Supporting Information

Surface-Initiated SET Living Radical Polymerisation for the Synthesis of Silica–Polymer Core–Shell Nanoparticles

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MATERIALS AND CHARACTERISATION METHODS

Materials. All materials were purchased from Sigma-Aldrich and used as received unless otherwise stated. Methyl acrylate (MA, 99 %), *tert*-butyl acrylate (*t*BA, Fluka, ≥ 98 %) and n-butyl acrylate (nBA, ≥ 99 %) were passed over two short columns of MEHQ inhibitor removal packing to remove methylethyl hydroquinone immediately prior to use. *N*-Isopropylacrylamide (NIPAAm, 97 %) was purified by recrystallisation from hexane, dried in a vacuum oven at ambient temperature and then stored in a freezer. Styrene (S, ≥ 99 %) was passed over a column of activated basic alumina to remove the 4-*tert*-butylcatechol inhibitor prior to use. The free initiator, ethyl 2-bromoisobutyrate (EBiB, ≥ 98 %), was used without further purification. *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA, 99 %) was used as received. Hexamethylated tris(2-aminoethyl)amine (Me_6TREN) was provided by Cheuk Ka Poon (Key Centre for Polymers and Colloids, University of Sydney), prepared in accordance with standard literature procedures.[1] The {[(2-bromo-2-methylpropionyl)oxy]propyl}triethoxysilane (BPE) initiator was synthesised and coupled to silica nanoparticles (130 nm) by Dr. John Moraes (Key Centre for Polymers and Colloids, University of Sydney) in collaboration with A/Prof. Kohji Ohno (Institute for Chemical Research, Kyoto University). The silica nanoparticles were supplied by Nippon Shokubai Co., Ltd., Osaka, Japan (SEAHOSTER KE-E10, average diameter = 130 nm, 20 wt. % suspension in ethylene glycol). Dimethyl sulfoxide (DMSO, Ajax Finechem, 99.9 %), trifluoroethanol (TFE, ≥ 99 %), ethanol (EtOH, Merck, 99.7 %) and toluene (Ajax Finechem, 99.9 %) were used as received. Copper(0) wire (1.0 mm diameter) was activated using glacial acetic acid (Merck), according to the procedure outlined by Percec and co-workers.[2] Copper(II) bromide ($CuBr_2$, 99 %) was used as received.

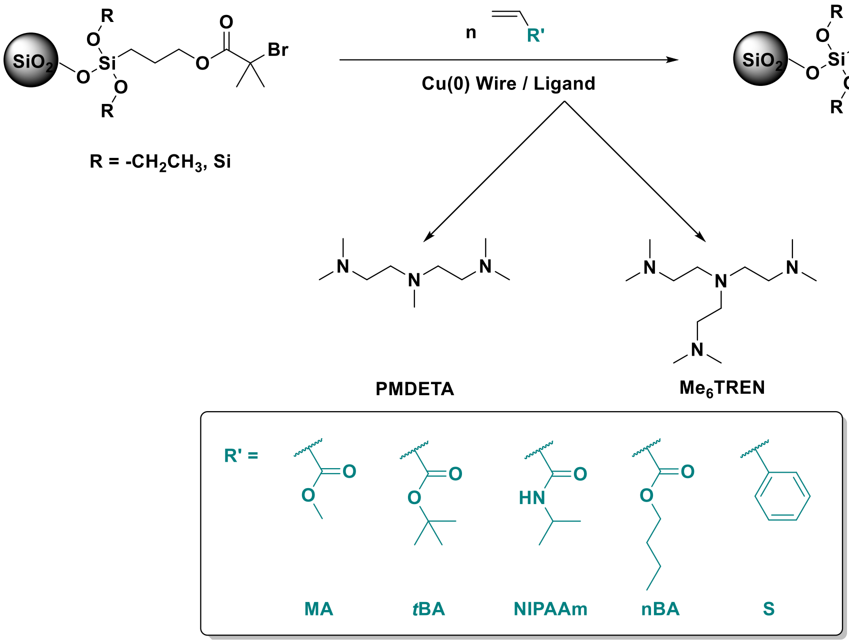
Analytical methods. ^1H-NMR spectra were recorded on a 200 MHz Bruker AVANCE NMR instrument to determine monomer conversion and the corresponding theoretical molecular weight based on the ratio of monomer to free initiator added. The solvent residual peak was used as an internal reference ($CDCl_3$, δ_H = 7.26 ppm; DMSO-d_6, δ_H = 2.50 ppm; acetone-d_6, δ_H = 2.05 ppm; MeOD, δ_H = 3.31 ppm). Two size exclusion chromatography (SEC) systems were used dependent upon polymer solubility to study the polymerisation kinetics and assess the control by monitoring the increase in molecular weight with time and the corresponding molecular weight distributions. THF soluble polymers (i.e. PMA, PnBA, P*t*BA and PS) were characterised using a UFLC Shimadzu LC-20AD prominence liquid chromatograph running LC Solutions software and equipped with a SIL-20A HT prominence auto sampler, DGU-$20A_3$ prominence degasser, Rid-10a Shimadzu RI detector, miniDAWN TREOS Wyatt LS detector and a Wyatt ViscoStar-II viscometer. The polymer samples were passed through a PLgel 5 µm guard (50 × 7.5 mm, Agilent Technologies), a Jordi Gel DVB column (new mixed bed, 10^4+ Å, 300 × 7.8 mm, Jordi Labs LLC) and a PLgel 5 µL Mixed C-column (300 × 7.5 mm, Agilent Technologies) using tetrahydrofuran (THF) as eluent containing 0.04 g L^{-1} hydroquinone at a flow rate of 1.0 mL min^{-1} at 40 °C. Analyte samples were passed over a column of basic alumina to remove residual copper salts before being concentrated under reduced pressure and redissolved in THF containing 0.04 g L^{-1} hydroquinone and 0.5 % (v/v) toluene as the flow rate marker. Prior to injection, samples were filtered through a PTFE membrane (0.45 µm pore size). The molecular weights and molecular weight distributions were determined using ASTRA6 software using a conventional calibration against linear polystyrene standards ranging from 6.82×10^2 to 1.67×10^6 g mol^{-1}. DMF soluble polymers (i.e. PHEA, PNIPAAm) were analysed using a Polymer Laboratories GPC-50 instrument equipped with a PL-RI differential refractive index detector. The polymer samples were passed through a Polymer Laboratories PolarGel 8 µm guard column, and two Polymer Laboratories PolarGel-M columns using *N*,*N*-

dimethylformamide (DMF) as eluent containing 0.04 g L^{-1} hydroquinone and 0.1 % (w/w) LiBr at a flow rate of 0.5 mL min^{-1} at 50 °C. Analyte samples were passed over a column of basic alumina, and concentrated under reduced pressure before being dissolved in DMF containing 0.04 g L^{-1} hydroquinone, 0.1 % (w/w) LiBr and 1.15 % (w/w) water as the flow rate marker. Prior to injection, samples were filtered through a PTFE membrane (0.45 µm pore size). The molecular weights and molecular weight distributions were determined using Cirrus^{TM} GPC software by conventional calibration with linear polystyrene standards ranging from 6.82×10^2 to 1.67×10^6 g mol^{-1}. Thermal gravimetric analysis (TGA) was used to determine the relative ratio of grafted polymer to silica by mass to evaluate the average number of synthetic polymers grafted to the silica core or the grafting density. Samples (0.5–10 mg) were heated from room temperature to 700 °C at a rate of 10 °C min^{-1} on a Hi-Res TGA 2950 thermogravimetric analyser under a nitrogen atmosphere (60 cm^3 min^{-1}). The sample was allowed to equilibrate at 100 °C to remove any residual water and solvent. The TGA thermograms were adjusted to 100 wt. % at approximately 200 °C or when the sample mass stabilised. The sample was then heated to 700 °C under a nitrogen atmosphere before the remaining organic material was consumed by the introduction of oxygen. The sample was isothermed at 700 °C until constant weight. The residual weight percent and degradation temperatures were determined using the TA Instruments Universal Analysis 200 software. Dynamic light scattering (DLS) and zeta potential measurements were performed using a Malvern Zetasizer Nano-ZS. Scanning electron micrographs were collected on a Zeiss ULTRA *plus* scanning electron microscope operating with an accelerating voltage at 30 kV and a working distance of ca 3 nm. Images were collected using an SE2 and STEM detector under bright field conditions. Transmission electron micrographs were taken on a JEOL JEM-1400 microscope operating at 120 kV under dark field regime. Image corrections and data analysis were conducted using ImageJ 1.47v software. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) was performed using a Bruker Tensor 27 spectrophotometer fitted with a diffuse reflectance accessory. The spectra were recorded between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1} using 32 scans in a KBr matrix. Spectra were subjected to a background subtraction using dry KBr and the spectra processed using OPUS 6.0 software. All spectra were averaged from a set of 3 measurements run in succession.

EXPERIMENTAL PROCEDURES

Activation of Copper(0) Wire using Glacial Acetic Acid. Typically, a two-necked 50 mL round bottom flask was charged with copper wire (1–30 cm, 1.0 mm diameter) wrapped around a Teflon coated magnetic stirrer bar before being sealed with a rubber septum and a quick-fit glass tap. The reaction vessel was then purged with nitrogen before glacial acetic acid (4–10 mL) was added via syringe. The flask was then placed in an oil bath preheated to 35 °C and allowed to equilibrate for 30 min before the copper wire was released into solution. After 10 min, the activated copper wire was removed from the acid by an external magnet and the acid removed from the reaction vessel by syringe. The flask was then evacuated and back-filled with nitrogen. The copper wire was then dried under a nitrogen stream for a further 60 min and stored under nitrogen until use.

Surface-Initiated Single-Electron Transfer Living Radical Polymerisation from Bromine-Functionalised Silica Nanoparticles. In a typical reaction, bromine-functionalised silica nanoparticles (SiP-Br), accounting for 1 % (w/w) of the total reaction mixture, excluding the zerovalent copper catalyst, was collected from ethanol (EtOH, 12.74 % (w/w)) and solvent-exchanged to the appropriate solvent by centrifugation and redispersion using a vortex mixer (3 times, 4 min, 14,500 rpm). The monomer and solvent containing the functionalised particles were measured into a 25 mL sample vial. The vial was then sealed with a rubber septum to prevent evaporation before the ligand and sacrificial initiator (EBiB) were added using a microsyringe. The mixture was then transferred to a 25 mL Schlenk tube charged with a magnetic stirrer wrapped with the activated copper(0) wire catalyst (1.0 mm diameter), fixed above the solution by an external magnet. The reaction flask was then sealed with a rubber septum and deoxygenated by 5 consecutive cycles of freeze-pump-thaw degassing before being back-filled with nitrogen. The flask was then placed in a thermostatted oil bath preheated to the appropriate temperature and allowed to equilibrate before the catalyst was released into solution to initiate the polymerisation. Samples were taken at various intervals by syringe for analysis by SEC and ^{1}H-NMR for molecular weight distribution and percentage conversion, respectively. The reaction was carried out similarly in the absence of functionalised silica nanoparticles to investigate their impact on the reaction mechanism. Due to the very high molecular weights targeted in this system, the ligand and initiator may have been introduced into the reaction mixture through stock solutions. Detailed experimental procedures for all investigations are given below.



