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Dithioesters and Trithiocarbonates as Anchoring Groups for the “Grafting-To” Approach

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Reversible addition fragmentation chain transfer (RAFT) polymerization is an extremely versatile, controlled radical polymerization technique that is becoming increasingly popular due to its tolerance toward functional monomers, enabling the synthesis of a vast range of (co)polymers. RAFT operates via a degenerative transfer mechanism in which a thiocarbonylthio compound acts as a chain transfer agent (CTA).[1,2] As a consequence of the mechanism, polymers prepared by this technique bear a dithioester end group or a trithiocarbonate group in the middle of the chain according to the type of CTA used. Polymers produced by RAFT are thus highly interesting for the functionalization of metal, and in particular gold, surfaces via the “grafting-to” approach. Up to now, the reported procedures to modify gold surfaces with RAFT polymers involve the prior transformation of the sulfur-containing group coming from the CTA into thiols by reaction with nucleophiles such as primary amines.[3−6] However, this step is incompatible with some polymers due to the reactivity of the main chain (e.g., poly(acrylic acid) or polymers bearing activated esters) and restricts thus the range of application. Moreover, it has been shown that it is rather difficult to selectively obtain thiols by this procedure and that disulfides are often formed, resulting from the coupling between two thiol-functionalized polymer chains.[7−9] In this paper we show for the first time that the prior transformation of dithioesters and trithiocarbonates into thiols is not mandatory for the functionalization of metal surfaces, these two species being able to chemisorb onto gold.

Preparation of monolayers based on a sulfur−Au bond has been extensively investigated,[10] including the use of thiols,[11] disulfides,[12] sulfides,[13] thiophene,[14] thiocarboxylic acids,[15] dithiocarboxylic acids,[16] xanthates,[17] thiocarbamates,[18] and dithiocarbamates.[19] However, to the best of our knowledge, the chemisorption of dithioesters and trithiocarbonates onto gold has never been reported.

We have prepared monolayers of two different CTA—benzyl dithiobenzoate (BDTB) and dibenzyl trithiocarbonate (DBTTC)—by immersing gold substrates into dilute solutions of these CTA for 4 h, followed by copious rinsing with pure solvent (see Supporting Information for more details). The monolayers were then characterized by X-ray photoelectron spectroscopy (XPS). Figure 1 shows the S 2p spectra recorded on monolayers of BDTB and DBTTC. Only one peak is observed on the spectrum of BDTB, indicating that both sulfur atoms experience the same chemical environment. Moreover, the location of this peak, around 162 eV, is in very good agreement with the value reported in the literature for chemisorbed dithiocarboxylic acid on gold.[16] These two observations demonstrate that BDTB is chemisorbed with both sulfurs attached to the gold substrate, as represented in Scheme 1. For DBTTC, the peak is clearly broader (much broader than the resolution of 1.5 eV), and the reconstruction of the spectrum evidences the presence of two doublets in a 2:1 ratio located around 162 and 163.5 eV. The binding energy and the width of the most intense doublet are identical to those observed for BDTB and is therefore associated with chemisorbed sulfurs. The minor doublet, located at 163.5 eV, is associated with the sulfur of the C−S bond not interacting with the gold substrate. Its binding energy is indeed in very good agreement with the values reported for a C−S bond in bulk compounds.[20] These observations evidence the chemisorption of DBTTC in a configuration where two of three sulfur atoms interact with the gold substrate, as shown in Scheme 1. This bridged configuration is reminiscent of the one found for xanthates and dithiocarbamates where only the two sulfur atoms are chelating gold.[17,19] This is likely due to geometrical constraints.

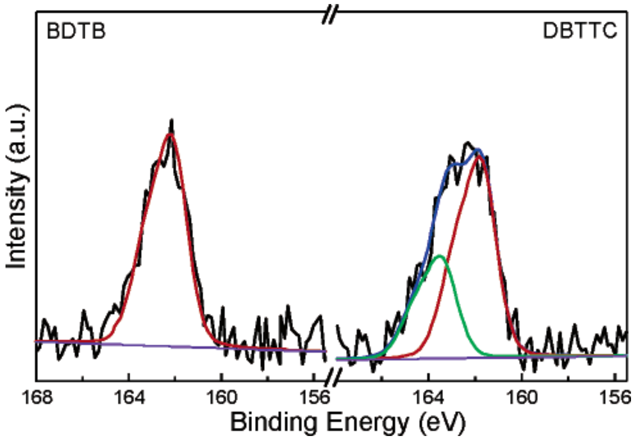
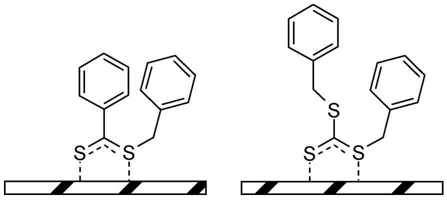


Figure 1. S 2p XPS spectra recorded on layers of BDTB and of DBTTC on gold. The red and green lines are the envelopes of doublets used to fit the spectra (see Supporting Information for details).

