silica (Si100-APS: 15g; Si500-APS: 25g) was added to the mixture and the suspension was stirred for 3h at -78°C and then for 4 h at -10°C. The product was then filtered, washed with THF and MeOH and dried under vacuum at room temperature. The surface density of RAFT agent calculated based on % mass loss by Thermogravimetry (TGA) was 0.72µmol/m^2 (Si100-RAFT) and 3.32µmol/m^2 (Si500-RAFT).

Film thickness estimation

The calculation of the film thickness *d* (nm) was performed assuming a homogeneous grafted layer as follows.

From elemental analysis:

(1) $$d = \frac{m_c \times M_w}{M_c \times \rho \times S} \times 10^3$$

$$m_c = \frac{\%C}{100 - \left(\frac{\%C \times M_w}{M_c}\right)}$$ (2)

where m_c = weight of carbon of the grafted polymer per gram of bare silica support, M_w = weighted average molecular weight of the grafted polymer assuming stoichiometric incorporation of reactive monomers, M_C = weighted average molecular weight of the carbon fraction of the grafted polymer, *r* = weighted average density of monomers (g mL^{-1}) and *S* = specific surface area of the bare silica support (m^{2}g^{-1}).

From average pore size:

$$d = \frac{D_{pi} - D_{pf}}{2}$$

where :

D_{pi} = pore diameter of the original starting material

D_{pf} = pore diameter in the resulting composite

1. C. Sulitzky, B. Rückert, A. J. Hall, F. Lanza, K. Unger and B. Sellergren, *Macromolecules*, 2002, **35**, 79-91.
2. B. Rückert, A. J. Hall and B. Sellergren, *J. Mat. Chem.*, 2002, **12**, 2275-2280.

Table S1. Characterisation of the iniferter and azoinitiator modified silica supports used for grafting

Modified support[a]	%C	%N	%S	Area density[b] (µmol/m^2)	Coverage[c] (%)	Distance[d] (nm)
Si-CPT	5.57	-	-	1.80	23	1.0
Si-DTC	5.96	0.32	1.70	0.74	6.4	1.8
Si-APS	3.79	1.34	-	2.9	36	0.8
Si-ACPA[a]	6.19	1.71	-	0.21	2.5	2.5
Si-ACPA[b]	11.76	3.93	-	1.5	18	1.1

a) The immobilizations were performed in two steps by consecutive coupling of p-(chloromethyl phenyl trimethoxysilane) (CPT) and diethyldithiocarbamate (DTC) on Si100 silica beads and the modified supports analyzed by elemental analysis. The Si100 silica beads (10µm average particle size) were mesoporous with a surface area (S) of 360m^2/g; an average pore diameter (D_p) of 13 nm and an pore volume (V_p) of 1,39 mL/g) except for Si-ACPA[a]. In this case the support was Licrosphere Si100 with the following charactersitics: (S=380m2/g, Dp=12 nm, Vp=1.26mL/g).

b) The area density (D) was calculated from the increase in carbon (Si-CPT) or average of the increase in sulfur and nitrogen (Si-DTC) content after the corresponding coupling as: $D=m_X/(M_X S)$, where $m_X=X\%/(100-X\%M_w/M_X)$, M_w=molecular weight of immobilized silane (Step 1) or dithiocarbamate (Step2), M_X=weight of carbon (X=C), nitrogen (X=N) or sulfur (X=S) per mole of immobilized species and S= surface area of the silica support. M_W and M_X were calculated assuming double substitution of the silane.

c) The coverage (C) was calculated as: C=100xD/8, assuming a maximum silanol group density of 8µmol/m^2.

d) The average distance d_L (nm) between the coupled ligands assuming a random ligand distribution was calculated as: $d_L = \sqrt{\frac{10^{18}}{D \times 10^{-6} \times N}}$, where N is the Avogadros number.