Scheme S1 General system used to prepare inorganic–organic core–shell materials from an initiator-fixed silica core by surface-initiated single-electron transfer living radical polymerisation using a copper-based catalytic system with a variety of synthetic monomers in the presence of a free initiator, EBiB, which has been omitted for simplicity.

Kinetic Study Investigating the Growth of Poly(methyl acrylate) Brushes from Initiator-Fixed Silica Nanoparticles. The use of a heterogeneous catalytic system exploited by SET-LRP systems to graft high molecular weight polymers from a solid-support (SiP-Br) was investigated using methyl acrylate (MA) as a model system. The conditions used are indicated in Table S1, Entries 1–5. Modifying the ratio of monomer to sacrificial initiator allowed the shell thickness to be tuned. Samples were collected by syringe at various intervals under nitrogen to monitor the reaction progress. The sampling syringe was rinsed with deuterated chloroform for analysis by ^{1}H-NMR to determine monomer conversion and theoretical molecular weight. The remaining sample was diluted with DCM or chloroform and washed by repeated centrifugation-redispersion cycles (3 times, 14,500 rpm). The supernatant was collected and the solvent removed under reduced pressure to collect the free polymer for analysis by SEC to determine the molecular weight and molecular weight distribution. In order to determine whether the presence of functionalised particles in the reaction medium has a significant impact on the polymerisation progress, the reactions were performed in the absence and presence of initiator-fixed silica nanoparticles. Detailed experimental procedures are given below. Changes in experimental procedure were based on equipment availability, reagent quantities and sensitivity to oxygen.

Grafting MA from SiP-Br, $DP_{\mathrm{n,target}}$ 250 (Table S1, Entry 1). The functionalised silica nanoparticles (SiP-Br) were solvent exchanged from EtOH to DMSO (3 times, 6 min, 14,500 rpm). MA (2.0 mL, 22 mmol) and DMSO (1.5 mL) containing the SiP-Br (37.5 mg) were measured into a 25 mL sample vial. The vial was then sealed with a rubber septum before ligand (Me$_6$TREN, 2.4 µL, 8.98×10^{-3} mmol) and initiator (EBiB, 13.2 µL, 8.90×10^{-2} mmol) were added using a microsyringe. The mixture was then transferred to a 25 mL Schlenk tube charged with a magnetic stirrer wrapped with the copper(0) wire catalyst (1.5 cm, 1.0 mm diameter) fixed above the solution by an external magnet. The flask was then sealed with a rubber septum and deoxygenated by 5 consecutive cycles of freeze-pump-thaw degassing before being back-filled with nitrogen. The flask was then placed in a thermostatted oil bath preheated to 30 °C for 5 min before the catalyst was released into solution to initiate the polymerisation.

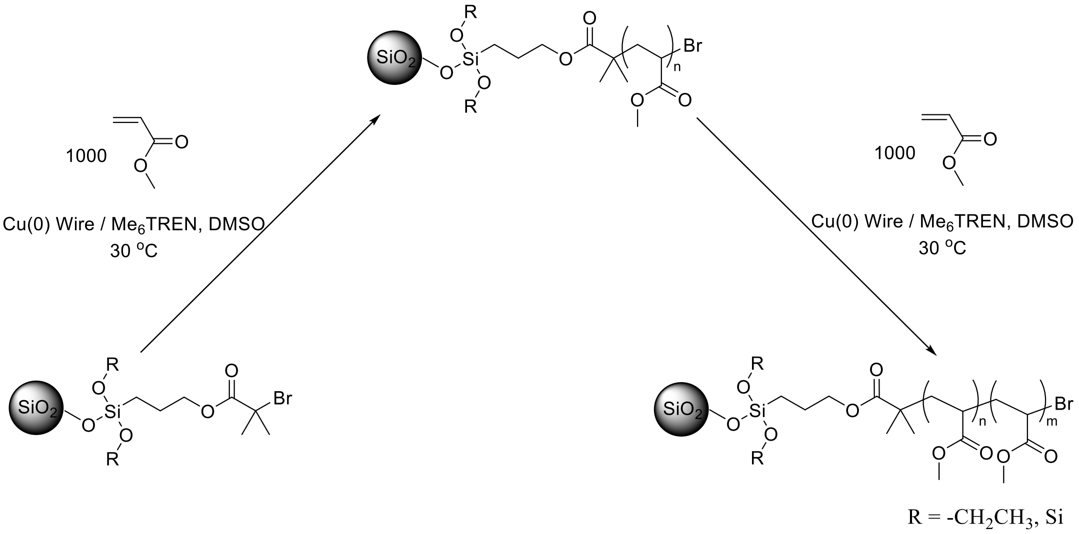
Grafting MA from SiP-Br, $DP_{\mathrm{n,target}}$ 500 - Concentrated Regime (Table S1, Entry 2). The functionalised silica nanoparticles were solvent exchanged from EtOH to DMSO (3 times, 4 min, 14,500 rpm). A 0.362 % (w/w) stock solution of Me$_6$TREN in DMSO was prepared. MA (4.0 mL, 44 mmol), the stock solution solvent (DMSO, 1.0 mL) containing the ligand (Me$_6$TREN, 4.0 mg, 1.7×10^{-2} mmol) and functionalised silica nanoparticles (0.061 g) in DMSO (1.0 mL) were then measured into a 25 mL Schlenk tube charged with the magnetic stirrer and copper(0) wire (10.0 cm, 1.0 mm diameter) which were kept out of the mixture using an external magnet. The flask was then sealed with a rubber septum and the reaction mixture degassed by 5 cycles of freeze-pump-thaw degassing before being back-filled with nitrogen and placed in a pre-heated thermostatted oil bath at 30 °C. After 30 min, the initiator (EBiB, 13 µl, 8.8×10^{-2} mmol) was added by syringe under nitrogen and the copper(0) wire dropped into the solution to initiate the polymerisation.

Grafting MA from SiP-Br, $DP_{\mathrm{n,target}}$ 500 - Dilute Regime (Table S1, Entry 3). Functionalised SiNPs were solvent exchanged from EtOH to DMSO (3 times, 4 min, 14,500 rpm). MA (2.0 mL, 22 mmol) and DMSO (1.5 mL) containing the functionalised SiNPs (36.1 mg) were measured into a 25 mL sample vial. The vial was then sealed with a rubber septum before Me$_6$TREN (2.4 µL, 8.98×10^{-3} mmol) and EBiB (6.6 µL, 4.45×10^{-2} mmol) were added using a microsyringe. The mixture was then transferred to a 25 mL Schlenk tube charged with a magnetic stirrer wrapped with the copper(0) wire catalyst (5 cm, 1 mm diameter) fixed above the solution by an external magnet. The flask was then sealed with a rubber septum and deoxygenated by 5 consecutive cycles of freeze-pump-thaw degassing before being back-filled with nitrogen. The flask was then placed in a thermostatted oil bath at 30 °C for 5 min before the catalyst was released to initiate the polymerisation.

Grafting MA from SiP-Br, $DP_{\mathrm{n,target}}$ 1000 (Table S1, Entry 4). A 1 mL stock solution of initiator (EBiB, 66 µl) and ligand (Me$_6$TREN, 20 mg) in solvent (DMSO) was prepared in a volumetric flask. Functionalised SiNPs (83.3 mg) were solvent exchanged from EtOH to DMSO (3 times, 4 min, 14,500 rpm) and transferred to a 20 mL sample vial containing MA (4.0 mL, 44 mmol) before being transferred to a 20 mL Schlenk flask charged with the copper(0) wire catalyst (6.0 cm, 1.0 mm diameter) wrapped around a magnetic stirrer bar.

The copper catalyst was kept above the solution by an external magnet. The flask was then sealed with a rubber septum before the addition of 100 µL of the stock solution containing initiator (EBiB, 6.6 µL, 4.5×10^{-2} mmol) and ligand (Me_6TREN, 2.3 µL, 8.7×10^{-3} mmol) in DMSO. The total volume of solvent (DMSO) added was 4.0 mL. The reaction mixture was then deoxygenated by 3 consecutive cycles of freeze-pump-thaw degassing. The reaction flask was then placed in a water bath at 30 °C for 30 min before the catalyst was dropped into solution to initiate the polymerisation.

Building Up Shell Size by Successive Chain Extensions. PMA was grown from the initiator-fixed particles targeting a DP_n of 1000 monomer units using the same conditions and stoichiometric ratios as in Entry 4(ii). After 130 min, the polymerisation was quenched by exposure to air and dilution with DCM (51 % conversion by ^{1}H-NMR). The PMA-grafted particles were then washed by repeated centrifugation-redispersion cycles (3 times, 14,500 rpm, 10 min) and redispersed in DMSO (4.0 mL) for subsequent chain extension. To the PMA-grafted silica nanoparticles, MA (4.0 mL, 44 mmol), ligand (Me_6TREN, 2.3 µL, 8.6×10^{-3} mmol) and sacrificial initiator (EBiB, 6.6 µL, 4.4×10^{-2} mmol) was added. The reaction mixture was then transferred to a 25 mL Schlenk tube charged with the activated copper(0) wire catalyst (6 cm, 1.0 mm diameter) wrapped around a magnetic stirrer before being sealed with a rubber septum. The reaction mixture was then deoxygenated by 5 consecutive cycles of freeze-pump-thaw degassing before being back-filled with nitrogen. The reaction mixture was then allowed to equilibrate in a thermostatted oil bath preheated to 30 °C for 5 min before the copper catalyst was released to initiate the polymerisation. The polymerisation was quenched by exposure to air after 4 h (24 % conversion by ^{1}H-NMR). The PMA-grafted particles were then washed by repeated centrifugation-redispersion cycles (3 times, 14,500 rpm, 10 min) with DCM.



Scheme S2 Synthetic strategy to build-up long polymer grafts from surface-bound initiators by successive block extensions.

