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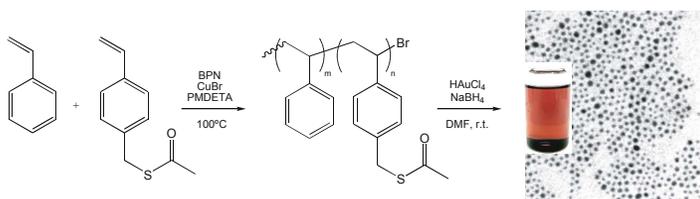
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Copolymers with acetyl-protected thiol pendant groups as highly efficient stabilizing agents for gold surfaces

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We showed the potential of novel multifunctional-sulfur containing polymers as model ligands for the preparation of sub-5 nm gold nanoparticles.



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

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Multifunctional-sulfur containing homo-, block and random copolymers with modulable number of noble metal affine groups were efficiently prepared by atom transfer radical polymerization of S-(4-vinylbenzyl) thioacetate, in case with styrene. Their potential as model ligands for stabilization of sub-5 nm noble metal nanoparticles is demonstrated through the one-step fabrication of well-controlled stable gold dispersions, in spite of working with gold precursor to ligand concentration ratio much lower than those typically used in the presence of more traditional mono-functional terminated polymers.

The use of polymers as a tool for the preparation of nanomaterials strictly depends on their functionalities, and any approach that introduces new functional group transformations or protection/deprotection protocols is expected to improve the potential of tailoring material properties.¹⁻³ Controlled radical polymerization methods and, in lesser extent, anionic polymerization are powerful means to control chain-end and side-chain functionalities, often in combination with more or less traditional techniques (from nucleophilic substitution reactions to click chemistry).⁴⁻⁶ As a matter of fact post-polymerization modification opened the way to polymers which cannot be prepared by direct polymerization of the functional monomer due to limited group tolerance.⁷

In the framework of an inclusive project aiming to develop novel hybrid nanomaterials resulting from the controlled arrangement of nanoparticles in (block co)polymers,⁸⁻¹¹ herein we focus on the

preparation of polymers containing functional groups with high affinity for noble metal surfaces, and more specifically of molecules bearing protected thiol functionalities. Even though it is well known that thiol-containing, and more generally, sulfur-containing molecules may potentially be used not only in the field of device fabrication, in molecular electronics or in sensors and biosensors^{12,13} (often in form of self-assembled monolayers),¹⁴ but also for stabilization of noble metal nanoparticles against aggregation,^{15,16} most of such uses are based on chains containing only terminal functional groups. On the other hand, synthesis and applications of multifunctional sulfur-containing compounds in nanotechnology are less common, in part due to a more complex synthetic route and also to their tendency to undergo rapid oxidative coupling. Polymers bearing pendant protected thiol groups may be prepared by two main approaches: i) radical addition of thiols to polymeric alkenes, usually 1,2-polybutadiene, through the so-called thiol-ene coupling^{7,17} or ii) polymerization of monomers containing protected thiol groups by, e.g., traditional radical polymerization¹⁸ or nitroxide-mediated radical polymerization¹⁹ Polymers prepared by the first approach are usually thought as intermediates to create different functional polymers,²⁰ whereas the interest for the second route is usually related to the easy manipulation by deprotection and redox control between thiol and disulfide to provide tunable cross-linked polymer aggregates.¹⁹

Protected thiol derivatives of styrene and especially S-(4-vinylbenzyl) thioacetate (VBTA) were already used to prepare styrenic polymers by traditional radical polymerization,²¹⁻²³ but in this work VBTA is subjected for the first time to atom transfer radical polymerization (ATRP) to produce homopolymer, random and block copolymers with styrene. The potential of these polymers to act as stabilizing agents for noble metal nanoparticles is preliminary illustrated with the fabrication of fairly monodisperse gold nanoparticles. Notwithstanding a number of groups have investigated monofunctional polymers as stabilizing ligands for gold nanoparticles, the studies reporting the formation of well-defined particles with dimensions below 5 nm were based on thiol or thioether terminated polymers, with the best results in terms of monodispersity actually obtained by employing dithiol and tetrathiol-terminated chains.^{24,25} In such sense, the polymers here reported, containing different and controlled amount of pendant gold-affine groups may be considered as model ligands, which allow

