Supporting Information

for *RSC Advances*, DOI: 10.1039/ #####

Copolymers with acetyl-protected thiol pendant groups as highly efficient stabilizing agents for gold surfaces

Daniel González-Fernández, Mercedes Torneiro, M. Arturo López-Quintela and Massimo Lazzari*

Content:

1. Polymer synthesis and characterization

Kinetic studies and ^{1}H NMR

The time dependence of ln($[M]_0$/[M]) and the dependence of Mn and dispersity on the comonomer conversion for RC2 are shown in Figure S1, herewith considered as an illustrative example.

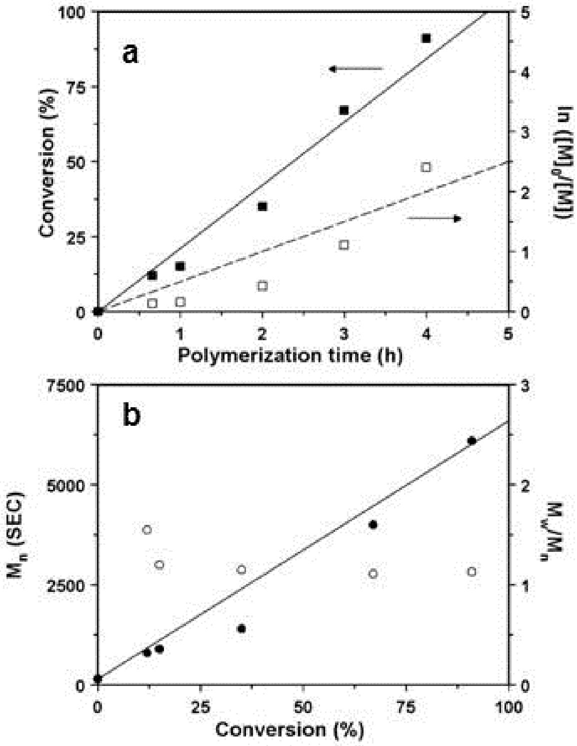


Figure S1. Time dependence of conversion (filled symbols) and ln($[M]_0$/[M]) (open symbols) (a) and conversion dependence of M_n (filled symbols) and dispersion (open symbols) (b) for the random copolymerization of VBTA and styrene (70/30) at 100ºC. Solid line in (b) indicates the theoretical value of molecular weight.

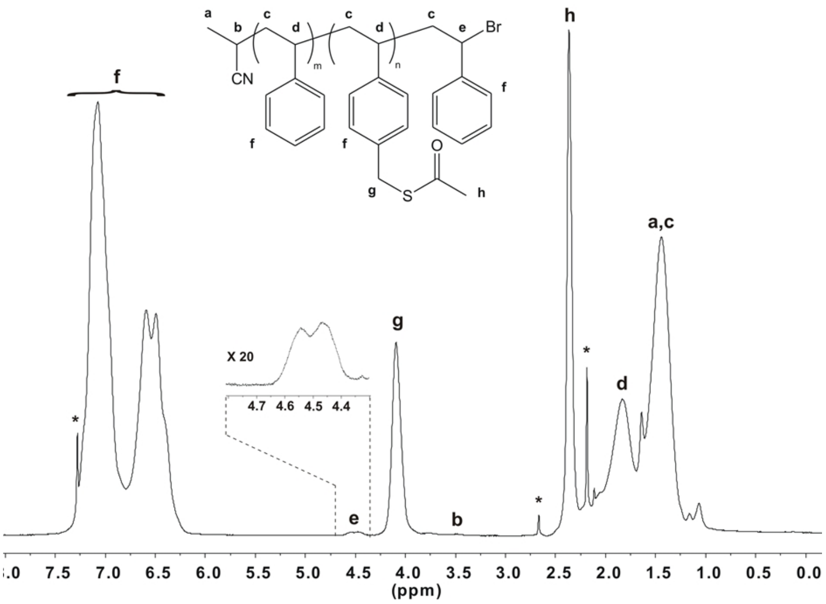


Figure S2. ^{1}H NMR spectrum of random copolymer **RC2**. In all the spectra it is worth pointing out the absence of unsaturated chain ends which may be formed by disproportionation, eventually responsible for signals at 6-6.2 ppm. Marks denote signals due to residual undeuterated solvent.