Grafting MA from SiP-Br, $DP_{n,target}$ 5000 at 60 °C (Table S1, Entry 5). Functionalised SiNPs were solvent exchanged from EtOH to DMSO (3 times, 5 min, 14.5×10^{3} rpm). MA (4.0 mL, 44 mmol) containing the ligand (Me_6TREN, 0.5 µL, 1.8×10^{-3} mmol) and initiator (EBiB, 1.3 µL, 8.9×10^{-3} mmol) was measured into a sealed 25 mL sample vial containing the SiNPs (64.7 mg) in DMSO (4.0 mL). The mixture was then transferred to a 25 mL Schlenk tube charged with a magnetic stirrer wrapped with the copper(0) wire catalyst (2 cm, 1.0 mm diameter) which was fixed above the solution using an external magnet. The reaction mixture was then sealed with a glass stopper before being deoxygenated by 5 consecutive cycles of freeze-pump-thaw degassing, and back-filled with nitrogen before being placed in a preheated oil bath thermostatted at 60 °C. The catalyst was then released into solution to initiate the polymerisation. The polymerisation was quenched by exposure to air after 13.5 h. An aliquot was removed and dissolved in deuterated chloroform for analysis by ^{1}H-NMR to determine monomer conversion and theoretical molecular weight. The remaining sample was diluted with DCM and washed by repeated centrifugation-redispersion cycles (3 times, 14,500 rpm).

Kinetic Study Investigating the Growth of Poly(*tert*-butyl acrylate) Brushes from Initiator-fixed Silica Nanoparticles. The conditions used to prepare the SiP-*g*-P*t*BA core–shell materials are given in Table S1, Entries 6–9. Samples were collected by syringe at various intervals under nitrogen to monitor the reaction progress. The sampling syringe was rinsed with deuterated chloroform for analysis by ^{1}H-NMR to determine monomer conversion and theoretical molecular weight. The remaining sample was diluted with DCM and washed by repeated centrifugation-redispersion cycles (3 times, 14,500 rpm). The supernatant was collected and the solvent removed under reduced pressure to collect the free polymer for analysis by SEC to determine the molecular weight and molecular weight distribution. Detailed experimental procedures are given below.

Grafting *t*BA from SiP-Br, $DP_{\mathrm{n,target}}$ 250 at 30 °C (Table S1, Entry 6). Functionalised SiNPs were solvent exchanged from EtOH to TFE (3 times, 4 min, 14,500 rpm). *t*BA (4.0 mL, 28 mmol) and TFE (2.0 mL) containing the functionalised SiNPs (62.7 mg) were measured into a 25 mL sample vial. The vial was then sealed with a rubber septum before Me_6TREN (2.9 µL, 1.1×10^{-2} mmol) and EBiB (16.3 µL, 1.1×10^{-1} mmol) were added using a microsyringe. The mixture was then transferred to a 25 mL Schlenk tube charged with a magnetic stirrer wrapped with copper(0) wire (3.0 cm, 1.0 mm diameter). The flask was then sealed with a rubber septum and deoxygenated by 3 consecutive cycles of freeze-pump-thaw degassing before being back-filled with nitrogen. The flask was then placed in a preheated oil bath at 30 °C and allowed to equilibrate for 10 min before the catalyst was released to initiate the polymerisation.

Grafting *t*BA from SiP-Br, $DP_{\mathrm{n,target}}$ 250 at 50 °C (Table S1, Entry 7). Functionalised SiNPs were solvent exchanged from EtOH to TFE (3 times, 4 min, 14,500 rpm). *t*BA (4.0 mL, 28 mmol) and TFE (2.0 mL) containing the bromine-functionalised SiNPs (64.1 mg) were measured into a 25 mL sample vial. The vial was then sealed with a rubber septum before Me_6TREN (2.9 µL, 1.1×10^{-2} mmol) and EBiB (16.3 µL, 1.1×10^{-1} mmol) were added using a microsyringe. The mixture was then transferred to a 25 mL Schlenk tube charged with a magnetic stirrer wrapped with the copper(0) wire catalyst (3.0 cm, 1.0 mm diameter) fixed above the solution by an external magnet. The flask was then sealed with a rubber septum and deoxygenated by 5 consecutive cycles of freeze-pump-thaw degassing before being back-filled with nitrogen. The flask was then placed in a preheated oil bath at 50 °C and allowed to equilibrate for 10 min before the copper wire catalyst was released to initiate the polymerisation.

Grafting *t*BA from SiP-Br, $DP_{\mathrm{n,target}}$ 370 at 50 °C (Table S1, Entry 8). Functionalised SiNPs were solvent exchanged from EtOH to TFE (3 times, 4 min, 14,500 rpm). *t*BA (4.0 mL, 28 mmol) and TFE (2.0 mL) containing the bromine-functionalised SiNPs (57.3 mg) were measured into a 25 mL sample vial. The vial was then sealed with a rubber septum before ligand (Me_6TREN, 6.6 µL, 2.5×10^{-2} mmol) and initiator (EBiB, 11 µL, 7.4×10^{-2} mmol) were added using a microsyringe. The mixture was then transferred to a 25 mL

Schlenk tube charged with a magnetic stirrer wrapped with the copper(0) wire catalyst (0.43 g, 6.0 cm, 1.0 mm diameter) fixed above the solution by an external magnet. The flask was then sealed with a rubber septum and deoxygenated by 5 consecutive cycles of freeze-pump-thaw degassing, back-filling with nitrogen before each thawing cycle. The flask was then placed under argon before being placed in a preheated oil bath at 50 °C. The catalyst was then released into solution to initiate the polymerisation.

Grafting *t*BA from SiP-Br, $DP_{\mathrm{n,target}}$ 745 at 50 °C (Table S1, Entry 9). Functionalised SiNPs were solvent exchanged from EtOH to TFE (3 times, 4 min, 14,500 rpm). *t*BA (4.0 mL, 28 mmol) and TFE (2.0 mL) containing the bromine-functionalised SiNPs (63.8 mg) were measured into a 25 mL sample vial. The vial was then sealed with a rubber septum before ligand (Me$_6$TREN, 8.3 µL, 3.1×10^{-2} mmol) and initiator (EBiB, 5.5 µL, 3.7×10^{-2} mmol) were added using a microsyringe. The mixture was then transferred to a 25 mL Schlenk tube charged with a magnetic stirrer wrapped with the copper(0) wire catalyst (4.0 cm, 1.0 mm diameter) fixed above the solution by an external magnet. The flask was then sealed with a rubber septum and deoxygenated by 5 consecutive cycles of freeze-pump-thaw degassing, back-filling with nitrogen before each thawing cycle. The flask was then placed under argon before being placed in a preheated oil bath at 50 °C. The catalyst was then released into solution to initiate the polymerisation.

Exploring the Versatility of SET-LRP to Prepare Silica–Polymer Hybrid Materials. The conditions used to prepare various core–shell materials are given in Table S1, Entries 10–12.

Grafting n-Butyl Acrylate (nBA) from SiP-Br, $DP_{\mathrm{n,target}}$ 250 (Table S1, Entry 10). The functionalised SiNPs were solvent exchanged from EtOH to DMSO (3 times, 5 min, 14,500 rpm). nBA (2.0 mL, 14 mmol) and DMSO (1.5 mL) containing the bromine-functionalised silica nanoparticles (34.9 mg) were measured into a 25 mL sample vial. The vial was then sealed with a rubber septum before ligand (Me$_6$TREN, 1.5 µL, 5.6×10^{-3} mmol) and initiator (EBiB, 8.3 µL, 5.6×10^{-2} mmol) were added using a microsyringe. The mixture was then transferred to a 25 mL Schlenk tube charged with a magnetic stirrer wrapped with the copper(0) wire catalyst (1.5 cm, 1.0 mm diameter) fixed above the solution by an external magnet. The flask was then sealed with a glass stopper and deoxygenated by 5 consecutive cycles of freeze-pump-thaw degassing before being back-filled with nitrogen. The flask was then placed in a thermostatted oil bath preheated to 30 °C for 5 min before the catalyst was released into solution to initiate the polymerisation. The polymerisation was quenched by exposure to air after 24 h. An aliquot was removed and dissolved in deuterated chloroform for analysis by ^1H-NMR to determine monomer conversion and theoretical molecular weight. The remaining sample was diluted with DCM and washed by repeated centrifugation-redispersion cycles (3 times, 14,500 rpm). The supernatant was collected and the solvent removed under reduced pressure to collect the free polymer for analysis by SEC to determine the molecular weight and molecular weight distribution. SEC (THF, 1 mL min^{-1}, 40 °C): $M_{\mathrm{n,SEC}} = 20{,}600$ g mol^{-1}, $M_{\mathrm{w,SEC}} = 21{,}800$ g mol^{-1}, $Đ = 1.06$. %C$_{\mathrm{NMR}}$ = 49 %, $M_{\mathrm{n,th}} = 16{,}000$ g mol^{-1}, $DP_{\mathrm{n,th}} = 123$. DRIFTS (cm^{-1}, KBr Matrix): 3659, 3269, 2961, 2877, 1736, 1463, 1108, 952, 807, 553, 468, 460.

Grafting *N*-Isopropylacrylamide (NIPAAm) from SiP-Br, $DP_{\mathrm{n,target}}$ 250 (Table S1, Entry 11). NIPAAm (2.0 g, 18 mmol) and EtOH (3.0 mL) containing the bromine-functionalised SiNPs (44.1 mg) were measured into a 25 mL sample vial. The vial was then sealed with a rubber septum before the ligand (PMDETA, 3.7 µL, 1.8×10^{-2} mmol) and initiator (EBiB, 10 µL, 6.7×10^{-2} mmol) were added using a microsyringe. The mixture was then transferred to a 25 mL Schlenk tube charged with a magnetic stirrer wrapped with the copper(0) wire catalyst (3.0 cm, 1.0 mm diameter, 0.22 g) fixed above the solution by an external magnet. The flask was then sealed with a glass stopper and deoxygenated by 5 consecutive cycles of freeze-pump-thaw degassing before being back-filled with nitrogen. The flask was then placed in a thermostatted oil bath preheated to 30 °C for 5 min before the catalyst was released into solution to initiate the polymerisation. The polymerisation was quenched by exposure to air after 24 h. An aliquot was removed, dried under ambient conditions and then dissolved in deuterated chloroform for analysis by ^{1}H-NMR to determine monomer conversion and theoretical molecular weight. The remaining sample was diluted with EtOH and washed by repeated centrifugation-redispersion cycles (3 times, 14,500 rpm). The supernatant was collected and the solvent removed under reduced pressure to collect the free polymer for analysis by SEC to determine the molecular weight and molecular weight distribution. SEC (DMF, 0.5 mL min^{-1}, 50 °C): $M_{\mathrm{n,SEC}}$ = 39,000 g mol^{-1}, $M_{\mathrm{w,SEC}}$ = 111,000 g mol^{-1}, $Đ$ = 2.8. %C$_{\mathrm{NMR}}$ = 20 %, $M_{\mathrm{n,th}}$ = 6100 g mol^{-1}, $DP_{\mathrm{n,th}}$ = 52. DRIFTS (cm^{-1}, KBr Matrix): 3271, 2976, 2933, 2876, 1868, 1652, 1542, 1458, 1367, 1151, 1105, 948, 801, 553, 465.