Table S2. Characterisation of the RAFT modified silica supports used for grafting

Modified support[a]	%C	%N	%S	Area density[b] (µmol/m^2)	TGA (% mass loss)	Area density[c] (µmol/m^2)	Coverage[d] (%)	Distance[e] (nm)
Si100-APS	3.96	1.38	-	1.25	8	1.23	16	1.2
Si100-RAFT	6.83	1.36	1.01	0.61	14	0.72	7.6	1.7
Si500-APS	1.80	0.80	-	5.82	3	3.84	73	0.5
Si500-RAFT	3.28	0.76	0.56	2.17	7	3.32	27	0.9

a) The immobilizations were performed in two steps by consecutive coupling of 3-aminopropyltrimethoxy silance (APS) and 4-cyanopentanoic acid dithiobenzoate (RAFT agent) on Si100 silica beads and the modified supports analyzed by elemental analysis and thermal gravimetric analysis (TGA). The Si100 silica beads (15µm average particle size) were mesoporous with a surface area (S) of 320m^2/g(After treatment with 17% HCl); an average pore diameter (D_p) of 11.6 nm and an pore volume (V_p) of 1.28mL/g whereas the Si500 beads (30µm average particle size) displayed a surface area (S) of 45m^2/g; an average pore diameter (D_p) of 48nm and an pore volume (V_p) of 0.81mL/g.

b) The area density (D) was calculated from the increase in carbon after the corresponding coupling as described in Table S1.

c) The area density (D) was calculated from the mass loss.

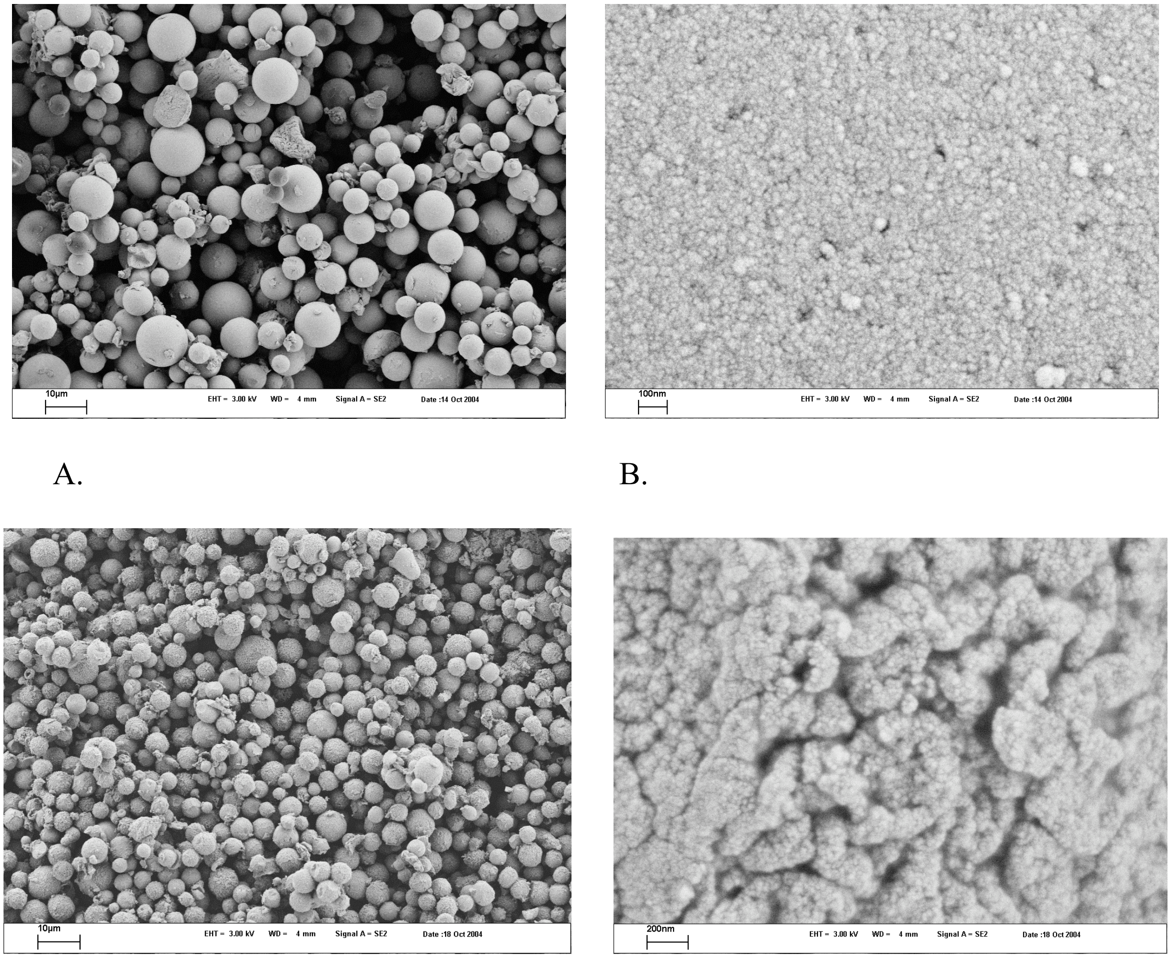
d) The coverage (C) and the average distance d_L (nm) between the coupled ligands were calculated as described in Table S1.