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producing gold dispersions in one step, with good control over particle size distributions for very low polymer concentration. Additionally, although for such application the thioacetate head groups are expected to adsorb to gold as thiolates,²⁶ we also developed a post-polymerization deprotection protocol to obtain polymers bearing a controlled amount of pendant thiol groups (details are reported in the Supporting Information).

The potential of VBTA for the preparation of well-defined (co)polymers with controlled molecular weight, narrow molecular weight distribution and controlled amount of pendant thiol groups, was verified through copper-mediated ATRP in bulk, and its behavior was compared with that of styrene. Detailed monomer and polymers synthetic methods and characterizations are reported in the Supporting Information. As far as we know, controlled polymerization of VBTA was not reported previously, but the weak electron-withdrawing effect of ethyl thioacetate on the aromatic ring predict a successful polymerization in any of the conditions already reported for styrene or other styrene derivatives.²⁷⁻²⁹ The idea of taking advantage of the properties of pendant thioacetate groups has also been recently explored through the preparation of methacrylic copolymers by ATRP.^{30,31}

Copolymerization of VBTA with styrene was carried out in bulk at 100°C using CuBr/PMDETA as catalytic system and BPN as initiator. A total monomers to initiator equivalents of 50/1 was maintained for all the series of three random copolymers, RC1-3, and the corresponding poly(S-4-(vinylbenzyl) thioacetate) (PVBTA) (details are provided in Table 1). Notwithstanding the atom transfer equilibrium should, in principle, be shifted toward the active species side by the VBTA unit with respect to bare styrene, very similar values of conversion after 4 h copolymerization suggest a limited stabilizing effect by the thioacetate. On the other side, the lower conversion observed for VBTA homopolymerization may be related to physical effects, i.e. the observed fast increase of viscosity of the reaction medium with respect to the case of styrene homopolymerization.

As for very high conversion values the composition of the

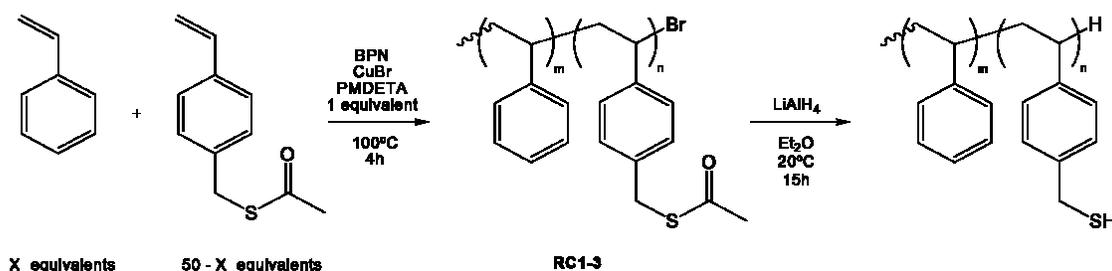
copolymers equals those of the feed composition, we also carried out kinetic studies with the purpose to get more information on both the polymerization fashion (Figure S1) and monomer reactivity. An almost linear relationship between logarithmic monomer conversion index ($\ln [M]_0/[M]$) and the polymerization time, the increase of the copolymer molecular weight with the conversion that matches the theoretical one, and narrow molecular weight distributions (as those visible in the SEC traces shown in Figure 1a) assess a good control of the polymerization, with an overall behavior of VBTA very similar to that reported for styrene polymerization.²⁷ Also ¹H NMR detection of high amount of bromo-end groups at around 4.5 ppm (> 80% in all cases) confirmed that termination by-products are formed in small amounts and, in any case, not continuously during polymerization. ¹H NMR spectrum of RC2 is shown in Figure S2. With respect to the relative reactivity of comonomers, the molar ratio of VBTA units incorporated into the copolymer (determined by ¹H NMR) with respect to reaction time decreases from the initial 47 mol % after 1 h down to 40 (2 h) and finally 30 mol % after 4 h reaction, thus matching the molar composition of the comonomer feed. Even though the reactivity ratios were not quantified, the initial copolymer composition moderately enriched with VBTA finally indicate a little higher reactivity ratio of this unit with respect to styrene.