Grafting Styrene (S) from SiP-Br, targeting a $DP_{\mathrm{n,target}}$ 250 (Table S1, Entry 12). The functionalised SiNPs were solvent exchanged from EtOH to toluene (3 times, 5 min, 14.5 × 10^{3} rpm). Styrene (4.4 mL, 38 mmol) and toluene (2.2 mL) containing the bromine-functionalised SiNPs (62.4 mg) were measured into a 25 mL sample vial containing $CuBr_2$ (3.3 mg, 1.5 × 10^{-2} mmol). The vial was then sealed with a rubber septum before ligand (PMDETA, 11.2 µL, 5.4 × 10^{-2} mmol) and initiator (EBiB, 22.8 µL, 1.5 × 10^{-1} mmol) were added using a microsyringe. The mixture was then transferred to a 25 mL Schlenk tube charged with a magnetic stirrer. The flask was then sealed with a glass quick-fit tap and deoxygenated by 5 consecutive cycles of freeze-pump-thaw degassing before being back-filled with nitrogen. The flask was then placed in a thermostatted preheated oil bath at 90 °C before the copper(0) wire (1 cm, 1.0 mm diameter, 0.08 g) was dropped into solution to initiate the polymerisation under nitrogen. The polymerisation was quenched by exposure to air after 24 h. An aliquot was removed and dissolved in deuterated chloroform for analysis by ^{1}H-NMR to determine monomer conversion and theoretical molecular weight. The remaining sample was diluted with toluene and washed by repeated centrifugation-redispersion cycles (3 times, 14,500 rpm) assisted by sonication, followed by washing with THF (3 times, 14,500 rpm). The supernatant was collected and the solvent removed under reduced pressure to collect the free polymer for analysis by SEC to determine the molecular weight and molecular weight distribution. SEC (THF, 1 mL min^{-1}, 40 °C): $M_{\mathrm{n,SEC}}$ = 19,100 g mol^{-1}, $M_{\mathrm{w,SEC}}$ = 20,900 g mol^{-1}, $Đ$ = 1.1. %C$_{\mathrm{NMR}}$ = 67 %, $M_{\mathrm{n,th}}$ = 17,800 g mol^{-1}, $DP_{\mathrm{n,th}}$ = 169. DRIFTS (cm^{-1}, KBr Matrix): 3651, 3239, 2926, 1868, 1493, 1453, 1109, 949, 800, 699, 545, 470.

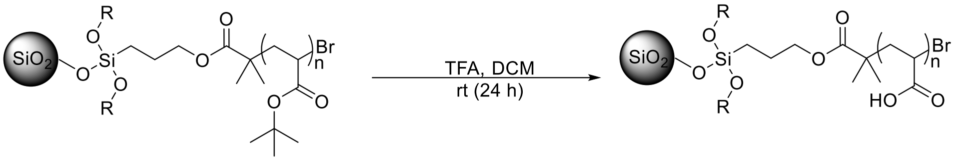
Table S1 Summary of the reagents, stoichiometric ratios, and quantities used to investigate the surface-initiated single-electron transfer living radical polymerisation from bromine-functionalised silica nanoparticles.

ENTRY		*Reagents*			*T*	*Molar Ratio*					*Dilution*			*Monomer*		*Initiator*[a]		*Ligand*		*Solvent*		*Cu(0)*	*SiP-Br*
		Monomer	*Ligand*	*Solvent*	(°C)	[M]	:	[I]	:	[L]	M	:	S	(ml)	(mmol)	(μL)	(mmol)	(μL)	(mmol)	(ml)	(mmol)	(cm)	(mg)
1	i	MA	Me_6TREN	DMSO	30	250	:	1.00	:	0.10	2	:	1.5	2.01	22.3	13.2	0.0890	2.4	0.0090	1.50	21.2	1.5	-
	ii					249	:	1.00	:	0.10	2	:	1.5	2.00	22.2	13.2	0.0890	2.4	0.0090	1.50	21.2	1.5	37.5
2	i				30	507	:	1.00	:	0.20	2	:	1	4.00	44.4	13.0	0.0876	4.7	0.018	2.00	28.1	10.0	-
	ii					506	:	1.00	:	0.20	2	:	1	4.00	44.4	13.0	0.0876	4.6	0.017	2.00	28.2	10.0	61
3	i				30	499	:	1.00	:	0.20	2	:	1.5	2.00	22.2	6.6	0.044	2.4	0.0090	1.50	21.1	5.0	-
	ii					499	:	1.00	:	0.20	2	:	1.5	2.00	22.2	6.6	0.044	2.4	0.0090	1.50	21.1	5.0	36.1
4	i				30	998	:	1.00	:	0.19	1	:	1	4.00	44.4	6.6	0.044	2.3	0.0086	2.76	38.8	6.0	-
	ii					997	:	1.00	:	0.19	1	:	1	4.00	44.4	6.6	0.044	2.3	0.0086	4.01	56.5	6.0	83.3
5	i				60	4999	:	1.00	:	0.21	1	:	1	4.00	44.4	1.3	0.0089	0.5	0.0018	4.00	56.4	2.0	-
	ii					4999	:	1.00	:	0.21	1	:	1	4.00	44.4	1.3	0.0089	0.5	0.0018	4.00	56.4	2.0	64.7
6	i	*t*BA	Me_6TREN	TFE	30	251	:	1.00	:	0.10	2	:	1	4.00	27.6	16.3	0.110	2.9	0.011	2.00	27.4	3.0	-
	ii					252	:	1.00	:	0.10	2	:	1	4.02	27.7	16.3	0.110	2.9	0.011	2.00	27.4	3.0	62.7
7	i				50	252	:	1.00	:	0.10	2	:	1	4.01	27.7	16.3	0.110	2.9	0.011	2.00	27.5	3.0	-
	ii					251	:	1.00	:	0.10	2	:	1	4.00	27.6	16.3	0.110	2.9	0.011	2.00	27.4	3.0	64.1
8	i				50	372	:	1.00	:	0.33	2	:	1	4.00	27.6	11.0	0.0742	6.6	0.025	2.00	27.4	6.0	-
	ii					372	:	1.00	:	0.33	2	:	1	4.00	27.6	11.0	0.0742	6.6	0.025	2.00	27.5	6.0	62.7
9	i				50	743	:	1.00	:	0.84	2	:	1	4.00	27.6	5.5	0.037	8.3	0.031	2.00	27.4	4.0	-
	ii					744	:	1.00	:	0.84	2	:	1	4.00	27.6	5.5	0.037	8.3	0.031	2.00	27.5	4.0	57.3
10	-	nBA	Me_6TREN	DMSO	30	253	:	1.00	:	0.10	2	:	1.5	2.03	14.2	8.3	0.056	1.5	0.0056	1.50	21.1	1.5	34.9
11	-	NIPAAm	PMDETA	EtOH	30	262	:	1.00	:	0.26	2	:	3	---	17.7	10.0	0.0674	3.7	0.018	3.00	51.4	3.0	44.1
12[b]	-	Styrene	PMDETA	Toluene	90	251	:	1.00	:	0.35	2	:	1	4.45	38.5	22.8	0.154	11.2	0.0536	2.22	20.9	1.0	62.4

[a] In all polymerisations, the free initiator ethyl 2-bromoisobutyrate (EBiB) was used as a structural mimic for the initiator-fixed to the surface of the silica nanoparticles.

[b] Styrene was polymerised in the presence of 10 mol% deactivator ($CuBr_2$) relative to the added free initiator.

Hydrolysis of SiP-*g*-P*t*BA to SiP-*g*-PAA. A fifty-fold molar excess with respect to *tert*-butyl ester groups of trifluoroacetic acid (TFA, 0.23 g, 0.21 mmol) was added to a dispersion containing SiP-*g*-P*t*BA (16 mg, 4.2×10^{-2} mmol *tert*-butyl ester) in DCM (4.1 g). The reaction mixture was then left at ambient temperature with vigorous stirring for 24 h. The reaction mixture was diluted with methanol and the material washed by repeated centrifugation-redispersion into methanol (3 times, 14,500 rpm, 10 min). $M_{\mathrm{n,th}}$ = 11500 g mol^{-1}, $DP_{\mathrm{n,th}}$ = 157. DRIFTS (cm^{-1}, KBr Matrix): 3652, 3274, 3041, 2979, 2939, 2564, 1970, 1870, 1720, 1708, 1459, 1449, 1421, 1393, 1369, 1146, 1106, 952, 797, 749, 472, 464, 450, 421.



Scheme S3 Preparation of water-dispersible core–shell materials by hydrolysis of the P*t*BA grafts to PAA using TFA.