Table S3. Etching results for composites prepared by interupted grafting from silica modified with iniferter or azoinitiator

Grafting method	Support	%C composite	%C etching 1	%C etching 2
Iniferter	Si-DTC	19	56	56
Azo-RAFT	Si-ACPA[a]	15	21	56

Etching 1: 1g composite was suspended in 10ml NH_4HF_2 (3M) in water and the etching allowed to proceed for 2 days. After washing with water they were submitted for elemental analysis.

Etching 2: As etching 1 but using more than 10ml/g of the solution. Fresh solution was added 3 times and the composites left shaking for 5 days. After washing with water they were submitted for elemental analysis.



A. B.

C. D.

Figure S1. Scanning electron micrographs of imprinted polymer corresponding to I_I^{240} (A,B) and A_{IR}^{120} (C,D) after removal of the silica by etching. See Table 1 for polymer assignements.

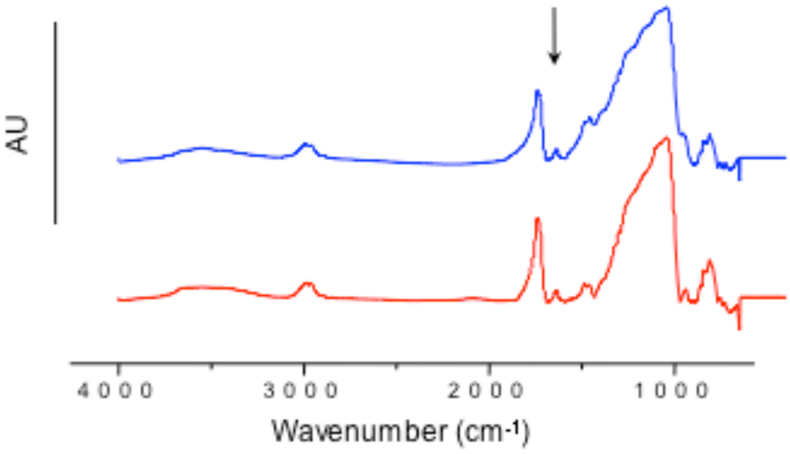


Figure S2. FT-IR transmission spectra (KBr) of an imprinted composite prepared using RAFT modified silica (A_{IR}^{90}) (lower spectrum), and one prepared using iniferter modified silica (I_I^{90}) (upper spectrum). The arrow indicate the position of the C=C stretch vibration at 1630 cm^{-1} corresponding to unreacted pendent double bonds.