Due to the living character of all the polymeric products, either the PVBTA with bromo-chain ends or the reference ω -bromo PS could be used as macroinitiators for the preparation of PS/PVBTA block copolymers. Copolymerization was initiated by ternary systems constituted of the macroinitiator, CuBr and PMDETA dissolved in the corresponding comonomer, using a 300/1 monomer to initiator ratio. The effective formation of PS-*b*-PVBTA and PVBTA-*b*-PS copolymers was verified by a combination of SEC, and ¹H NMR and FTIR spectroscopies. Spectra of the PS-*b*-PVBTA were consistent with the expected structures, in particular, new peaks are visible at around 4 (CH_2 -S) and 2.15 ppm (CO- CH_3) in the ¹H NMR spectra, and at 1690 cm^{-1} (carbonyl thioacetate stretching) in the FTIR spectra. On the other side, the addition of styrene to

Tab. 1 Experimental parameters for the 4 h polymerization in bulk of styrene and/or VBTA at 100°C, with $[BPN]_0/[CuBr]_0/[PMDETA]_0$: 1/1/1.

(Co)polymer	Sty/VBTA ^a [equivalents]	Molar composition sty/VBTA ^b	Yield ^c [%]	$M_{n,th}$ ^d [KDa]	$M_{n,SEC}$ ^e [KDa]	D^e	$T_g^{(exp)}$ ^f [°C]	$T_g^{(th)}$ ^g [°C]
RC1 ^h	45/5	90/10	95	5.4	5.5	1.07	82	85
RC2 ^h	35/15	70/30	91	5.9	6.1	1.13	72	76
RC3 ^h	25/25	52/48	96	6.9	7.2	1.15	65	68
PS	100/0	100/0	74	7.4	6.4	1.04	91	-
PVBTA	0/50	0/100	54	5.9	4.4	1.27	56	-

^a) With respect to the initiator equivalents; ^b) determined by ¹H NMR; ^c) conversion as determined by gravimetry; ^d) $M_{n,th} = M_{BPN} + (M_{sty} \cdot \chi_{sty} + M_{VBTA} \cdot \chi_{VBTA}) \cdot [Sty + VBTA]_0 / [BPN]_0 \cdot (\text{conversion})$; χ = initial molar fraction; ^e) polydispersity determined by SEC equipped with a RI detector against PS standards; ^f) Determined by DSC; ^g) calculated on the basis of the weight composition assuming the additive contribution of the T_g of the corresponding homopolymers (Fox relation); ^h) reaction's scheme for the random copolymers, RC1-3 as follows (X= 45, 35 or 25), also showing the deprotection of the VBTA units to form thiol-containing polymers:



PVBTA do not entail the appearance of new significant signals in both types of spectroscopies, exactly because entering comonomer moiety is very similar to that of its derivative; indeed also the diblock copolymer compositions were calculated from the ratio of the methyl group of the thioacetate to the aliphatic protons of the main chain from both monomeric units (Table S1). As an example, a typical evolution of the SEC traces, relative to the copolymerization from PS to VBTA is shown in Figure 1b, where monomodal distributions and a shift of the peak toward lower retention time after 4 h reaction confirm an efficient chain extension.