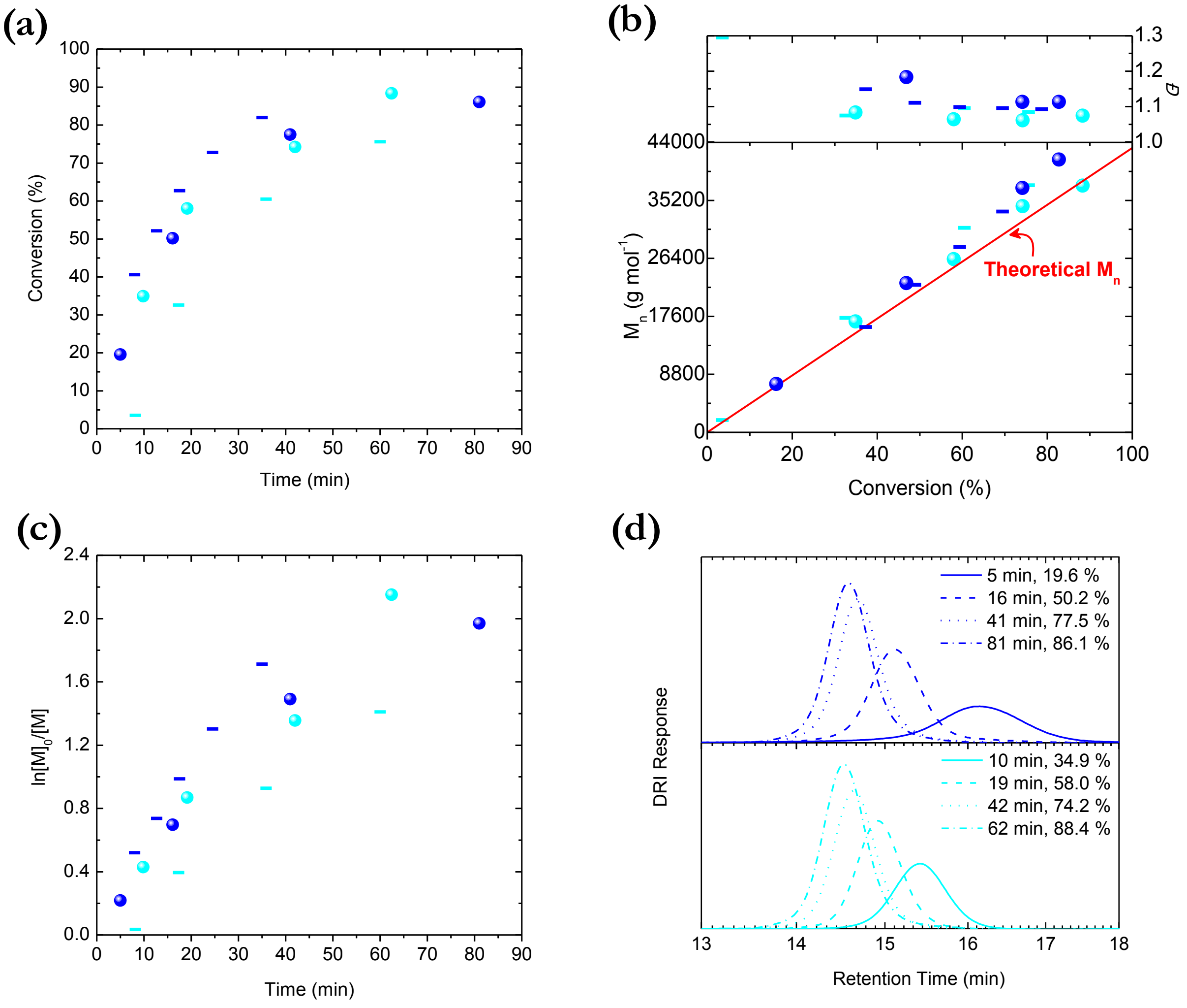


Figure S1 (a)–(d) Kinetic plots monitoring the polymerisation of MA by SET-LRP in DMSO in the absence (–) and presence (●) of 1 % (w/w) SiP-Br. The SEC traces shown in (d) correspond to the free polymers formed in the presence of initiator-functionalised silica nanoparticles. *Reaction Conditions*: [MA]:[EBiB]: [Me$_6$TREN] = 500:1.00:0.20, at M:S ratios of 2:1 (blue markers) and 2:1.5 (light teal markers) (v/v), 30 °C. Glacial acetic acid activated copper(0) wire.

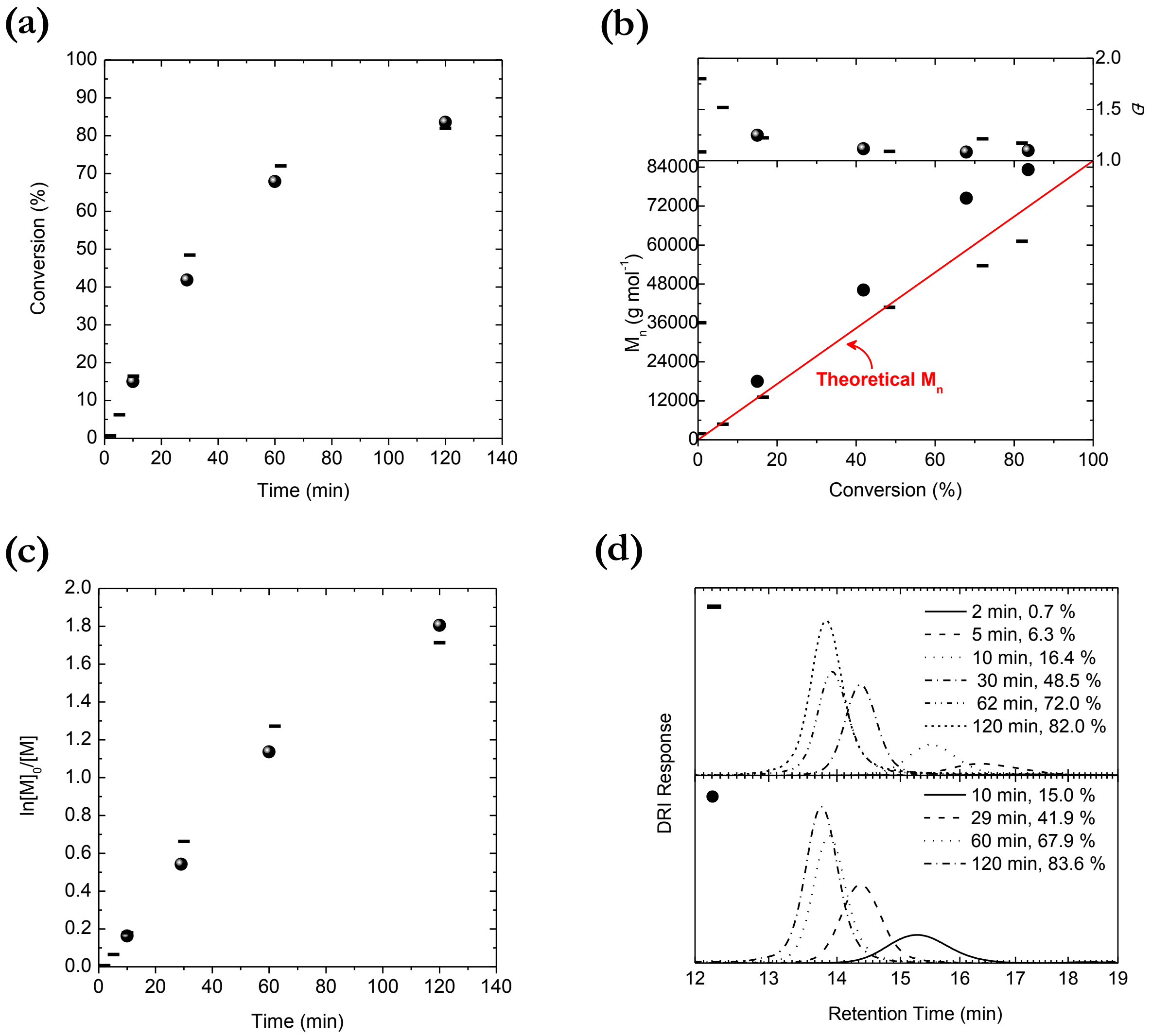


Figure S2 (a)–(d) Kinetic plots monitoring the polymerisation of MA by SET-LRP in DMSO in the absence (–) and presence (●) of 1 % (w/w) SiP-Br. The SEC traces shown in (d) correspond to the polymers formed in the absence (top) and presence (bottom) of initiator-functionalised silica nanoparticles. *Reaction Conditions*: [MA]:[EBiB]: [Me$_6$TREN] = 1000:1.00:0.20, MA = 4.0 mL, 1:1 v/v M:S, 30 °C. Glacial acetic acid activated copper(0) wire (6 cm, 1 mm diameter).

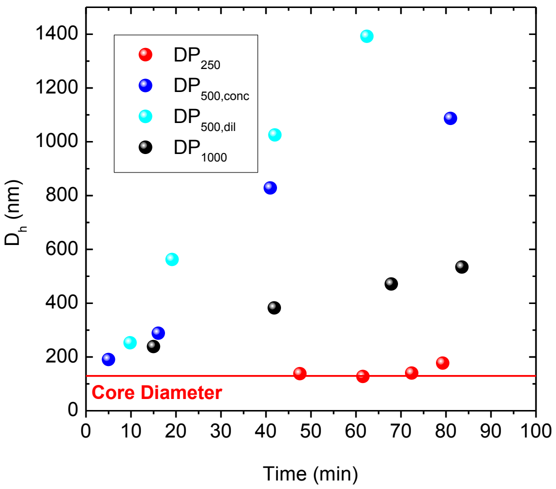


Figure S3 DLS results showing the average hydrodynamic diameter, D_h, of SiP-*g*-PMA with increasing monomer conversion targeting a DP_n of 250, 500, and 1000.

Thermal Gravimetric Analysis.

The grafting density (σ) (chains nm^{-2}) is calculated according to the following equation:

$$\sigma = \frac{\rho \cdot D \cdot N_A \cdot m_{organics}}{6 \cdot M_n \cdot m_{inorganics}} \tag{S1}$$

Where $\boldsymbol{\rho}$ and $\boldsymbol{D}$ are the density (1.9×10^{-21} g nm^{-3}) and diameter (130 nm) of the silica nanoparticle core respectively, $\boldsymbol{N_A}$ is Avogadro's number (6.022×10^{23} mol^{-1}), $\boldsymbol{M_n}$ is the number average molecular weight of the free polymer, $\boldsymbol{m_{organics}}$ and $\boldsymbol{m_{inorganics}}$ are the corrected weight percent of the organic and inorganic material obtained from the thermolysis of the material at 700 °C under an oxygen atmosphere.