Block copolymer synthesis and characterization

Table S1. Experimental parameters for the block copolymerization from PS or PVBTA to VBTA or Sty, respectively, at 100ºC in bulk for 4 h, with $[\text{monomer}]_0/[\text{macroinitiator}]_0/[\text{CuBr}]_0/[\text{PMDTA}]_0$: 300/1/1/1.

Copolymer	Molar composition sty/VBTA^a	Yield^b [%]	$M_{n,\,th}$^{c} [KDa]	$M_{n,\,SEC}$^{d} [KDa]	D^d	$T_{g\,(exp)}$^{e} [ºC]
PS-*b*-PVBTA	67/33	10	12.1	9.9	1.18	51, 92
PVBTA-*b*-PS	69/31	17	9.7	10.5	1.12	58, 87

$^{a)}$ Determined by ^{1}H NMR; $^{b)}$ conversion as determined by gravimetry; $^{c)}$ $M_{n,th} = M_{macroinitiator} + (M_{monomer})\cdot[\text{monomer}]_0/[\text{macroinitiator}]_0\cdot(\text{conversion})$; $^{d)}$ polydispersity determined by SEC equipped with a RI detector against PS standards; $^{e)}$ determined by DSC.

DSC characterization enlightened the thermal and phase separation properties of the copolymers. In the case of the random copolymers, the values of glass transition temperature (T_g) may be strictly related to the copolymer composition and each monomeric unit makes a specific partial contribution to the glass transition in proportion to the T_g of the corresponding homopolymer and its weight fraction in the copolymer. In all the series the experimental values are very similar to those calculated on the basis of a direct additivity (Table 1). In contrast, the DSC traces of the block copolymers show two glass transitions (Table S1), denoting that the blocks are sufficiently long to exhibit mesophase segregation in the bulk material. Traces of PVBTA and PVBTA-*b*-PS are compared in Figure S3.

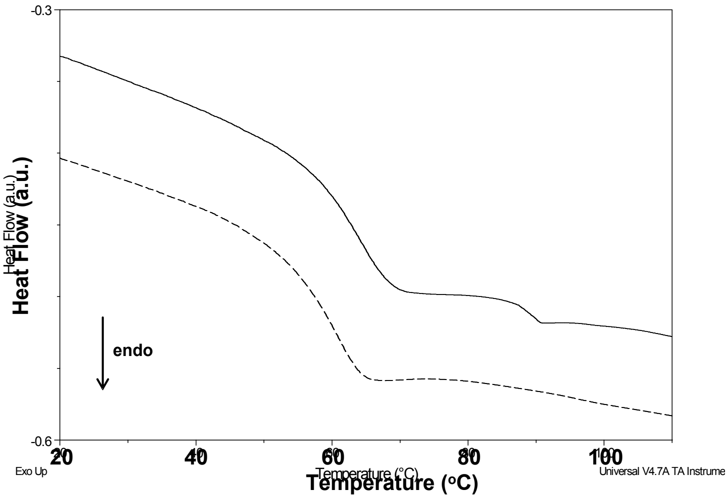


Figure S3. DSC traces of PVBTA-*b*-PS (solid line) and PVBTA (dashed line).

Deprotection of the copolymers

Although not necessary for this application, we also tested the feasibility of the post-polymerization deprotection of the VBTA-copolymers. The complete removal of the acetyl-protecting groups was demonstrated for RC1 as a model, upon treatment with $LiAlH_4$ in Et_2O.[4] The IR spectrum of the resulting deprotected polymer PS-*r*-PVPMT showed the disappearance of the carbonyl streching band at 1690 cm^{-1} and the presence of the characteristic weak band of the thiol group at 2565 cm^{-1} (Figure S4). Accordingly, the ^1H NMR showed the absence of the CO-CH_3 signal at around 2.3 ppm and the up-field displacement of the benzylic (CH_2-SH) signal. The high solubility of the PS-*r*-PVPMT in conventional organic solvents and in particular, the absence of any displacement or widening of the corresponding SEC traces suggests a negligible degree of cross-linking by disulfide bridges.