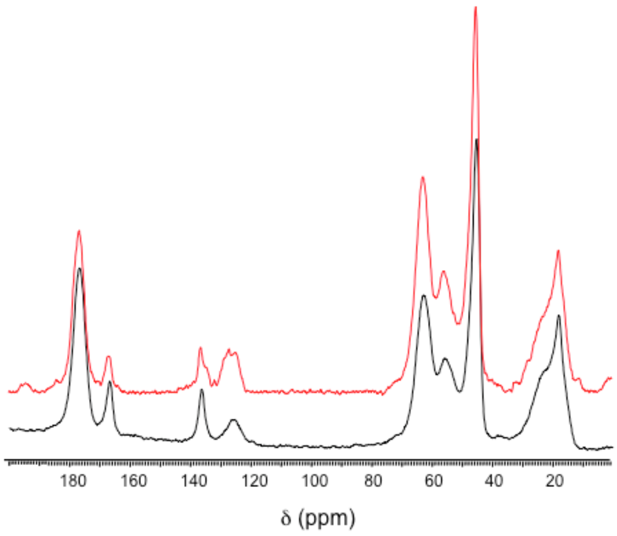


Figure S3. CP-MAS solid state ^{13}C-NMR spectra of a composite prepared using iniferter modified silica (I_I) (upper spectrum) and a corresponding composite prepared using azoinitiator modified silica (A_I) (lower spectrum).

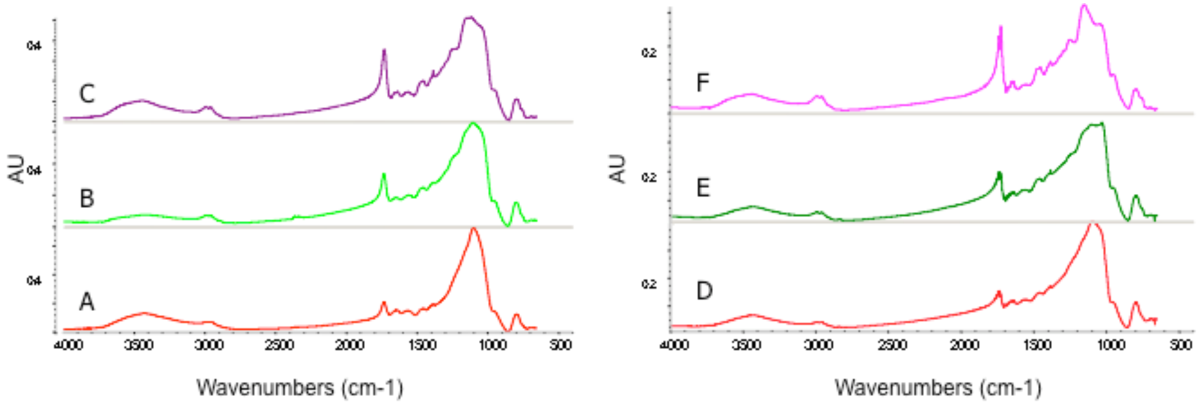


Figure S4. FT-IR transmission spectra (KBr) of imprinted composites prepared using azoinitiator modified silicas (A) A_{FD}^{1}, (B) A_{FD}^{2}, (C) A_{FD}^{3}, (D) A_{F}^{1}, (E) A_{F}^{2} and (F) A_{F}^{3}.