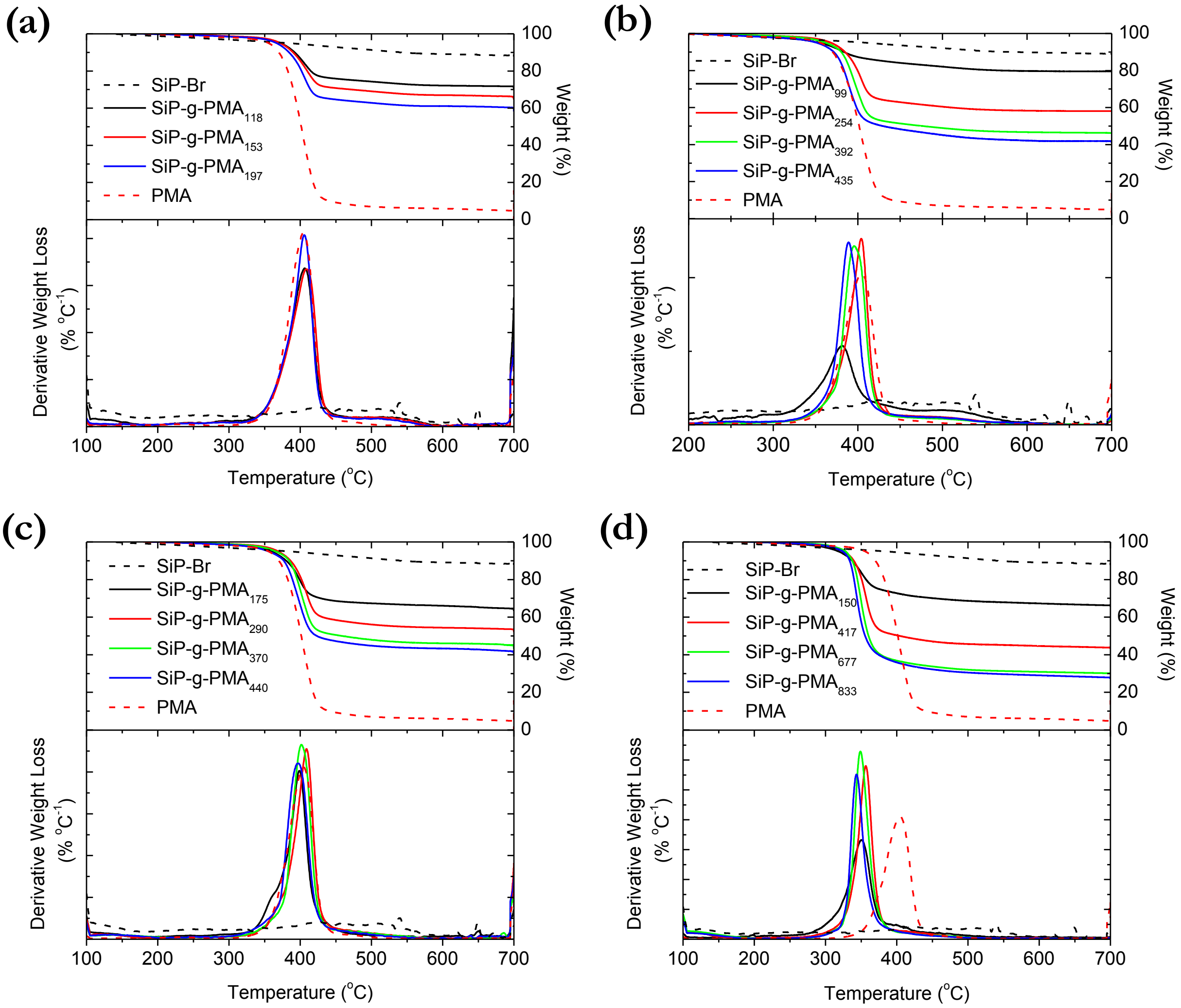


Figure S4 TGA and corresponding DTG curves of SiP-*g*-PMA with increasing monomer conversion (solid curves) in comparison to SiP-Br (broken black curve) and free PMA (broken red curve), targeting a *DP*$_n$ of 250 (a), 500 under concentrated (b) and dilute (c) conditions, and 1000 (d) monomer units.

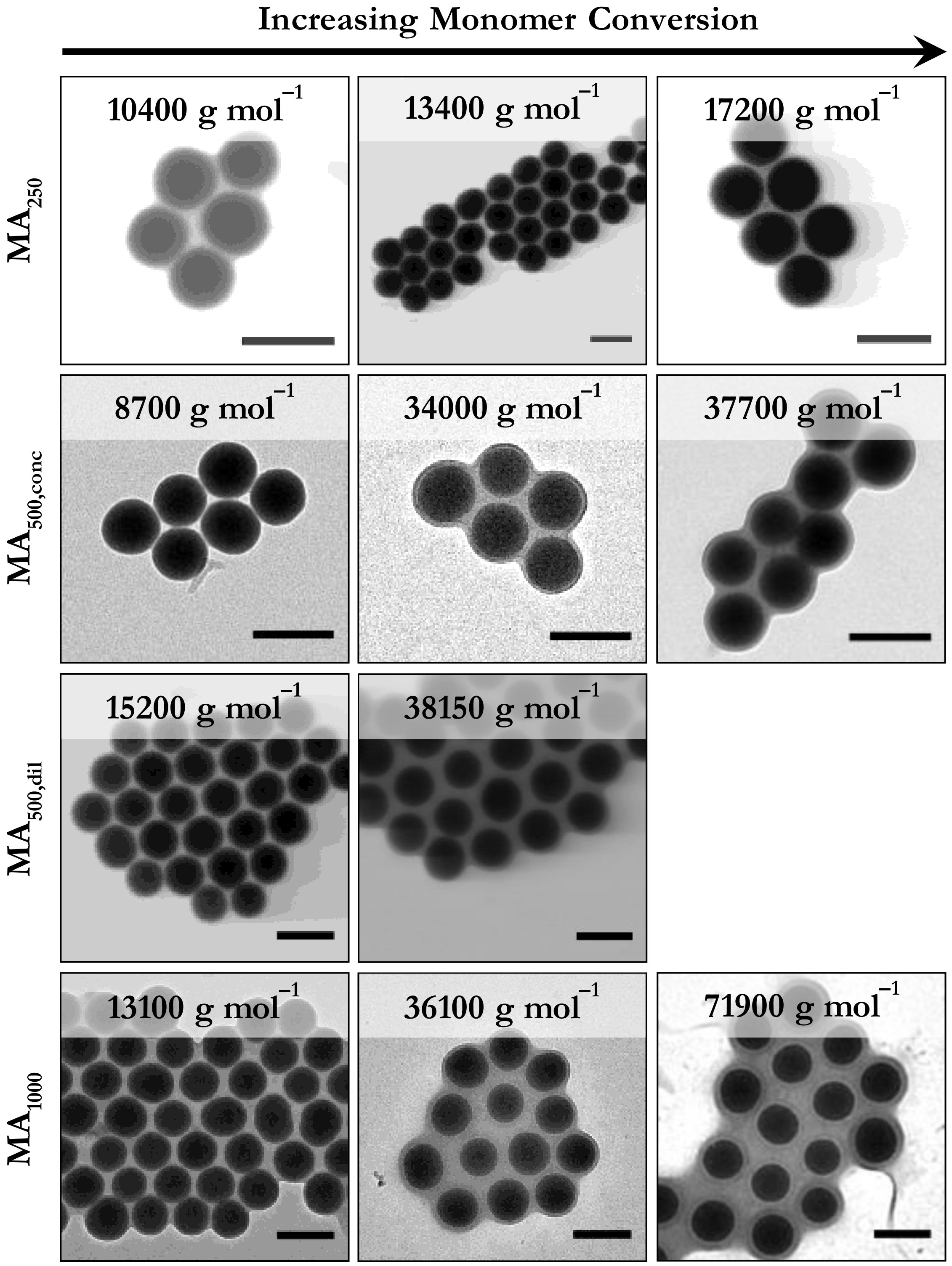


Figure S5 Electron micrographs of SiP-*g*-PMA in order of increasing monomer conversion, targeting a DP_n of 250, 500, and 1000 monomer units. $M_{n,free}$ is indicated on each micrograph. Scale bar represents 200 nm.

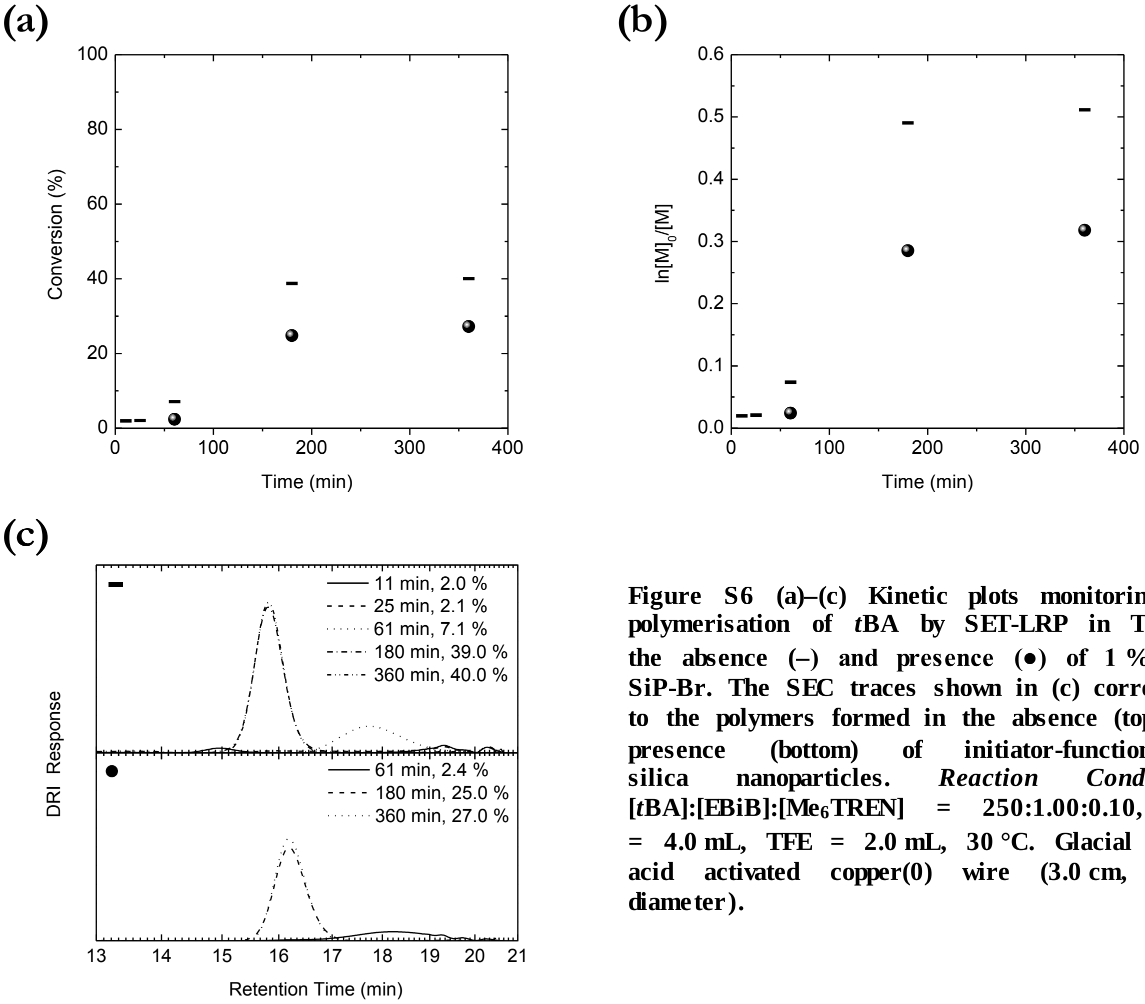


Figure S6 (a)–(c) Kinetic plots monitoring the polymerisation of *t*BA by SET-LRP in TFE in the absence (–) and presence (●) of 1 % (w/w) SiP-Br. The SEC traces shown in (c) correspond to the polymers formed in the absence (top) and presence (bottom) of initiator-functionalised silica nanoparticles. *Reaction Conditions*: [*t*BA]:[EBiB]:[Me_6TREN] = 250:1.00:0.10, *t*BA = 4.0 mL, TFE = 2.0 mL, 30 °C. Glacial acetic acid activated copper(0) wire (3.0 cm, 1 mm diameter).

