Surface Science 603 (2009) 3205–3211

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Tandem diazonium salt electroreduction and *click* chemistry as a novel, efficient route for grafting macromolecules to gold surface

Samia Mahouche [a], Nejib Mekni [b], Leila Abbassi [a], Philippe Lang [a], Christian Perruchot [a], Mohamed Jouini [a], Fayna Mammeri [a], Mireille Turmine [c], Hatem Ben Romdhane [b,*], Mohamed M. Chehimi [a,*]

[a] *ITODYS, University Denis Diderot & CNRS (UMR 7086), 15 rue Jean de Baïf, 75013 Paris, France*
[b] *Laboratoire de Chimie Organique Structurale-Synthèses et Analyses Physico-chimiques, Faculté des Sciences de Tunis, Campus Universitaire, 2092 Manar II, Tunisia*
[c] *LISE, CNRS (UPR 15) and University Pierre & Marie Curie, Case 133, 4, Place Jussieu, 75005 Paris, France*

ARTICLE INFO

Article history:
Received 18 July 2009
Accepted for publication 2 September 2009
Available online 9 September 2009

Keywords:
Diazonium salts
Click chemistry
Macromolecules
Gold
XPS
PMIRRAS
Contact angles

ABSTRACT

Bis-alkynylated oligoethyleneglycol (OEG) and a monopropargyl-functionalized perfluorinated ethylene glycol (FEG) were *clicked* to azide-functionalized gold surface (Au–N_3) at room temperature via the well known 1,3 cycloaddition *click* chemical reaction. The Au–N_3 substrate was obtained by nucleophilic attack of NaN_3 on gold substrates modified by the electrochemical reduction of the BF_4^-, $^+N_2$–C_6H_4–CH_2Br diazonium salt. This electrochemical process yields aryl layer-modified gold of the type Au–C_6H_4–CH_2Br (hereafter Au–Br). The untreated and modified gold plates were examined by XPS, PMIRRAS and contact angle measurements. XPS brought evidence for electrografting aryl layers by the detection of Br3d; azide functionalization by the increase of the N/Br atomic ratio; and *click* reaction of OEG with Au–N_3 by the increase of O/N ratio. In addition, the perfluorinated plate (Au-FEG) exhibited F1s and characteristic C1s peaks from -$(CF_2)_7$- chain and terminal CF_3. Infra red spectroscopy (PMIRRAS) evidenced (i) grafting N_3 to Au–Br; (ii) characteristic stretching bands, from ethylene glycol units, C–O–C (1100–1300 cm^{-1}); CF_2 (1000–1100 cm^{-1}) and CF_3 (1100–1350 cm^{-1}) from FEG grafts; and (iii) suppression of alkynyl bands from OEG and FEG after surface *click* chemistry. More importantly, PMIRRAS results support an important bridging of the bispropargyl oligoethylene glycol at the gold surface. Water drop contact angles were found to be 48.7° and 83.0° for Au-OEG and Au-FEG, respectively, therefore highlighting the control over the hydrophilic/hydrophobic character of the *clicked* substrate.

This work shows that *clicking* macromolecules to grafted, diazonium salt-derived aryl layers is a novel, simple and valuable approach for designing robust, functional surface organic coatings.

1. Introduction

Modification of (semi)conductors by aryl diazonium salts has attracted several research teams and witnessed a quantum jump in the number of publications recently [1]. Aryl layers are attached to surfaces by electrochemical [1] or electroless [2] reduction of the parent diazonium salts. The grafted layers strongly bind covalently to carbon [3] and various metals [4,5] and have a nanometer-scale thickness [6] that can, under certain circumstances, be extended to micrometer-thick coatings [2b].

Aryl layers permit to design coatings with controlled redox [7], bioactive [8], wetting [9], adhesive [10], metal chelating properties [11], to name but a few applications. As far as macromolecular species are concerned, (i) polystyrene was grafted to 4-benzoylphenyl layers used as photoactivators [12]; (ii) glucose oxidase was covalently attached to carboxylic acid-functionalized aryl layers in order to devise diamond-based biosensors [13]; (iii) brominated aryl layers on iron [14] and carbon [15] served for the surface-confined atom transfer radical polymerization of a variety of vinylic monomers.

Despite the various surface chemistry routes and potential applications of grafted aryl layers, they were only recently been subjected to *click* chemistry [16] as a versatile approach to design bioactive surfaces.

