Electronic supplementary information for Journal of Materials Chemistry

Materials. All thiophene derivatives, amine (TEA), 2-bromoisobutyrylbromide, triethyl pentamethyldiethylenetriamine (PMDETA), copper bromide (Cu(I)Br) and Cu(0) were used as received without further purification. *t*-butyl acrylate monomer (noted *t*-BuA) was dried and distilled over CaH_2. THF was dried and distilled over CaH_2 and sodium/benzophenone respectively. CH_2Cl_2 was dried and distilled over CaH_2.

Cyclohexane (J.T. Baker, 99%) utilized as dispersant medium was used as received. Ethylene glycol (EG) (Aldrich, 99%), tolylene-2,4-diisocyanate (TDI) (Aldrich, 98%) were used as received. Dibutyl tin dilaurate (DBTDL) was used as received; a 1% stock solution was prepared by dissolving 2.48×10^{-3} moles of DBTDL in 25g of paraffin.

Trifluoroacetic acid (TFA) (Aldrich, 99%) and potassium tetrachloroaurate(III) ($KAuCl_4$) (Acros, 98%) were also used as received.

Instrumentations. Molecular weights and molecular weight distributions were determined by size exclusion chromatography (SEC) on a Varian 5500 apparatus equipped with high-speed PSS columns, a refractive index detector and a UV-vis detector. The temperature of the analysis was 298 K and the eluant rate 1ml/min. Carefully dried THF containing BHT antioxidant was used as the eluant. Average molecular weight values were calculated from the polystyrene calibration curve using a correction coefficient.

^{1}H NMR spectra were recorded on a Bruker AC400 spectrometer operating at 400 MHz. The samples of each fraction were dissolved in $CDCl_3$.

Transmission electron microscopy (TEM) was performed on a JOEL, JEM-100S electron microscopy. The samples were placed on a copper grid and were let to dry at room temperature.

Syntheses.

Synthesis of a new thiophene-based ATRP initiator <u>1</u>.

To a three neck round-bottom flask was added, under nitrogen stream, 2-bromoisobutyrate ethanol (6.9 mmol, 1.456 g) with 1 eq of 3-thiophene acetic acid (0.981 g) in the presence of 4-(dimethylamino)pyridinium-p-toluene (DPTS) (0.2 eq) and N,N-diisopropyl-1,3-carbodiimide (DiPC) (1.3 eq). The reaction was carried out in 40 ml of CH_2Cl_2. The reaction mixture was stirred overnight at room temperature. Once the reaction was completed, the solution was filtered off over a paper filter and the solvent removed. At this point the residual product was eluted with CH_2Cl_2 through a silica gel column. The appropriate fractions were collected and the solvent was removed to give the pure product (1.827 g, yield : 79%). ^1H NMR (400 MHz, $CDCl_3$) : δ (ppm) = 1.90 (s, 6H), 3.69 (s, 2H), 4.38 (s, 4H), 6.95 (d, 2H), 7.03-7,30 (3H).

Synthesis of α-thienyl, ω-hydroxy poly(*t*-butyl acrylate) "surfmer" <u>2</u>.

For the synthesis, we followed and adapted the procedure described by Coessens *et al.* (V. Coessens and K. Matyjaszewski *Macromol Rapid Commun* **20:**127 (1999)).

A round-bottom flask equipped with a gas inlet/outlet and a rubber septum was flame dried under vacuum. To the mixture of initiator **<u>1</u>** (1 eq), CuBr (1 eq) and PMDETA (1 eq) previously introduced in the flask under nitrogen was added the appropriate amount of *t*-butyl acrylate monomer (targeted M_n = 12000 g/mol or 7000g/mol). The reaction mixture was degassed by means of three freeze-thaw cycles. Then the reactor was placed in an oil bath thermostated at 80°C, and kept under stirring during 16 min. After cooling down to room temperature, an excess of allyl alcohol (> 30 eq.) and 0.5 eq of Cu(0) were added to the reaction medium. The latter was allowed to reach 50°C and let to react during 16 hours. The flask was cooled to room temperature, the content was dissolved in THF and then passed through a column of neutral alumina to remove copper derivatives. The final α-thienyl, ω-hydroxy poly(*t*-butyl acrylate) **2** was recovered by precipitation in a mixture of $MeOH/H_2O$ (70/30) (v/v) and dried under vacuum. All the thiophene-functionalized surfmers thus obtained were characterized by size exclusion chromatography (SEC) and by ^1H NMR spectroscopy.

Synthesis of polyurethane particles.