Scheme 1. Chemisorption Configuration of the BDTB (Left) and of the DBTTC (Right)



To further evidence the chemisorption of dithioesters and trithiocarbonates and their utility as anchoring groups in the “grafting-to” approach, we have prepared polymer brushes on gold substrates, using polystyrene made by RAFT with the two CTA. The brushes were prepared by immersing gold substrates into PS solutions in toluene for 24 h followed by careful rinsing with toluene. These samples were then characterized by AFM-based force spectroscopy, steric forces being a well-known characteristic of polymer brushes.[21−24] Figure 2 shows the approach profile obtained in toluene between a bare silicon nitride tip and a layer of the PS prepared from BDTB. The monotonically increasing repulsive forces, which are typical of

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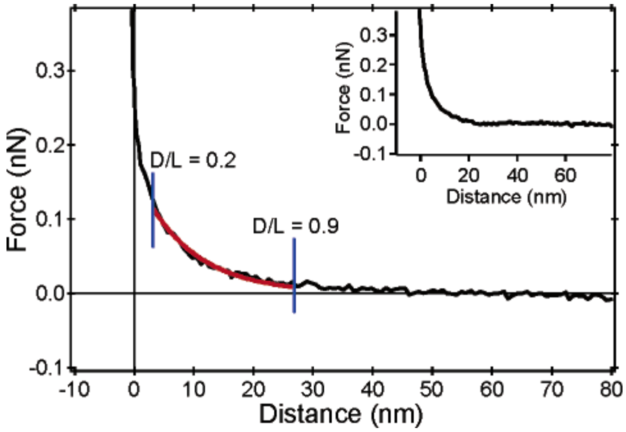

Figure 2. Approach profile of a force curve obtained in toluene between a bare silicon nitride tip and a layer of the PS, prepared from BDTB, on gold. The red line is a fit of the compression profile by a function based on the Alexander–de Gennes model, in the distance range for which the model is valid. Inset: corresponding retraction curve showing that the profile is reversible.

a polymer brush under compression in a good solvent,[21] are caused by the reduced configurational entropy of the polymer chains which increases osmotic pressure upon approach of the surface.[22] This is an indication that the polymer films behave like a brush. The force profile can be represented by a function based on the Alexander–de Gennes scaling concept,[23] describing the forces resulting from the compression of polymer brushes. The Alexander–de Gennes model provides a good approximation for the calculation of the steric repulsion for moderate grafting densities (typically between 0.1 and 5 chains/100 nm^2)[21,24] but fails to describe the behavior of very dense brushes (above 5 chains/100 nm^2).[25] The force per unit area between an AFM tip and a surface coated with a polymer brush can be approximated by the following exponential expression, for $0.2 < D/L < 0.9$:[24]

$$F(D) \approx 50 k_B T \Gamma^{3/2} e^{-2\pi D/L} \tag{1}$$

where D is the distance between the two surfaces, L is the thickness of the polymer brush, and Γ is the grafting density (m^{-2}). From this function, the grafting density can be estimated, as illustrated in ref 24 and references therein. To test whether the measured forces decay as predicted, the region of the force profiles corresponding to $0.2 < D/L < 0.9$ was fitted by an exponentially decaying function:

$$F(D) = \alpha e^{-D/z} \tag{2}$$

where the amplitude α and the decay length z are the fitting parameters (Figure 2, red curve). A grafting density of 1.3 ± 0.3 chains per 100 nm^2 has been estimated from this equation. That corresponds to a typical distance between grafting sites of 8.8 nm. Only one exponential was required to fit the approach profiles, indicating that the chains are firmly attached to the surface and laterally immobile (solid brush). Liquid brushes which can diffuse on the surface often show more than one decaying component, characteristic of an escape transition occurring in the brush.[24] The complete reversibility of the profile is also a characteristic of terminally attached brushes. Physisorbed polymers often display a hysteresis between compression and decompression due to nonequilibrium relaxation effects.[21] Similar force profiles were obtained for the PS prepared from DBTTC. A grafting density of 0.66 ± 0.3 chain per 100 nm^2, which corresponds to a typical distance between grafting sites of 12 nm, was estimated. For both samples, the chains are in the brush regime. Indeed, the Flory radius can be calculated from the following equation:[23]

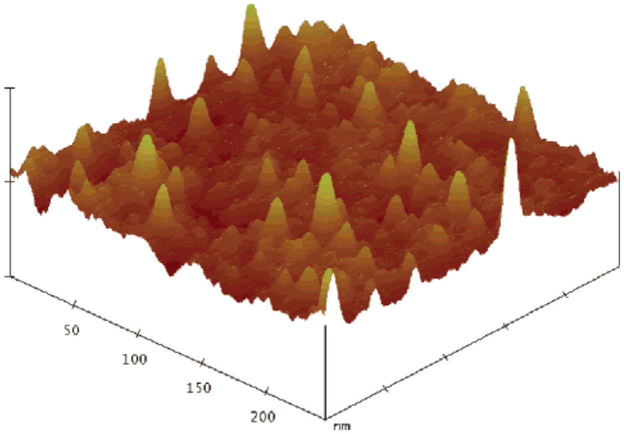

Figure 3. AFM topography image of a PS brush in the dry state prepared from BDTB on an atomically flat terrace of gold on mica (tapping mode in air, maximum z scale: 3 nm).

$$R_F \approx a N^{3/5} \tag{3}$$

where a is the statistical segment length and N the degree of polymerization of a chain. For PS made from BDTB ($N = 346$), $R_F \cong 22$ nm, and for PS made from DBTTC (N of one arm $= 149$), $R_F \cong 13$ nm. The diameter of the coils is thus larger than the distance between grafting points, indicating that we are indeed in the brush regime. Figure 3 shows an AFM topography image recorded in air in tapping mode on a PS brush prepared from BDTB on an atomically flat terrace of gold on mica. This picture shows "pinned micelles", typical of a brush in its collapsed state.[26]

In conclusion, we have demonstrated that polymers synthesized by RAFT with dithioesters or trithiocarbonates as CTA can be used directly to prepare brushes on gold surfaces, without prior transformation of these moieties into thiols. This simplifies the conventional approach, broadens the range of applications, and especially opens the way to surfaces functionalized with reactive polymers of high interest such as poly(N-succinimidyl acrylate) or poly(pentafluorophenyl acrylate) in a one-step approach.

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Supporting Information Available: Synthesis details and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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