Among the various heteroatom coupling procedures, the copper (I)-catalyzed 1,3 dipolar cycloaddition between an azide and terminal alkyne, is considered as the very promising *click* reaction strategy for the preparation of polymers and other materials with well defined structures and functionalities [17]. This is due to the simplicity, high efficiency, the satisfactory selectivity of the reaction, and its applicability under soft working conditions [18].

This approach has been widely used for the modification of polymers, by post-functionalization of their side chains or by

* Corresponding authors. Tel.: +33 1 57276863; fax: +33 1 57277263 (M.M. Chehimi).
E-mail addresses: hatem.benromdhane@fst.rnu.tn (H.B. Romdhane), chehimi@univ-paris-diderot.fr (M.M. Chehimi).

0039-6028/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2009.09.004

coupling of preformed polymer segments in order to prepare new macromolecules [19]. Recently, this useful alternative was extended to material surface modification [20,21] owing to the very high stability of the 1,2,3-triazole cycle resulting from the *click* reaction [22]. Particularly, Ciampi et al. reported an efficient *click* chemistry approach for grafting oligoethylene glycols (OEGs) on acetylene-terminated monolayers on Si (1 0 0) [23] and on porous silicon Rugate filters [24].

In order to fill the gap, we combined the fast and efficient electrografting of aryl layers and surface *click* chemistry as a novel route for binding macromolecules to gold plates at room temperature. This accounts for an alternative method to the well accepted *click* reaction on gold modified by thiol self-assembled monolayers (SAMs) [25]. The advantage of the present approach is that the very fast cleavage (less than 1–2 min) of dinitrogen gives an aryl radical which binds to gold with an energy as high as 24 kcal/mol [5] much higher than 5 kcal/mol reported for thiol SAMs on gold (case of octanethiol in hexane) [1]. One can thus anticipate that electrografted aryl layers combined to the efficiency of *click* chemistry would permit, in an original way, to design organic coatings on gold with excellent adhesion properties.

Towards this end, gold was modified by electrochemical reduction of the diazonium salt BF_4^-, $^+N_2$–C_6H_4–CH_2Br. The resulting Au–C_6H_4–CH_2Br plates (Au–Br) were further modified by NaN_3 leading to Au–C_6H_4–CH_2N_3 (Au–N_3). Mono- or bispropargyl-functionalized (oligo)ethylene glycols of the types HC≡C–CH_2–O–CH_2–CH_2–$(CF_2)_7CF_3$ and HC≡C–CH_2–O–$(CH_2CH_2O)_4$–CH_2–C≡CH were clicked to the azide-functionalized aryl layers Au–N_3. The grafted oligomers are expected to impart differing hydrophilic/hydrophobic characters to the substrate. The Au-OEG and Au-FEG hybrids, and their precursors were characterized by XPS, PM-IRRAS and contact angle measurements.

2. Experimental

2.1. Synthesis and NMR analysis of mono- and bispropargyl (oligo)ethylene glycols

The silica gel used is of Merck 7734 type. Propargyl bromide, polyoxyethylene glycols, tetrabutylammonium hydrogen sulfate (TBAHS), sodium hydroxide (NaOH) are Fluka commercial products, and the *F*-octylethanol is an ATOCHEM product.

To a vigorously stirred mixture of sodium hydroxide (6 g, 0.15 mol), 0.5 ml of water, 0.2 g of TBAHS, and 25 mmol of OEG (or FEG) at 50 °C, 0.15 mol of propargyl bromide (or 75 mmol) was added. After 40 min, the mixture was filtered, and the salt was washed with methylene chloride (2 × 25 mL). After drying on Na_2SO_4, the solvent was evaporated, the excess of propargyl bromide was removed and the residue was purified on chromatographic column by using methylene chloride as eluent (Scheme 1).

2.1.1. 4,7,10,13,16-pentaoxanonadeca-1,18-diyne (n = 4) [OEG]

^{1}H NMR ($CDCl_3$): δ 2.49 (t, 2H, 2≡CH), 4.16 (d, 4H, ≡C–CH_2–O), 3.65–3.70 (m, 4H, CH_2–O), 3.52–3.62 (m, 12H, 6CH_2–O); ^{13}C NMR ($CDCl_3$): δ 79.7 (s, 2C, ≡CH), 74.8 (s, 2C, *C*≡CH), 58.3 (s, 2C, *C*H_2–O), 69.5 (s, 2C, ≡C–CH_2–O), 70.3 (s, 6*C*H_2–O).