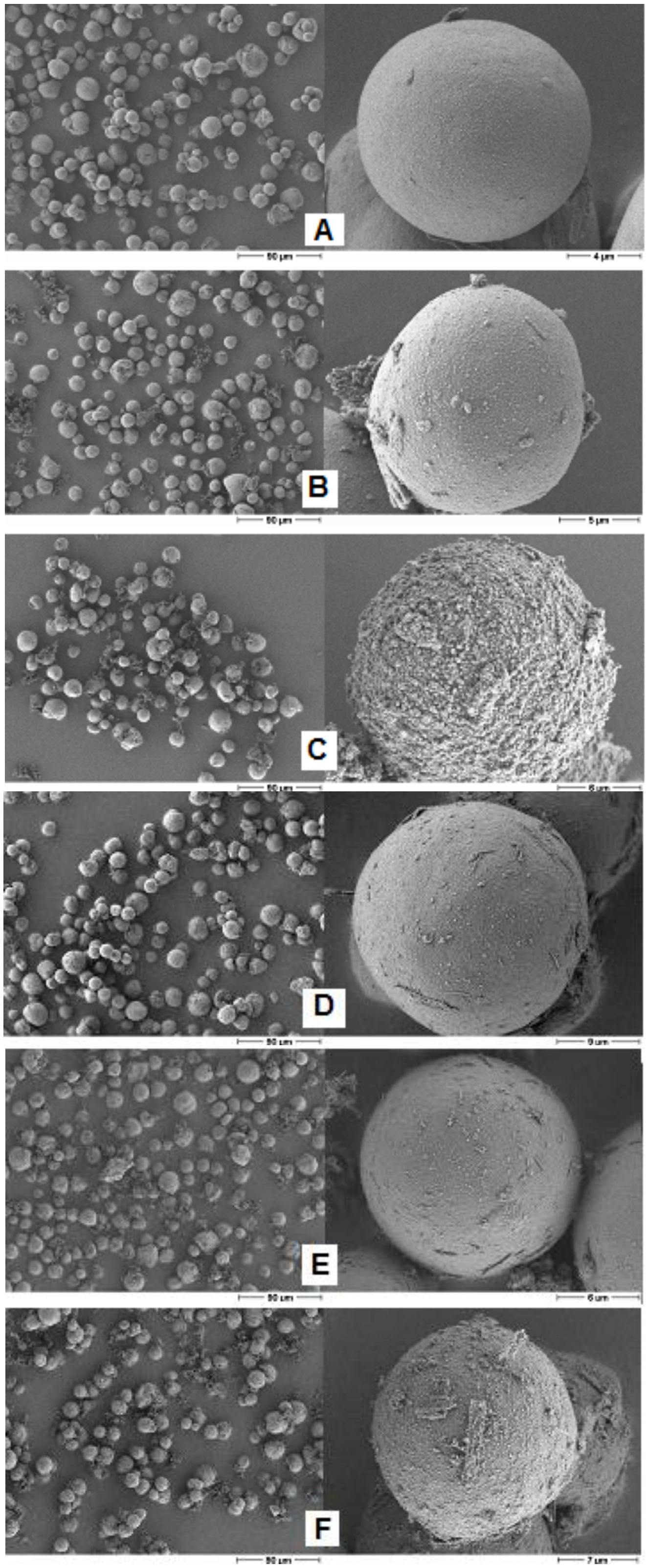

A
50 µm
4 µm
B
50 µm
5 µm
C
50 µm
6 µm
D
50 µm
9 µm
E
50 µm
6 µm
F
50 µm
7 µm

Figure S5. Scanning electron micrographs of imprinted composites (A) A_F^1, (B) A_F^2, (C) A_F^3, (D) A_{FD}^1, (E) A_{FD}^2 and (F) A_{FD}^3.

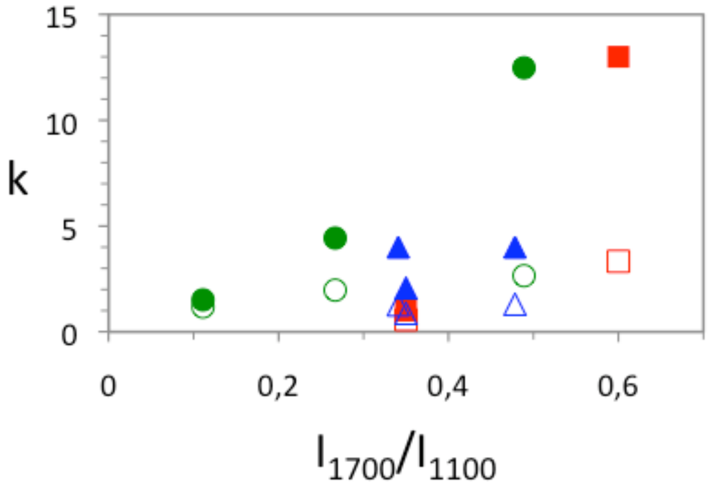


Figure S6. Plot of retention factors (k) for L-PA (solid symbols) and D-PA (open symbols) versus the normalized FTIR band intensities of the C=O stretch at ca 1700cm^{-1} (referenced to the SiOSi vibration at ca 1100cm^{-1}) for A_I (red squares) and A_{IR} (blue triangles) and A_{FD} (green circles). Mobile phase: MeCN/H2O/HOAc:92.5/5/2.5 (v/v/v).