The possibility of using such polymers as protecting agents for noble metal surfaces was explored through the fabrication of gold nanoparticles. A series of syntheses were performed in DMF through the reduction of the gold precursor (0.25 mM) by the addition of a

freshly prepared solution of sodium borohydride, in the presence of 4 different PBVTA-containing polymers, herewith considered as model stabilizing agents (experimental parameters and details of synthesis are reported in Table 2 and in the Supporting Information, respectively).

FTIR analysis of the resulting polymer/nanoparticle hybrid composites showed the disappearance of the carbonyl thioacetate stretching band, suggesting that the acetyl group is lost as a consequence of nanoparticle formation and growth due to covalent attachment of the sulfur atoms to the gold surface (reasonably in form of thiolates).²⁶ Although a partial thioacetate deprotection may, in principle, not be excluded, it is worth pointing out that the polymers treated under a similar reducing system, i.e. in the presence of low sodium borohydride concentration for short times, did not show any significant structural changes.

Color of the colloidal solutions and corresponding UV-vis spectra (examples in Figure 2a; UV-vis maximum in Table 2) are significantly different from each other, revealing the formation of particles of different dimensions and stability. Position and intensity of the broad plasmon absorption bands, with maximum between 510 and around 580 nm, are strongly dependent on the particle sizes and their distributions, and seem to indicate the presence of particles at least bigger than 10 nm.^{32,33} On the other hand, TEM images such as those shown in Figure 2b-e revealed narrow average size distributions in the range 2-5 nm (estimation of size distribution were obtained from much larger and representative areas and are summarized in Table 2), thus implying that broadening of the bands and red-shifting from the expected 510-520 nm of the maxima for individual spherical S-capped particles to the observed values may be related to the multidentate nature of the stabilizing agent.

It is important to note that nanoparticles were synthesized in the presence of two diverse polymer concentrations (0.01 and 0.1 mM, with the exception of RC3 with which 1 mM was also used) but, due to different compositions, the amount of groups that may interact with gold is variable and also the ratio between thioacetate and gold concentration, R , should be taken into account when discussing colloid formation. First of all, a minimum value of R , i.e. $R \geq 0.55$ (for RC2), is necessary to form a stable dispersion, whereas a further increase entails the formation of smaller and smaller nanoparticles. The effect of polymer molecular weight may be neglected for the series of random copolymers but in the case of the homopolymeric ligand the use of shorter molecules induced the formation of particles bigger than those stabilized by random copolymers, independently on the ligand concentration. This effect is the opposite

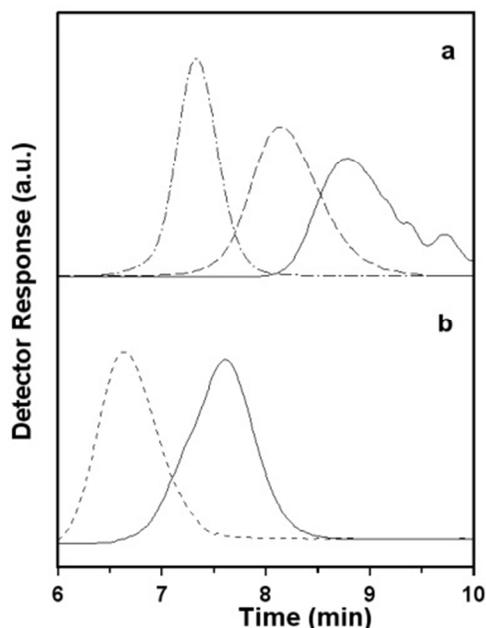


Fig. 1 Evolution of the SEC curves of the random copolymers of VBTA and styrene (70/30) (a) obtained after 1 h (solid line), 2 h (dashed line) and 4 h (RC2, dash-dotted line) polymerization at 100°C, and overlay (b) of PVBTA (solid line) and PVBTA-*b*-PS curves (dashed line).

Tab. 2 Experimental parameters for the synthesis of gold nanoparticles in DMF at room temperature, using HAuCl₄ (gold precursor, 0.25 mM), NaBH₄ (reducing agent, 2.5 mM) and PBVTA-containing polymers as stabilizing agents.

