



# Grafting of polymeric platforms on gold by combining the diazonium salt chemistry and the photoiniferter method



Randa Ahmad<sup>a</sup>, Adrien Mocaer<sup>a</sup>, Sarra Gam-Derouich<sup>a</sup>, Aazdine Lamouri<sup>a</sup>,  
Hélène Lecoq<sup>a</sup>, Philippe Decorse<sup>a</sup>, Philippe Brunet<sup>b</sup>, Claire Mangeney<sup>a,\*</sup>

<sup>a</sup> Univ Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 15 rue J-A de Baïf, 75205 Paris Cedex 13, France

<sup>b</sup> Univ Paris Diderot, Sorbonne Paris Cité, MSC, UMR 7057 CNRS, 10 rue Alice Domon et Léonie Duquet, 75205 Paris Cedex 13, France

## ARTICLE INFO

### Article history:

Received 17 September 2014

Received in revised form

5 December 2014

Accepted 8 December 2014

Available online 13 December 2014

### Keywords:

Diazonium salts

Iniferter polymerization

Gold nanoparticles

## ABSTRACT

The grafting of stable and strongly attached polymeric platforms on gold is a key factor for successful applications in biology, catalysis and sensing. Here, we report on the use of a combination of the iniferter method and the diazonium salt chemistry for preparing smart polymeric platforms attached through covalent bonds on gold. For this, bifunctional molecules bearing aryl diazonium coupling agents for anchoring on gold and *N,N*-diethyldithiocarbamate groups for initiating the growth of polymer chains were used. These two moieties were separated by oligo(ethylene oxide) spacers of various lengths allowing a fine tuning of the hydrophilic properties of the grafted photoinitiator layers. Cross-linked copolymers of methacrylic acid (MAA) and *N,N'*-methylenebisacrylamide (MBAm) were then grown from the gold surfaces under UV light. The polymer films were characterized in terms of chemical composition and wettability by X-ray photoelectron spectroscopy and contact angle measurements, respectively. The grafting procedure was simple, rapid and effective in producing polymer-grafted Au surfaces at room temperature. The diethyldithiocarbamil groups remaining at the end of the growing tethered chains could then be easily exchanged by a UV-light induced radical-exchange experiment in order to obtain terminal amino moieties able to immobilize citrate-capped gold nanoparticles, through electrostatic interactions. The results obtained in the present work highlight the efficiency of the diazonium salt chemistry coupled to the photo-iniferter based surface grafting approach to spontaneously functionalize gold surfaces through covalent bonds. This strategy opens new opportunities for the preparation of “smart” hybrid platforms made of pH-responsive polymers and nanoparticle assemblies.

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## 1. Introduction

Surface-initiated polymerization (SIP) on gold has received an increasing interest these recent years because gold surfaces are compatible with a large range of analytical techniques (SPR [1–3], electrochemistry [4], SERS [5]) and present unique properties at nanoscale. The use of photochemically activated initiators is especially convenient for grafting polymers to gold surfaces, since the

process can readily be controlled and confined by the selective application of long wavelength UV light. Dithiocarbamate species, introduced as photoinitiators (or iniferter: initiator-transfer-terminator agents) by Otsu [6–8], have the peculiarity of cleaving upon UV irradiation, forming a radical pair constituted by a reactive carbon radical that initiates the polymerization and a less reactive, sulfur-centered radical that can act as a reversible capping agent during the polymerization process. This polymerization process addresses a wide range of economical and ecological concerns, compared to corresponding thermal reactions, with low cost and mild reaction conditions. Conventionally, the universal platform for grafting iniferters on gold is based on the self-assembly of thiol [9–12] or disulfide [13,14] molecules. However, the UV-initiated polymerization from SAMs on Au is considered as a difficult task because of the instability of the thiol–Au bond upon UV irradiation [15]. To overcome this limitation, Benetti et al. [13] proposed to use

*Abbreviations:* XPS, X-ray photoelectron spectroscopy; SEM, scanning electron microscopy; CA, contact angles; MAA, methacrylic acid; *N,N'*-methylenebisacrylamide, MBAm.

\* Corresponding author. Tel.: +33 1 57276878; fax: +33 01 57277263.