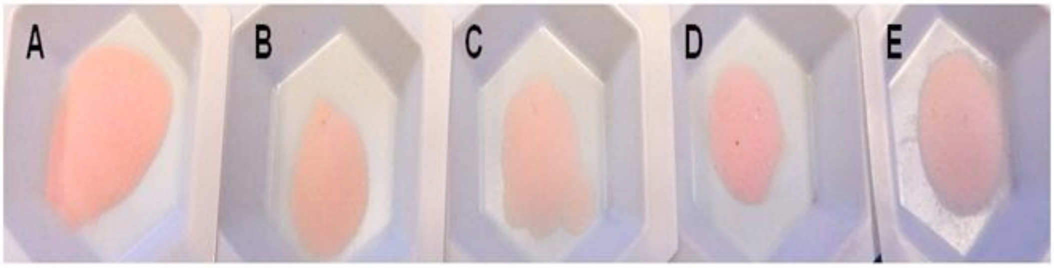


Figure S7. Picture of imprinted composite RAFT (A) Si-500 RAFT agent (B) R_F^{Si500} (C) R_{FE}^{Si500} (D) R_F^{Si100} (E) R_F^{Si100} (after etching)

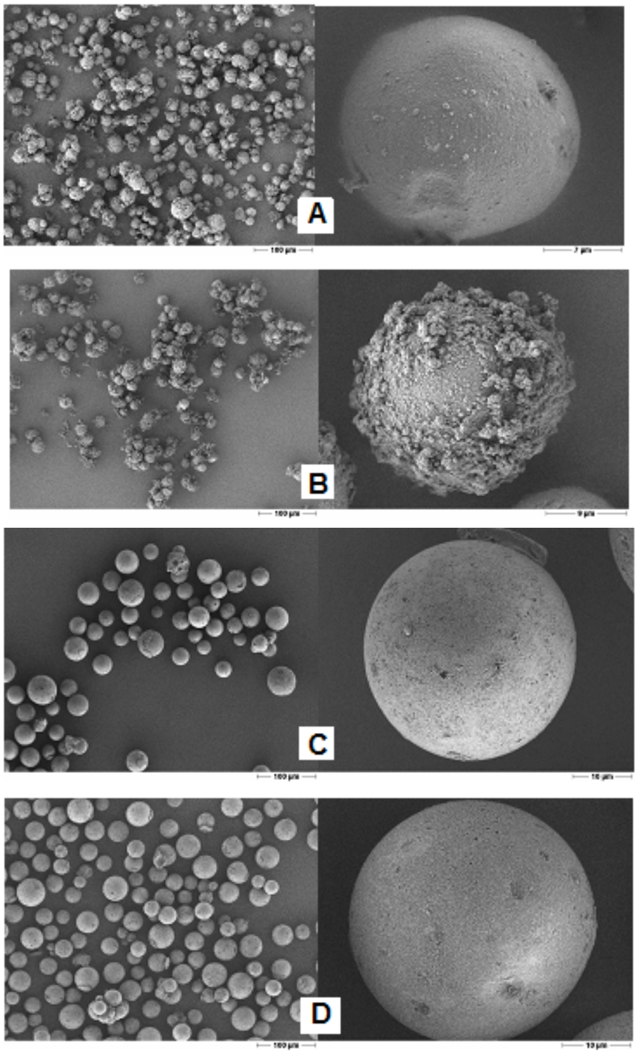


Figure S8. Scanning electron micrographs of imprinted composites (A) R_F^{Si100}, (B) R_{FE}^{Si100}, (C) R_F^{Si500} and (D) R_{FE}^{Si500} at two magnifications