Sample	Polymer	[Polymer] [mM]	R^a	UV-Vis max ^b [nm]	NP diameter ^c [nm]	Aggregate diameter ^d [nm]	Stability ^e
A	RC1	0.01	0.19	582	-	-	< 1 h
B	RC1	0.1	1.9	580	-	-	< 1 h
C	RC2	0.01	0.55	540	-	> 200	10 h
D	RC2	0.1	5.5	548	3.9±0.9	> 200	100 h
E	RC3	0.01	1.8	552	3.8±0.6	> 200	16 h
F	RC3	0.1	18	528	3.5±0.7	> 200	> 1 year
G	RC3	1	178	510	2.9±0.8	6	> 1 year
H	PVBTA	0.01	1.8	542	5.5±1.0	> 200	16 h
I	PVBTA	0.1	18	526	4.8±0.9	15, > 100	> 1 year

^{a)} Molar ratio of sulfur containing units to gold ions; ^{b)} maximum of the plasmon absorption band as determined by UV-vis spectroscopy;

^{c)} Determined by TEM; ^{d)} determined by DLS; approximate values refer to broad distributions; ^{e)} approximate time of partial precipitation of nanoparticles in form of dark aggregates.

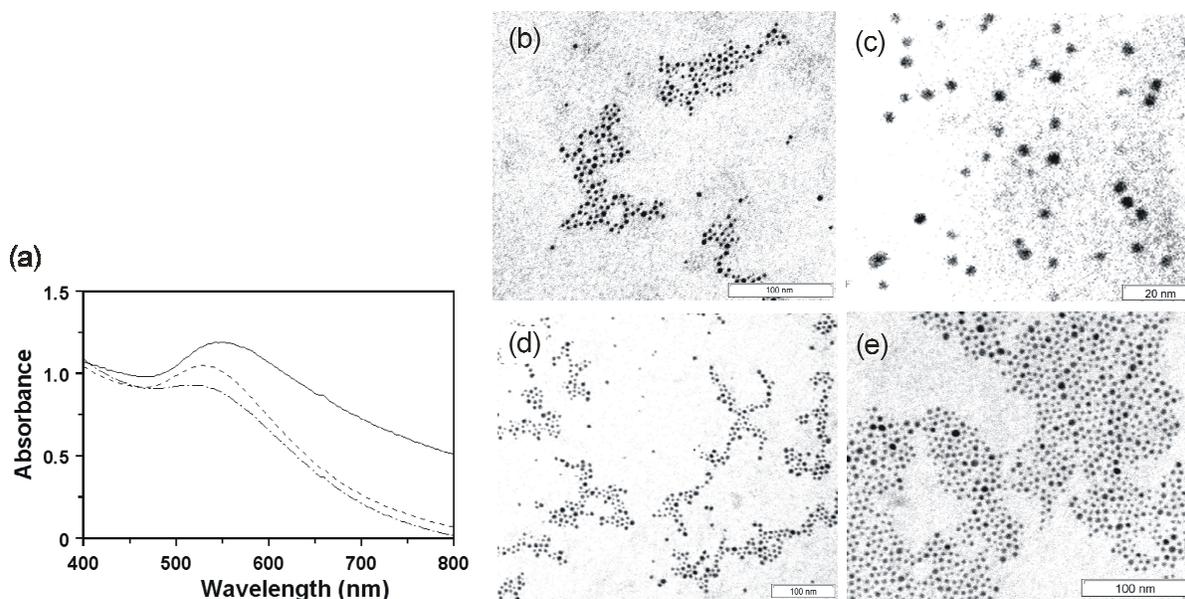


Fig. 2 UV-vis spectra of RC3-stabilized gold nanoparticles obtained with polymer concentration of 0.01 (solid line), 0.1 (dashed line) and 1 mM (dash-dotted line) (a), and TEM images of gold-nanoparticles stabilized with RC3 0.01 (b) and 0.1 mM (c), and PVBTA 0.01 (d) and 0.1 mM (e).