2.1.2. 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro-4-oxatetradeca-1-yne [FEG]

^{1}H NMR ($CDCl_3$): δ 2.46 (m, 2H, *CH*$_2$–CF_2, $^3J_{HF}$ = 15.1 Hz), 2.54 (t, 1H, ≡CH), 4.24 (d, 2H, ≡C–CH_2–O), 3.86 (t, 2H, O–*CH*$_2$–CH_2–CF_2); ^{13}C NMR ($CDCl_3$): δ 31.7 (t, 2C, *C*H_2–CF_2, $^2J_{CF}$ = 24.7 Hz), 80.1 (s, 1C, ≡*C*H), 75.1 (s, 1C, *C*≡CH), 58.9 (s, 1C, ≡C–*C*H_2–O), 77.7 (s, 1C, O–*C*H_2–CH_2–CF_2), 104–125 (m, 8C, CF); ^{19}F NMR ($CDCl_3$): δ −125.82 (m, 2F, $CF_{2\omega}$), −123.09 (m, 2F, $CF_{2\gamma}$), −122.40 (m, 2F, $CF_{2\delta}$), −121.57 (m, 4F, 2$CF_{2\varepsilon}$), −121.31 (m, 2F, $CF_{2\beta}$), −114.82 (m, 2F, $CF_{2\alpha}$, $^3J_{HF}$ = 15.1 Hz), −80.52 (t.t., 3F, CF_3, $^3J_{FF}$ = 10.53 Hz) ppm.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Brüker AC 300 spectrometer at 300, 75 and 282 MHz, respectively. TMS was used as standard reference for ^{1}H and ^{13}C NMR spectra and $CFCl_3$ for ^{19}F one.

2.2. Synthesis of the diazonium salt BF_4^-, $^+N_2$-C_6H_4–CH_2–Br (DS)

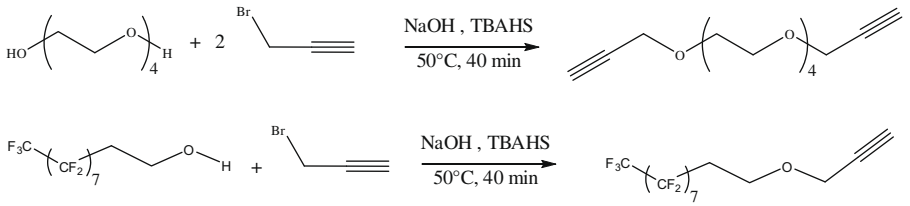
The diazonium salt was obtained in a 50 ml flask from the commercially available 4-(hydroxymethyl) aniline (Aldrich, 0.5 g) and tetrabutylammonium bromide (Aldrich, 1.63 g) by heating at 150 °C in 48% HBr (5 ml) for 16 h. The diazotation of the obtained yellow precipitate was then achieved by the standard method that consists in adding at 0 °C a solution of HBF_4 (4.5 ml) and a cold solution of $NaNO_2$ (0.34 g) dissolved in 2 ml of Milli-Q water. The mixture was left to react at 0 °C for 30 min and the precipitated brown diazonium tetrafluoroborate was filtered and washed with 5% $NaBF_4$, methanol and ether, then dried under vacuum and stored in the freezer. ^{1}H NMR (DMSO), δ 5.01 (s, 2H, CH_2–Br), 8.02 (d, 2H, C*H*–CH_2–Br), 8.68 (d, 2H, CH–C–N_2^+).

2.3. Electrochemical treatment of gold slides

Electrochemical grafting of the aryl layers was achieved on gold-coated silicon slides cut from commercial wafers (Aldrich) as working electrode, using a platinum counter electrode, and a SCE (saturated KCl) reference electrode. Grafting was carried out in a degassed solution of acetonitrile (ACN) containing 5 mM of BF_4^-, $^+N_2$–C_6H_4–CH_2–Br and 0.1 M of supporting electrolyte NBu_4BF_4, for 300 s. After modification, the slide was rinsed by sonication in acetonitrile, ethanol then dichloromethane, and subsequently dried under an argon flow. The as-modified substrates are abbreviated Au–Br.

2.4. Preparation of azido-terminated gold plates

One hundred milliliters solution of dimethyl formamide (DMF) containing 0.05 M of NaN_3 were added to five Au–Br slides placed in a Schlenk flask. After 8 h of stirring at room temperature, the slides (hereafter abbreviated by Au–N_3) were removed from the solution, and thoroughly washed with DMF and dichloromethane, then dried under argon flow.



Scheme 1. Schematic synthesis of OEG and FEG.