PUR synthesis was carried out in a 250 ml jacketed glass reactor fitted with a reflux condenser, a stainless steel half-moon type stirrer, a sampling device and a nitrogen inlet tube. The reactor was charged with the surfmer (10 wt% *vs* monomers), x mole of TDI (2 eq with respect to the OH functions) and all of the solvent (18 g). The mixture was allowed to react in the presence of DBTDL as the catalyst for 2h at 60°C at a stirring speed of 500 rpm. EG (0.733 g, 0.0118 mol) was then added drop-wise and allowed to react for 30 min. Then ($0.013-x$) mol of TDI was added over a period of 6 h. The mixture was kept at 60°C over a period of 1 h. The final product was washed by a number of cycles re-dispersion in cyclohexane/centrifugation. With the objective to determine the particle size the latexes were analyzed by TEM. Moreover, ^1H NMR spectroscopy analysis allowed us to determine the percentage of stabilizer that readily took part to the polyaddition reaction in cyclohexane (*i.e.* about 80 %).

Re-dispersion of polyurethane particles in water. A round-bottom flask equipped with a gas inlet/outlet and a rubber septum was flame dried under vacuum and charged with PUR latex (1.7 g, 2.2×10^{-5} mol of "surfmer"). A cyclohexane/distilled water mixture (35/35 V/V in mL) was added and the reaction was allowed to stir for 20 min to obtain a uniform suspension. Then a large excess (*vs* the "surfmer") of TFA (1.4 g, 0,013mol) was added drop-wise, under nitrogen, and the reaction was kept under stirring overnight at room temperature. The TFA excess was removed by evaporation of the solvents at the rotary evaporator. The final product was washed by a number of cycles re-dispersion in water/centrifugation. The particles thus obtained were characterized by TEM.

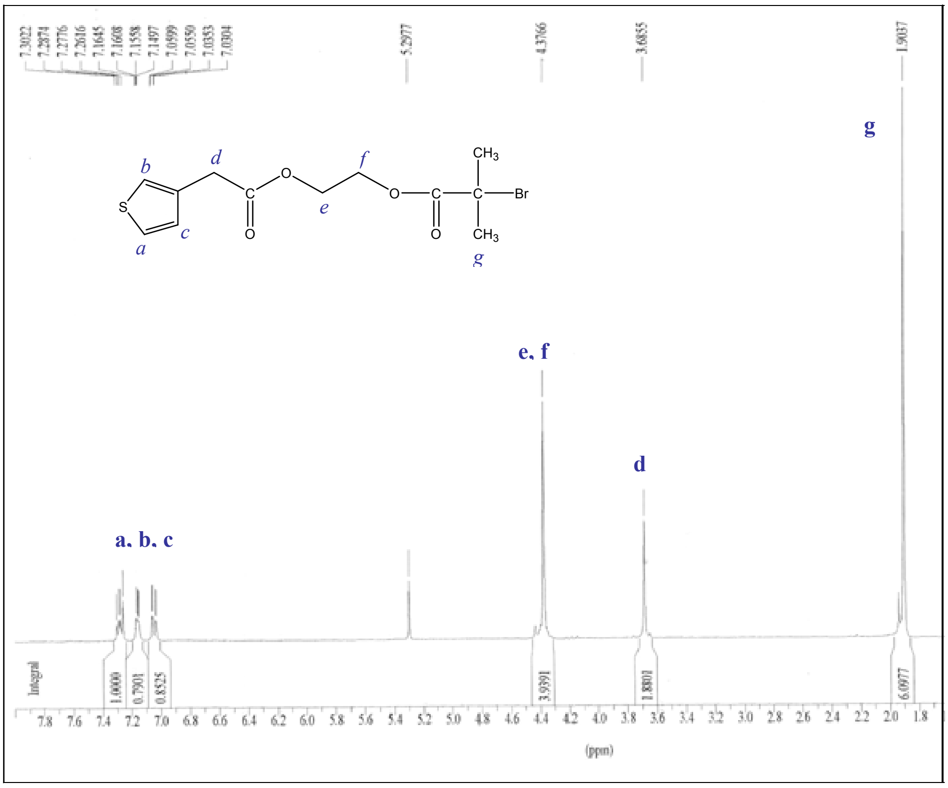
Direct-assembly of gold nanoparticles on polyurethane particles (Au@PUR).

50 mg of the PUR latex were dispersed in 8 mL of distilled water. Two kinds of latexes were investigated where the PUR average particle size was respectively of 3.5 µm and 0.8 µm. Then different concentrations (10^{-3}-10^{-4} M) and volumes of aqueous solution of potassium tetrachloroaurate ($KAuCl_4$) were added. Three gold/surfmer molar ratios were studied, respectively r = 1.2, 1.4 and 2.2. The mixture was kept under stirring at room temperature during various time (from 1 h to 50 h), depending on the brightness conditions. Experiments were carried out under UV radiation, at the room light and also in the dark. The as-synthesized hybrid materials were washed several times with water, recovered by centrifugation (10000 $tr.min^{-1}$, at 10°C during 5 min) and finally dried in air and characterized by TEM and XPS.