of that observed for thiol-terminated stabilizers, where smaller nanoparticles are produced with lower molecular weight polymers,²⁵ and is possibly due to adjacent binding sulfur functionalities that are less efficient than in random copolymers where they are intercalated with neutral units, i.e. styrene repetitive units. On the other hand, it is also worth noticing that in the random copolymer with just few sulfur containing units (RC1, with around 5 VBTA per molecule), their stabilizing effect is possibly partially shielded by the presence of longer styrene sequences.

With respect to the unexpected position and shape of the UV-vis absorption bands, it is well known that surface plasmon resonance in metallic nanoparticles is drastically changed if they are densely packed, so that the individual particles are electronically coupled to each other.³⁴ When particles come into close proximity to one another, electromagnetic coupling of clusters becomes effective for particle-to-particle distances smaller than five times the particle radius and increasingly important at smaller distances. Aggregation has the effect of causing a coupling of the nanoparticle's plasma modes, which results in a red shift and broadening of the longitudinal plasma resonance of effectively isolated particles. In the case of our system, it may be inferred that multiparticle aggregates are formed in the reaction medium, as also supported by the DLS measurements summarized in Table 2. Size of aggregates and corresponding red-shift would depend on the molecular weight, concentration and multidenticity of the polymeric stabilizers. Differently from monofunctional stabilizing agents, any molecule of these VBTA-based polymers, having a theoretical chain length of tens of nanometers and a number of gold-affine groups that depends on the polymer composition, may bind to more than one nanoparticle at the same time. Low VBTA content and low polymer concentration favor the formation of bigger aggregates which display plasma absorption bands with a significant red-shift with respect to those of isolated nanoparticles, and shortly become unstable with flocculation of nanoparticles in form of a dark precipitate (Table 2). On the other side, either the availability of increasing amount of stabilizer and higher content of gold affine groups affect not only the dimension of the synthesized nanoparticles but also reduce the

tendency of macromolecules to participate to the process of formation and stabilization of several particles at the same time, i.e. the tendency to form multiparticle aggregates. As an example, in the case of the gold reduction in the presence of RC3 (i.e. the copolymer with the highest VBTA content) an increase in the polymer concentration from 0.01 to 1 mM (entries E, F and G in Table 2) corresponds to a decrease in the absorption maximum from 552 to 510 nm, eventually associated to a decrease of aggregate dimension down to almost isolated nanoparticles.

Conclusions and outlook

An acetyl protected-thiol derivative of styrene, VBTA, could be efficiently synthesized from 4-vinylbenzyl chloride, and corresponding homo- and copolymers with styrene were obtained by ATRP with a good control over dispersity. We displayed the potential of such novel multifunctional polymers as a tool for the preparation of nanomaterials. Specifically, we showed that multifunctional stabilizing agents afford the preparation of gold nanocolloids with a good control over particle size, at least as good as those obtained in the presence of monofunctional thiol- or alkylthioether-terminated polymers,^{11,24,25} in spite of working with similar gold precursor concentration, i.e. 0.25 mM, and polymer concentration as low as 0.01 mM, possibly as a consequence of the multifunctionality of the polymeric ligands. In particular, stable and dimensionally uniform sub-5 nm gold colloids used as modifiers for block copolymers nanocomposites¹¹ could be prepared in the presence of thiol-terminated polystyrenes (molecular weights between 2.8 and 17.5 KDa) only at polymer concentration higher than 0.1 mM and gold precursor concentration 0.24 mM.³⁵

In addition, the preparation of block copolymers which exhibits a mesophase separation with molecular weight as low as around 10000 will also open the way to the preparation of block copolymer/metal nanoparticles composites with controlled localization of nanoparticles through the reduction in situ of

noble metal precursors with high affinity for one of the blocks.¹¹

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