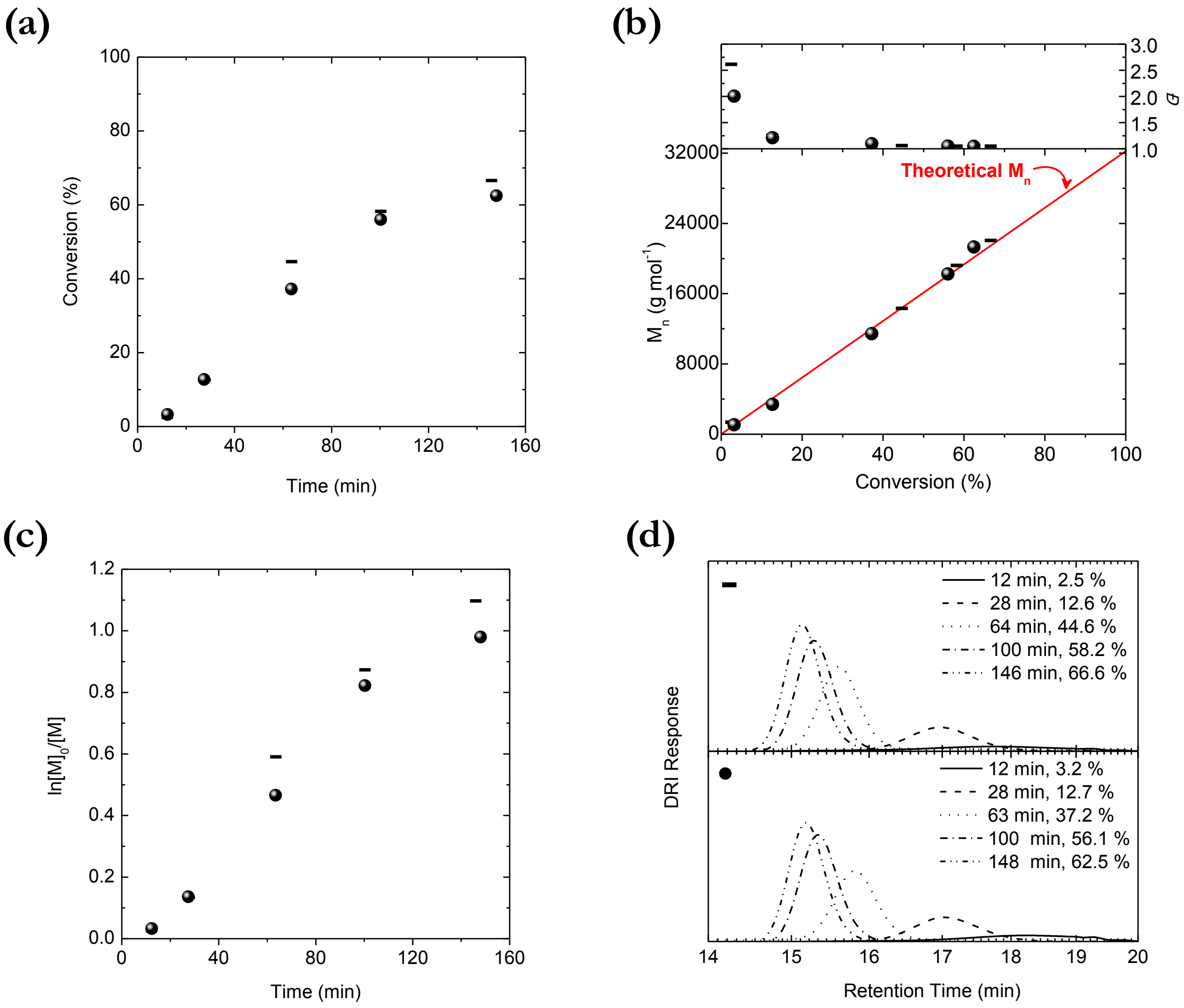


Figure S7 (a)–(d) Kinetic plots monitoring the polymerisation of *t*BA by SET-LRP in TFE in the absence (–) and presence (●) of 1 % (w/w) SiP-Br. The SEC traces shown in (d) correspond to the polymers formed in the absence (top) and presence (bottom) of initiator-functionalised silica nanoparticles. *Reaction Conditions*: [*t*BA]:[EBiB]:[Me$_6$TREN] = 250:1.00:0.10, *t*BA = 4.0 mL, TFE = 2.0 mL, 50 °C. Glacial acetic acid activated copper(0) wire (3.0 cm, 1 mm diameter).

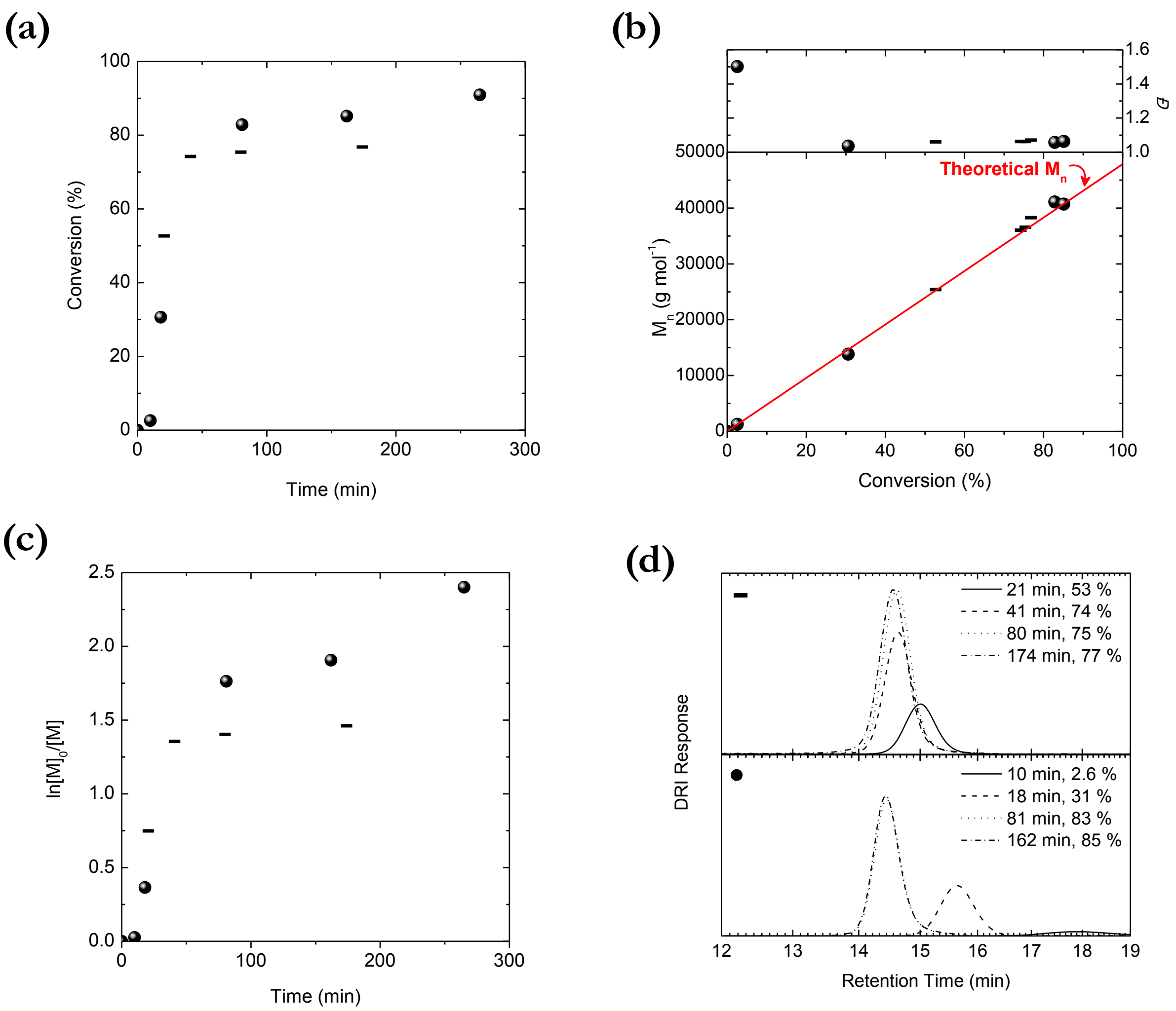


Figure S8 (a)–(d) Kinetic plots monitoring the polymerisation of *t*BA by SET-LRP in TFE in the absence (–) and presence (●) of 1 % (w/w) SiP-Br. The SEC traces shown in (d) correspond to the polymers formed in the absence (top) and presence (bottom) of initiator-functionalised silica nanoparticles. *Reaction Conditions*: [*t*BA]:[EBiB]: [Me_6TREN] = 370:1.00:0.33, *t*BA = 4.0 mL, TFE = 2.0 mL, 50 °C. Glacial acetic acid activated copper(0) wire (6.0 cm, 1 mm diameter).

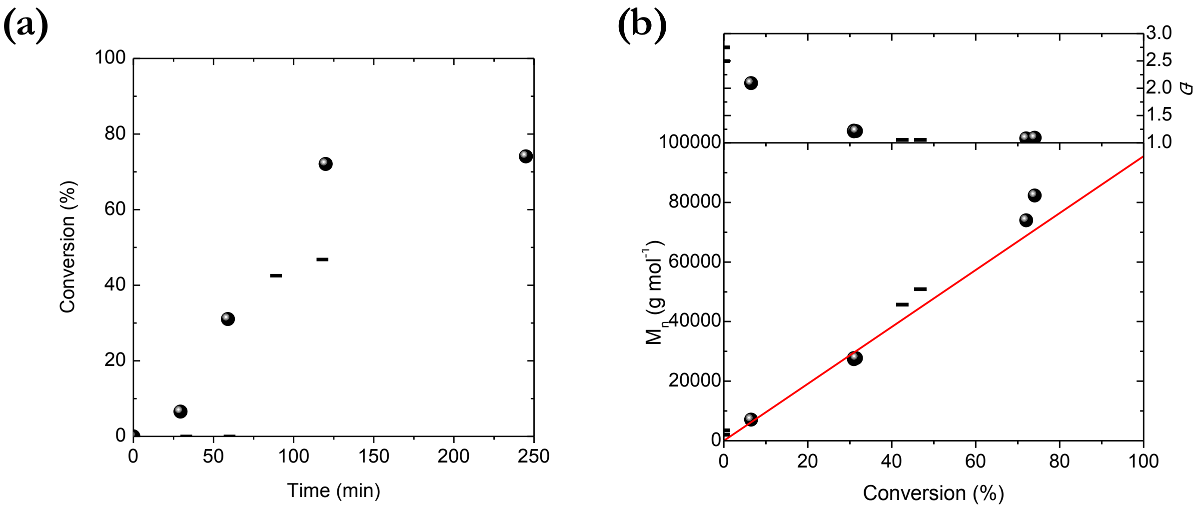


Figure S9 (a)–(b) Kinetic plots monitoring the polymerisation of *t*BA by SET-LRP in TFE in the absence (–) and presence (●) of 1 % (w/w) SiP-Br. *Reaction Conditions*: [*t*BA]:[EBiB]:[Me$_6$TREN] = 745:1.00:0.84, *t*BA = 4.0 mL, TFE = 2.0 mL, 50 °C. Glacial acetic acid activated copper(0) wire (4.0 cm, 1 mm diameter).

