Supplementary Information

In situ Synthesis of Gold-Cross-linked Poly(ethylene glycol) Nano Composites by Photoinduced Electron Transfer and Free Radical Polymerization Processes

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EXPERIMENTAL

Materials

The photocurable acrylic resin, poly(ethlenglycol) diacrylate (PEGDA) (Ebecryl 11, UCB), gold(III)chloride hydrate (HAuCl₄, Aldrich), and the radical photoinitiator (1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propane-1-one) (Irgacure 2959, Ciba) were used as received.

Sample preparation, UV-curing and characterization

HAuCl₄ was dispersed into the acrylic resin in the range between 1-5 wt%. The radical photoinitiator was added, in all the formulations, at 4 wt%. The mixtures were stirred and coated on glass substrates. The curing reaction was performed by irradiation with UV lamp with a light intensity of about 30 mW/cm² for one minute under nitrogen. The colors turn from yellow of the solution to purple of cured films.

The kinetics of the photopolymerization was determined by Real-Time FT-IR spectroscopy, employing a Thermo-Nicolet 5700. The formulations were coated onto a silicon wafer. The sample was exposed simultaneously to the UV beam, which induces the polymerization, and to the IR beam, which analyze *in situ* the extent of the reaction. A medium pressure mercury lamp equipped with an optical guide was used to induce the photopolymerization (light intensity on the surface of the sample of about 30 mW/cm²). Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. To this aim, acrylic double bond conversion was followed by monitoring the decrease in the absorbance due to acrylic double bond centred at 1638 cm⁻¹.

DSC measurements were performed under nitrogen flux, in the range between -80 °C to 150 °C, with a DSCQ 1000 of TA Instruments equipped with a low temperature probe. Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration.

The Gel Content was determined on the cured films by measuring the weight loss after 24 hours extraction with chloroform at room temperature (ASTM D2765-84).

Samples were prepared for TEM observation by Ar⁺ ion polishing system GATAN PIPS, working at 3.5 keV at an angle of 7°. They were examined in a 300 keV transmission electron microscope (TEM) Philips CM30. TEM micrographs were processed with a slow scan CCD camera and analyzed with the Digital Micrograph program. The TEM observations were

always performed using a very low electron flux in order to avoid any structural modification of the sample induced by the electron beam.

Table S1 Properties of UV cured films Obtained by Irradiation of Poly(ethlenglycol) diacrylate (PEGDA) Containing HAuCl₄ and 1-[4-(2-Hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propane-1-one (Irgacure 2959) (4 wt %).

| Sample | HAuCl ₄ | Conversion ^a | Gel content ^b | $T_{ m g}^{\ c}$ |
|---------|--------------------|-------------------------|--------------------------|------------------|
| | (wt%) | (%) | (%) | (°C) |
| PEGDA-1 | - | 95 | 95 | -50 |
| PEGDA-2 | 3 | 86 | 93 | -52 |
| PEGDA-3 | 5 | 80 | 90 | -61 |

^{*a*}Determined by Real-time FT-IR

^bDetermined by solvent extraction

^{*c*}Determined by dynamic-mechanical thermal analysis.



Fig. S1 Real-time kinetic conversion curves for the UV curing of poly(ethlenglycol) diacrylate containing different concentrations of HAuCl₄ and 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propane-1-one (Irgacure 2959) (4 wt %). 5 wt % HAuCl₄ (curve A), 3 wt % HAuCl₄ (curve B), and in the absence of HAuCl₄ (curve C)).