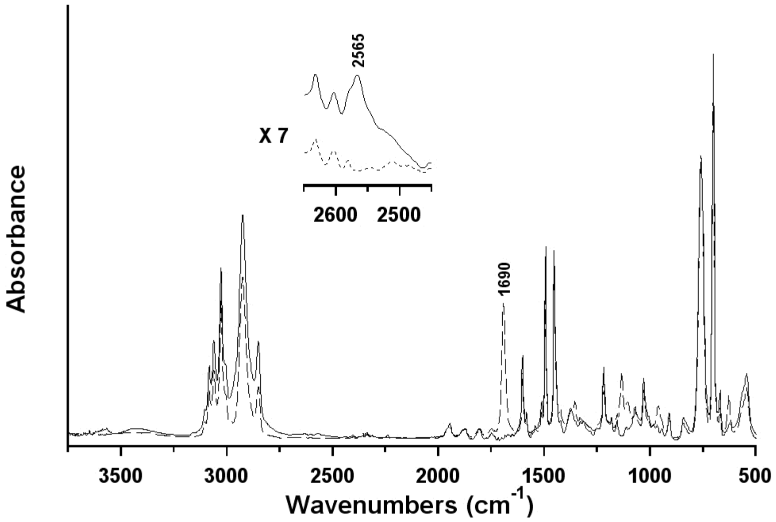


Figure S4. Comparison of the FTIR spectrum of PS-*r*-PVPMT (solid line) with that of **RC1** (dashed line).

Synthesis of gold nanoparticles

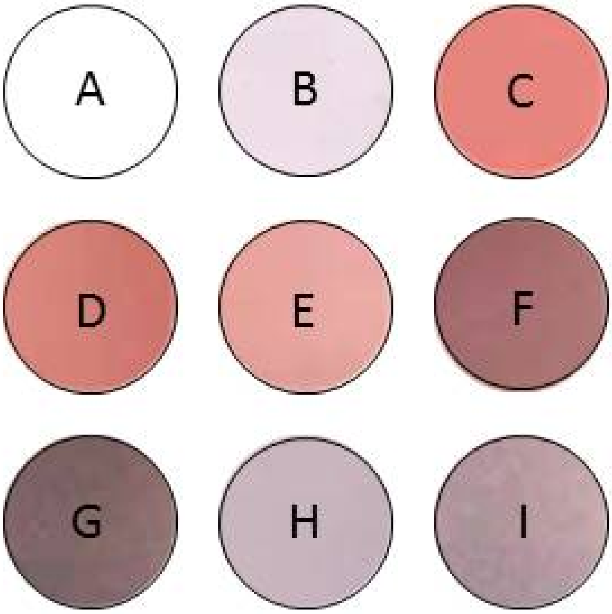


Figure S5. Optical images of gold solutions after 10 days, as reported in Table 2. Images were taken with a white background and refer to lateral views of the vials were the synthesis was carried out; please note that some solutions also showed partial precipitation of nanoparticles in form of dark aggregates, as detailed in the stability column of the table.

2. Experimental section

Materials and instrumentation

The following reagents, unless otherwise specified, were purchased from Sigma-Aldrich and used as received: 4-vinylbenzyl chloride (90%, with 500 ppm *tert*-butylcatechol as inhibitor), potassium thioacetate (KSAc, 98%), styrene (Sty, 99%), N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA, 99%), Cu^IBr (98%), 2-bromopropionitrile (BPN, 97%), hydrochloric acid (37%), lithium aluminum hydride (95%), hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥99.5%), sodium borohydride (98%), N,N-dimethylformamide (DMF, 99.8%), hexane (98%), ethyl acetate (EtOAc, 99.7%), diethyl ether (Et_2O, 99.8%), chloroform (99.8%), methanol (Fluka), 2-propanol (99.8%), tetrahydrofuran (THF, Fluka), deuterated chloroform (99.8% atom D).

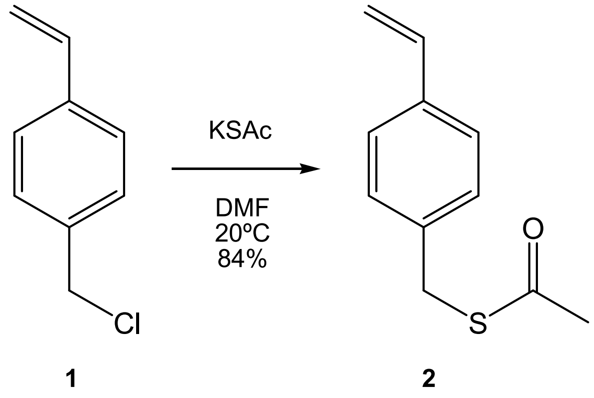
Dry Et_2O was distilled under argon from Na/benzophenone immediately prior to use. Organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated using rotary evaporator at aspirator pressure (20-30 mm Hg). The reaction for preparation of monomer **2** was monitored by thin-layer chromatography using aluminium-backed MERCK 60 silica gel plates (0.2 mm thickness). After visualization under ultraviolet light at 254 nm, the plates were developed by immersion in a solution containing a solution of ceric ammonium nitrate (0.5 g) and ammonium molybdate (4.8 g) in H_2O (100 mL) and H_2SO_4 (5.6 mL) followed by heating with a hot gun. Flash column chromatography was performed with Merck silica gel (230-400 mesh).