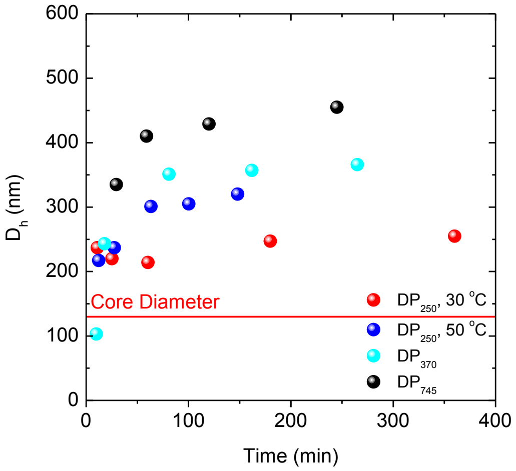


Figure S10 DLS results showing the average hydrodynamic diameter, D_h, of SiP-*g*-P*t*BA with increasing monomer conversion, targeting a DP_n of 250, 370, and 745 in comparison to the core diameter.

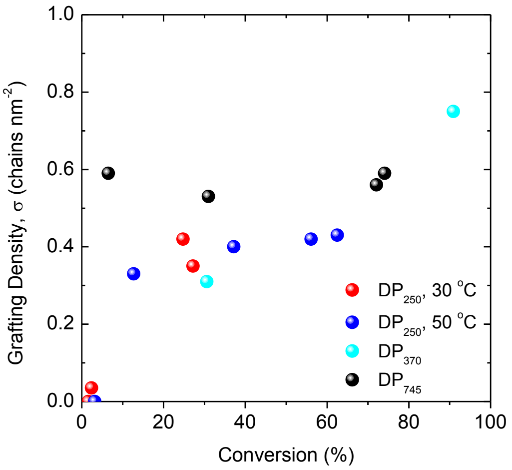


Figure S11 Evolution of grafting density with increasing monomer conversion targeting a degree of polymerisation of 250 at 30 °C (red markers) and 50 °C (blue markers), 370 (light teal markers), and 745 (black markers) monomer units.

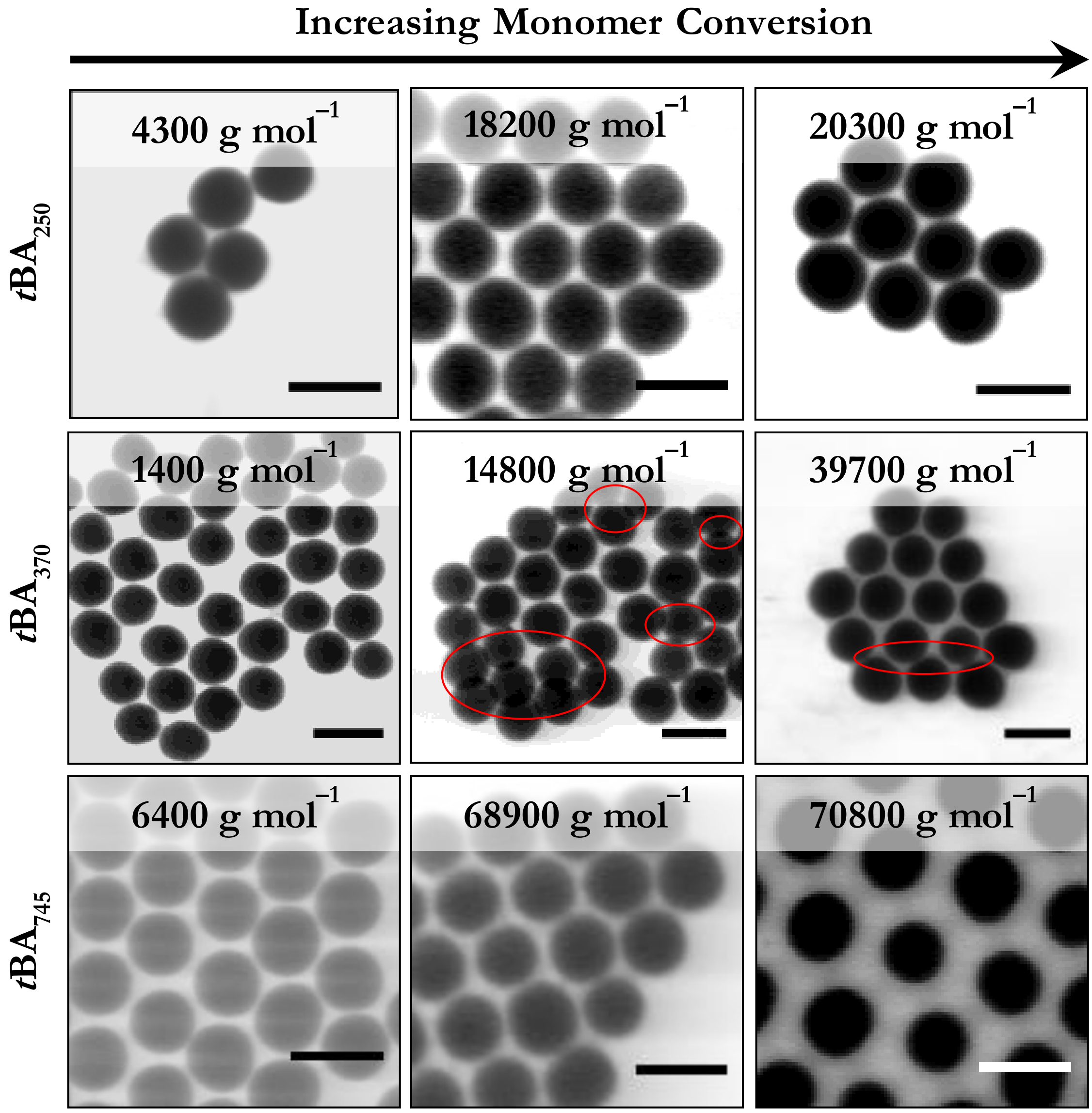


Figure S12 Electron micrographs of SiP-*g*-P*t*BA in order of increasing monomer conversion, targeting a DP_n of 250, 370, and 745 monomer units. $M_{n,free}$ is indicated on each micrograph. Evidence of crosslinking between particles is clearly indicated using red circles. Scale bar represents 200 nm.

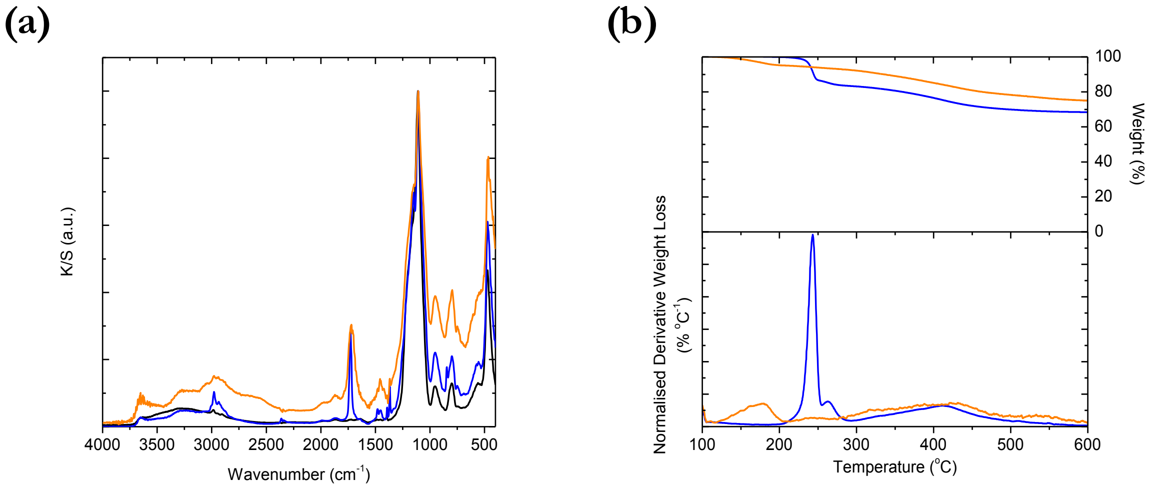
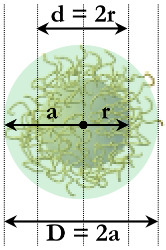


Figure S13 (a) DRIFTS spectra and (b) TGA chromatograms of SiP-Br (black curve) and P*t*BA-*grafted* silica nanoparticles before (blue curve) and after hydrolysis (orange curve) with TFA.

CORE–SHELL MODELLING TO DETERMINE SHELL THICKNESS



The compact core–shell model assumes the volume occupied by the polymer shell is equal to the volume occupied by a polymer of bulk density, and was used to determine the mean nearest neighbour distance, *D*, in nanometres.[1]

$$D = \left[\left(\frac{6d^2\sigma M_n}{N_A\rho}\right) + d^3\right]^{\frac{1}{3}} \tag{S2}$$

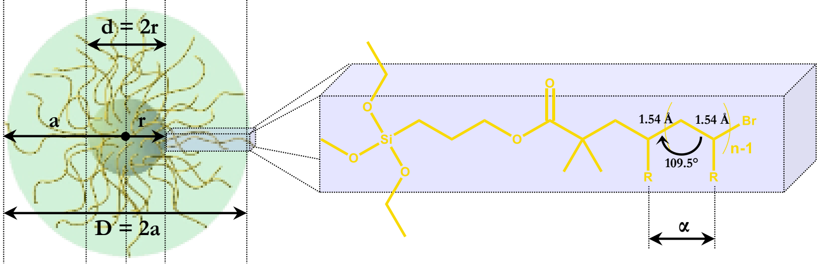
Where *d* is the core diameter (130 nm), M_n is the graft molecular weight (g mol^{-1}), σ is the surface grafting density (nm^{-2}), ρ is the bulk polymer density (g nm^{-3}), and N_A is Avogadro's Number (6.022 × 10^{23} mol^{-1}).

The mean nearest neighbour distance was then used to estimate the collapsed shell thickness, l, adopted in the dry state:

$$l = \frac{1}{2}(D - d) \tag{S3}$$

Where *D* is the particle diameter or mean nearest neighbour distance (nm) determined from the compact core–shell model, and *d* is the silica nanoparticle core diameter (130 nm).

The maximum particle size achievable when the polymer grafts are swollen was estimated using the fully-stretched or extended core–shell model.



This model assumes the polymer chains are radially stretched away from the silica core in an all-trans conformation such that the shell thickness is equal to the chain length.

$$l = \alpha \times DP_n \tag{S4}$$

The polymer chain length or shell thickness, l, was determined by taking the product of the length of one monomer unit, α, determined to be 0.252 nm using the cosine rule, and the degree of polymerisation, DP_n. The core–shell particle diameter, *D*, was then calculated in nanometres:

$$D = (2 \times l) + d \tag{S5}$$

Where l is the shell thickness (nm), and *d* is the silica nanoparticle core diameter (130 nm).

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[1] Morinaga, T., *et al.*, Two-dimensional ordered arrays of monodisperse silica particles grafted with concentrated polymer brushes. *Eur. Polym. J.* 2007, *43* (1), 243-248.