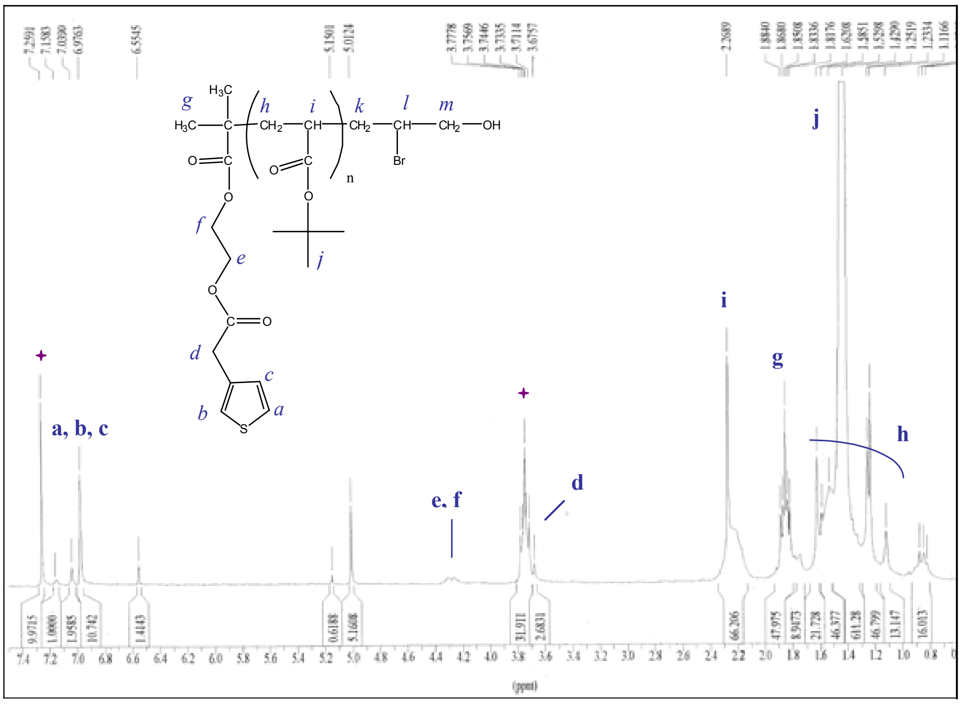
Electronic supplementary information for Journal of Materials Chemistry

^{1}H NMR analysis:

a)



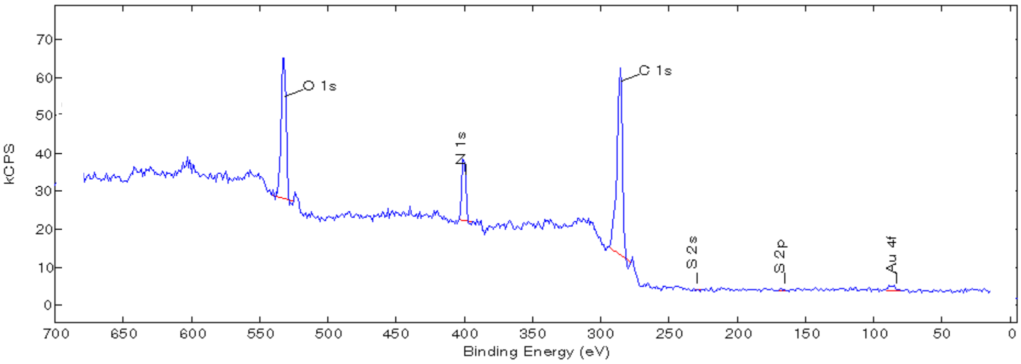
b)



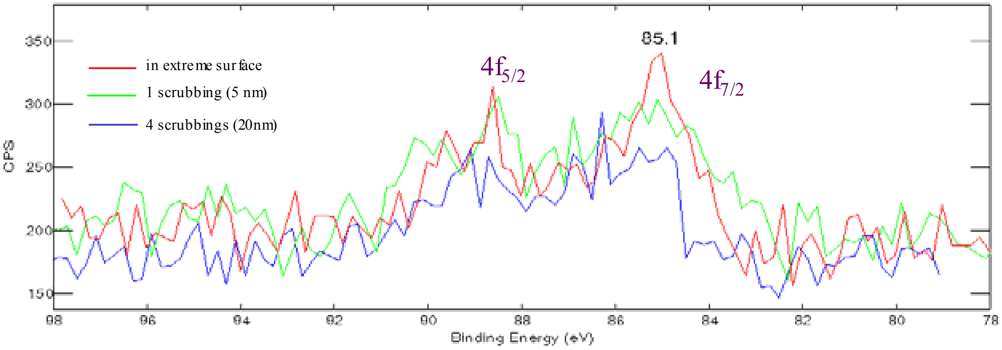
S1. (a) ^{1}H NMR of the initiator **1** ($CDCl_3$, *400MHz*)

(b) ^{1}H NMR of α-(3-thienyl), ω-hydroxy poly(*t*-butyl acrylate) **2** ($CDCl_3$, *400MHz*)

XPS analysis.



S2. XPS spectrum of the Au@PUR-2a.



S4. XPS spectra of the reduced gold by scrubbing in depth Au@PUR-2a.