NMR spectra were recorded in $CDCl_3$ on either a Bruker DPX 250 MHz at room temperature (monomer characterization) or a Bruker AMX 500 MHz at 50ºC (polymer characterization). Chemical shifts are reported on the δ scale (ppm) downfield from tetramethylsilane ($\delta = 0.0$ ppm) using the residual solvent signal at $\delta = 7.26$ ppm (^1H, $CDCl_3$) as internal standard; coupling constants (J) are reported in Hz. Size exclusion chromatography (SEC) was performed by using a PL-GPC 50 (Agilent) apparatus equipped with a MIXED E column (3 μm, 7.5 x 300 mm) with a nominal exclusion limit of 30000 g/mol and a high resolution for low molecular weights. Sample solutions, approximately 0.1% (w/v) concentration, were prepared in THF (stabilized with 200 ppm 2,6-dibutyl-4-methylphenol), which was also used as eluent at a flow rate of 1 mL min^{-1}, at 40ºC. A refractive index detector was used and column calibration was performed with PS narrow distribution standards and a third-order polynomial equation was obtained from regression analysis.

Infrared (IR) spectra were recorded on a Thermo Nicolet FTIR 6700 instrument at 4 cm^{-1} resolution. The samples in the form of thin films were casted from chloroform solutions onto KBr windows. Spectroscopic acquisition and data treatment were performed using Omnic version 6.1 (Thermo Nicolet). Differential scanning calorimetry (DSC) analyses were carried out with a Q200 (TA Instruments) calorimeter equipped with a refrigerated cooling system in the temperature range from 20 to 120ºC, with a scanning rate of 20ºC min^{-1} and under nitrogen atmosphere. UV-visible spectra were measured with a diode array Hewlett-Packard HP8452 spectrophotometer. The samples were placed in a 1 cm x 1 cm x 3 cm quartz cuvette and spectra recorded at room temperature. TEM was performed with a Philips CM-12 microscope operated at an accelerating voltage of 100 kV. Samples were prepared by dropping a dispersion of the particles on carbon coated copper grids. The low contrast, especially in the case of the higher magnification images, is possibly due to the polymer-coating of the nanoparticles. Particle diameters were determined using ImageJ software to analyze at least 4 TEM images for each sample. Particle size distribution and the average particle diameters were obtained by measuring between 1000 and 6000 particles. Dynamic light scattering (DLS) measurements were performed with a Zetasizer Nano ZS (Malvern UK) equipped with a 4 mW HeNe laser, using a 1 cm optical path cell; solutions was filtered by using Millipore Fluoropore (FHLP 0.45 μm) filters, and each sample was analyzed three times.

Synthesis of [S-(4-vinylbenzyl) thioacetate, VBTA]

The protected thiol derivative of styrene **2** [S-4-(vinylbenzyl) thioacetate, VBTA] was obtained by nucleophilic substitution from 4-vinylbenzyl chloride, **1** (Scheme S1).



Scheme S1. Synthesis of the thioacetate-protected thiol (VBTA)

Following a modified procedure by Wulff et al.,[1] 4-vinylbenzyl chloride (8.0 mL, 56.8 mmol) was added to a solution of potassium thioacetate (10.1 g, 88.6 mmol) in DMF (50 mL) and the reaction mixture was stirred for 1 h. Brine (10 mL) was added and the mixture was extracted with hexanes (10 x 10 mL). The combined organic phase was dried, filtered and concentrated. The residue was purified by column chromatography (SiO_2, 5 x 15 cm, 4% EtOAc and 96% hexanes mixture) to provide **2** as a pale yellow oil [9,16 g, 84%, Rf= 0.7 (20% EtOAc and 80% hexanes mixture)]. ^1H NMR ($CDCl_3$, 250 mHz): 7.15 (2H, d, *J*= 8.2 Hz), 7.05 (2H, d, *J*= 8.2 Hz), 6.50 (1H, dd, *J*=17.5 and 10.9 Hz), 5.55 (1H, d, *J*=17.5 Hz), 5.05 (1H, d, *J*= 10.9 Hz), 3.92 (2H, s), 2.13 (3H, s). Density: 1.11 g/mL.