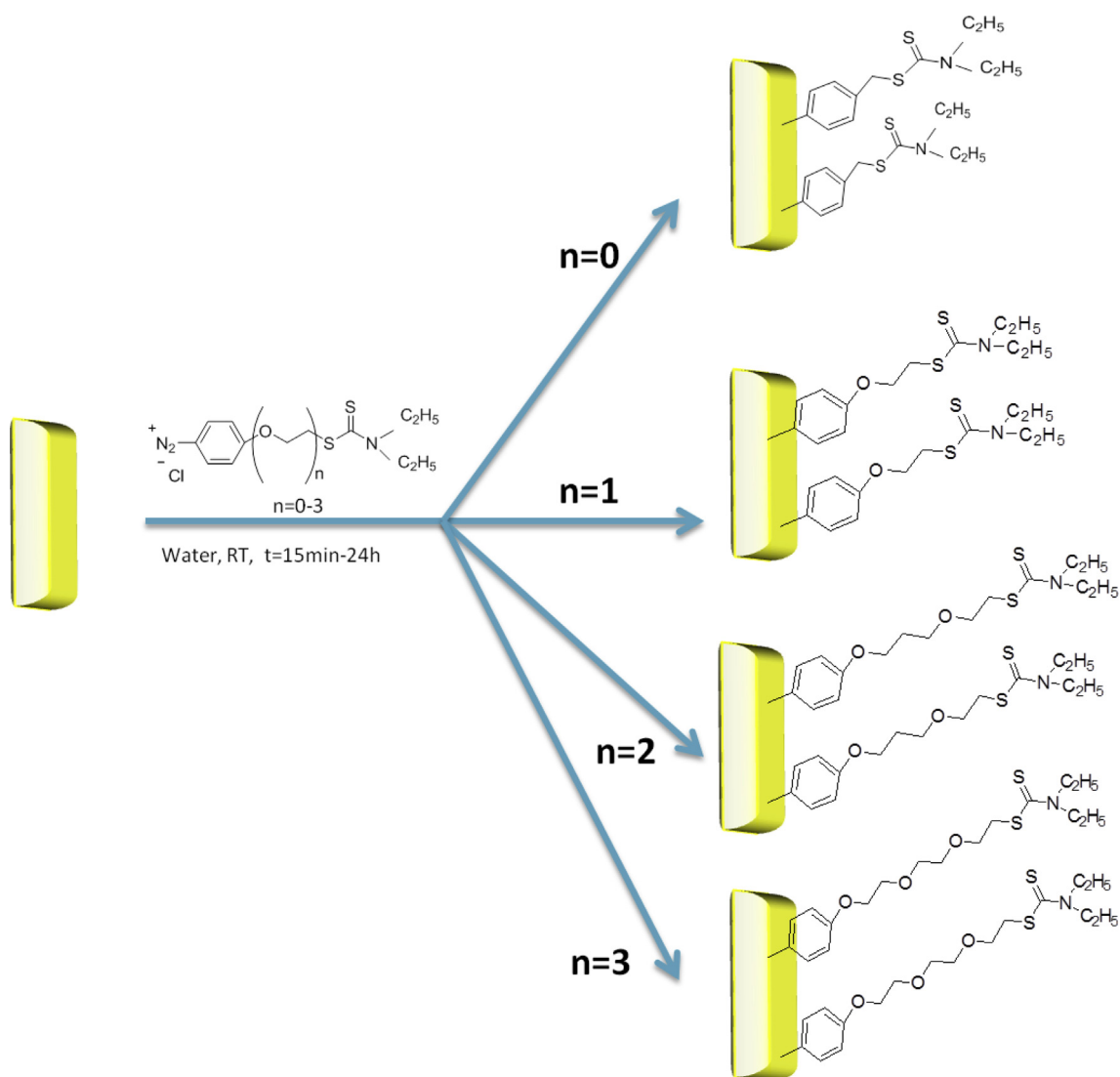
*E-mail addresses:* [mangeney@univ-paris-diderot.fr](mailto:mangeney@univ-paris-diderot.fr), [Claire.mangeney@univ-paris-diderot.fr](mailto:Claire.mangeney@univ-paris-diderot.fr) (C. Mangeney).

lamps emitting at 300 nm coupled with a 280 nm cut-off filter to perform the photopolymerization and avoid any degradation of the starting monolayer. However, the Au–S bond at the interface between the organic polymer coating and the gold surface remains labile upon certain conditions (UV light or heating) which causes instability problems for storage under light or any post-functionalization reaction above 60 °C.

Therefore, the development of versatile and efficient surface modification iniferter strategies [16–20] able to provide strong and stable linkages between the gold surface and the polymer coating still remains challenging. We address this issue in the present paper by developing a facile methodology to surface-initiated photopolymerization (SIP) of vinylic monomers from gold surfaces via an aryl diazonium salt-derived iniferter. Aryl diazonium salts have been shown recently to be useful coupling agents for the grafting of polymer coatings on carbon-based [21–27] and metallic [28–40] (gold, platinum, palladium, ruthenium and titanium) planar or nanoparticle surfaces, affording strong carbon or metal–carbon linkages. Nevertheless, the combination of the diazonium salt chemistry and the iniferter method, which has proved to be efficient in order to grow dense polymer layers from the surface of

aluminum [41] and oxide nanoparticles [42–44] has never been extended til now to the functionalization of gold surfaces.

In this paper, we fill this gap by exploring the propensity of aryl diazonium coupling agents bearing *N,N*-diethyldithiocarbamate (DEDTC) [9] groups to photo-initiate the growth of polymer chains from gold surfaces, as depicted in Fig. 1. The diethyldithiocarbamyl groups remain at the end of the growing tethered chains [6,7], which allows one to tune the chain length by variation of the irradiation time. In addition, the use of this polymerization reaction gives control over the end groups, which can be easily exchanged or chemically modified. The biocompatibility of this technique should also be underlined: no organic solvents are used and no toxic metal/compounds are involved in the polymerization process. By introducing oligo(ethylene oxide) spacers of various lengths between the aryl anchoring moieties and the DEDTC groups, we could play on the hydrophilic character of the initiating layer, which is of prime importance when the functionalization steps have to be performed in a water environment. We demonstrate this approach by grafting cross-linked copolymer layers of methacrylic acid (MAA) and *N,N'*-methylenebisacrylamide (MBAm) on gold surfaces. This grafting procedure is simple, rapid and effective in producing



**Fig. 1.** General method for the functionalization of gold surfaces by bifunctional molecules bearing a diazonium moiety and an iniferter end group separated by oligo(ethylene oxide) chains of various lengths.

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