Polymerization

Although the thioacetate may be easily deprotected to generate the thiol,[2] the expected significant transfer in the polymerization of thiol-containing monomers through the selected polymerization method, i.e. ATRP,[3] and the eventual crosslinking of thiol groups during the synthesis,[4] forced to directly use VBTA as monomer, in case performing the deprotection onto the polymer. In a typical random copolymerization, i.e. Table 1 entry RC2, 4 mL of styrene (34.9 mmol), 2.6 mL of VBTA (15 mmol), 0.21 mL of PMDETA (1.01 mmol) and 144 mg of CuBr (1.00 mmol) were added to flame-dried 25 mL Schlenk, maintaining an overpressure of dry nitrogen. After four freeze/pump/thaw cycles, 90 μL of BPN (1.01 mmol) were added to the frozen mixture and the flask finally placed in a silicon oil bath at 100ºC for 4 h. At the end, 10 mL of chloroform were added to dissolve the reaction mixture and the polymer was precipitated into a large excess of a 75% methanol and 25% propanol mixture. The polymer was filtered, washed several times with methanol and water, dissolved in chloroform and precipitated again, repeating the washing procedure. The polymer was finally dried under vacuum to constant weight. In the case of chain extension to prepare block copolymers, 1 mmol of the purified polymeric macroinitiator was dissolved in 300 mmol of the corresponding comonomer previously to the addition to flame-dried 25 mL Schlenk. A procedure similar to those used for a typical random copolymerization was then applied to perform block copolymerization.

Deprotection of RC1 to prepare polystyrene-*random*-poly-S-4-(vinylphenyl) methanethiol (PS-*r*-PVPMT)

A solution of **RC1** (500 mg) in dry Et_2O (20 mL) was slowly added *via cannula* to a suspension of $LiAlH_4$ (500 mg) in dry Et_2O (45 mL) and the mixture was stirred for 22 h under argon. The reaction was quenched by the addition of EtOH (55 mL) and the resulting mixture was washed with a solution of HCl (1M, 100 mL) and water (3 x 10 mL). The combined organic phase was dried, filtered, concentrated and dried *in vacuo* to afford PS-*r*-PVPMT as a white solid (0.391 mg, >79% yield). ^{1}H NMR ($CDCl_3$, 250 mHz): 7.1-6.4 (aromatic H), 4.5-4.4 (terminal PhC*H*-Br), 3.5 (CH_2-S), 2.0-1.7 (PhC*H*), 1.7-1.3 ppm: (PhCH_2).

Preparation of gold nanoparticles

In a typical synthesis, 20 mL of the random copolymer solution in DMF (0.01, 0.1 or 1 mM) and 50 μL of a freshly prepared 0.1 M aqueous solution of $HAuCl_4$ (pH=2) were added to a 25 mL vial. After 20 min stirring, 50 μL of a freshly prepared 1 M aqueous solution of $NaBH_4$ were added under stirring. UV-vis spectra and DLS measurements were recorded after further 20 minutes at room temperature.

3. References and notes

1 Removal of thioacetate groups in polymers prepared by radical polymerization of 2 with styrene and/or divinylbenzene was previously carried out by reduction with diborane (G. Wulff and I. Schulze, *Isr. J. Chem.* 1978, **17**, 291-297) or with $NaBH_4$-$AlCl_3$ in diglyme (G. Wulff and I. Schulze, *Angew. Chem.* 1978, **90**, 568-570).

2 P.A. Bobbio, *J. Org. Chem.* 1961, **26**, 3023-3024.

3 W.A. Braunecker and K. Matyjaszewski, *Prog. Polym. Sci.* 2007, **32**, 93-146.

4 N.V. Tsarevsky and K. Matyjaszewski, *Macromolecules* 2002, **35**, 9009-9014.