

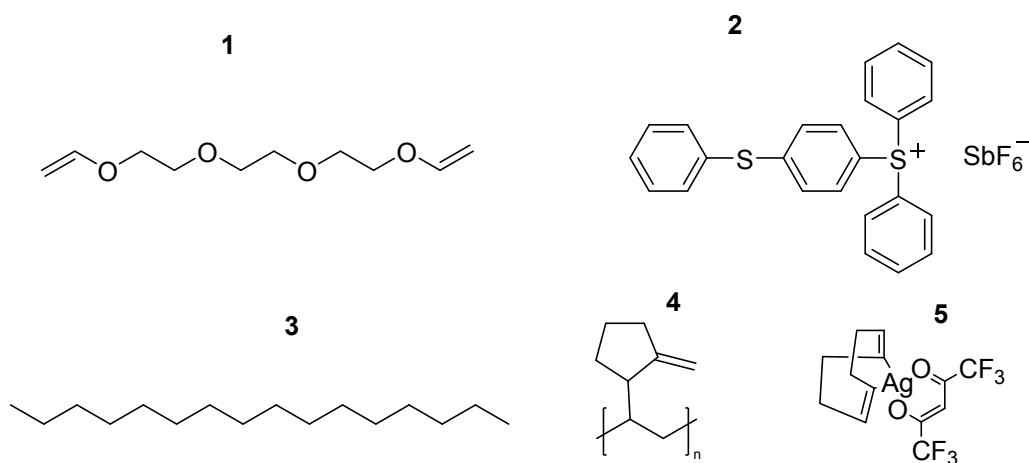
Supporting Information

## 2. EXPERIMENTAL

### 2.1 Materials

Triethylene glycol divinyl ether 98% **1** (**DVE3**) employed as a monomer in this work had a density of  $0.99 \text{ g mL}^{-1}$  at  $25 \text{ }^\circ\text{C}$ . The photoinitiator was triarylsulfonium hexafluoroantimonate salts **2** (**PI**), mixed 50 wt. % in propylene carbonate. In order to generate the interface polymerization, n-hexadecane 99% **3** has been used. polyvinylpyrrolidone (**PVP**) **4** powder  $M_w$  55,000  $\text{g mol}^{-1}$  was used as surfactant. For the silver functionalization of the polymeric capsules the silver precursor 1,5-cyclooctadiene (hexafluoroacetylacetonato) silver(I) **5** was used and added into the supercritical  $\text{CO}_2$  solution. All materials employed in this investigation were reagent quality and were used as purchased from Sigma-Aldrich.

Figure S1: Chemical structures of the materials employed



### 2.2 Synthesis of the polymeric nanoparticles

A typical photopolymerization is detailed as follows: The aqueous suspending medium (200 mL) composed of deionized water and 0.4 g of PVP were put into a 500 mL round-bottom flask. The deionized water and PVP form the *aqueous solution*. The solution was stirred at 1000 rpm for 10 min in order to obtain an optimal PVP solubilization.

Suspension cationic photopolymerization conducted in aqueous solution environment require a stabilizer to obtain spherical microparticles. The PVP surfactant was selected after different experimental trials comparing different surfactants and it was found PVP was the most appropriate. In a separate vial the *oil solution* was prepared consisting of 24 mL of n-hexadecane and 0.4 g of photoinitiator. Finally, the *non-aqueous solution* was made of 1.6 mL of *oil solution* and 10 g of DVE3. The flask of the aqueous solution was placed in the ultrasonic bath. The sonicator was switched on, then the prepared *non-aqueous solution* containing the DVE3 monomer was added dropwise to the flask over approximately 2 min. The solution was continually sonicated for 10 min and then the sonicator was switched off.

After this operation, the UV lamp probe was put on the flask to start the irradiation of the solution. UV-radiation was supplied by an OmniCure S2000 (Excelitas Technologies Corp, Canada) High Pressure 200 W mercury vapor lamp. A 320-390 nm filter was used in order to achieve the maximum absorption for the photoinitiator without added light. The light intensity used for all the photopolymerizations was 1 W/cm<sup>2</sup>. Irradiation of the solution was continued for 10 min, after which the UV lamp was switched off. The solution was then dried into a powder using a Mini Spray Dryer B-290 (BÜCHI Labortechnik, Switzerland). The following optimized settings were used: spray air flow = 1 kg/h; inlet temperature = 170 °C feed rate = 0.024 m<sup>3</sup>/h (this value corresponds to 20% of the maximum capacity of the peristaltic pump); aspirator power = 90 % of the maximum power aspiration of the aspirator. This mixture was characterized initially by <sup>1</sup>H-NMR, then in dry state by SEM, TEM and light scattering.

### **2.3 Silver functionalization of the polymeric particles by using supercritical CO<sub>2</sub>.**

In order to obtain polymer nanocomposite particles, previously synthesised polymer particles were placed in supercritical carbon dioxide containing a silver precursor. The following is a typical experimental procedure employed in order to obtain polymer-silver nanocomposite particles in sCO<sub>2</sub>.

The initial mixture was loaded in the reactor at atmospheric pressure: it was formed by 5 mg of dry DVE3 polymer particles and 0.5 mg of 1,5-cyclooctadiene hexafluoro acetyl acetonato silver (I). It is important that, the mass of silver precursor be from 5% to 10% of the mass polymer<sup>1</sup> in order to obtain a good dispersion of silver nanoparticles throughout the polymer within the polymer microparticles. The reactor was subsequently pressurised by the introduction of CO<sub>2</sub>. The operating conditions selected for the reactor have been: T = 65 °C and P = 207 bar. The autoclave was held at reaction conditions for 5 h, cooled then depressurised over a 10 min period.

### **2.4 Characterization methods**

<sup>1</sup>H-NMR analyses were recorded with a Bruker Avance 400MHz (Bruker, USA). All the NMR spectra are recorded in solution of deuterated chloroform CDCl<sub>3</sub> at an approximate ratio of 5 mg mL<sup>-1</sup>.

Particle size distribution was measured by using a Mastersizer, where a laser diffraction measuring particles sizes between 0.02 and 2000 µm. A Mastersizer 2000 (Malvern Instrument, UK) with software Mastersizer 2000 (Malvern Instrument, UK) was employed in this work. In a typical measurement 30 mL of the polymerized solution was placed in the analysis cell. Using the software Mastersizer2000, Mie model was chosen in order to obtain the particle size distribution. From the curve some parameters could be determined:

Each parameter value has a specific meaning: D (0.1) is the size of the particles for which 10% of them are below the size; D (0.5) is the size of the particles for which 50% of them are below the size; D (0.9) is the size of particles for which 90% of them are below the size. The span is the measurement of the width of the distribution. The narrower the distribution the smaller the span becomes.

Small Angle X-ray Scattering (SAXS) was used to determine the structure of particle system in terms of averages particles sizes, morphology or shapes. SAXS data are reported as a graph where *I* is on the ordinate and *q*, “length of the scattering vector” or “momentum transfer” is reported in the x-axis.

Using a Guinier plot<sup>2</sup> it was possible to obtain the average diameter of the particles where the logarithm of the intensity is reported versus  $q^2$ . From the slope of the fitting curve it is possible to evaluate  $R_G$ , or radius of gyration, of the analysed particles. This is an independent model, that means it contains no information about the shape or internal structure of the particle. But if the structure of the particles could be assumed, then  $R_G$  could be used to calculate the particle dimension. Since in this work the particles are known to be spherical (by SEM analyses), then the average radius of such particles could be calculated from the radius of gyration by the Equation S1:

$$R = \sqrt{5/3} \cdot R_G$$

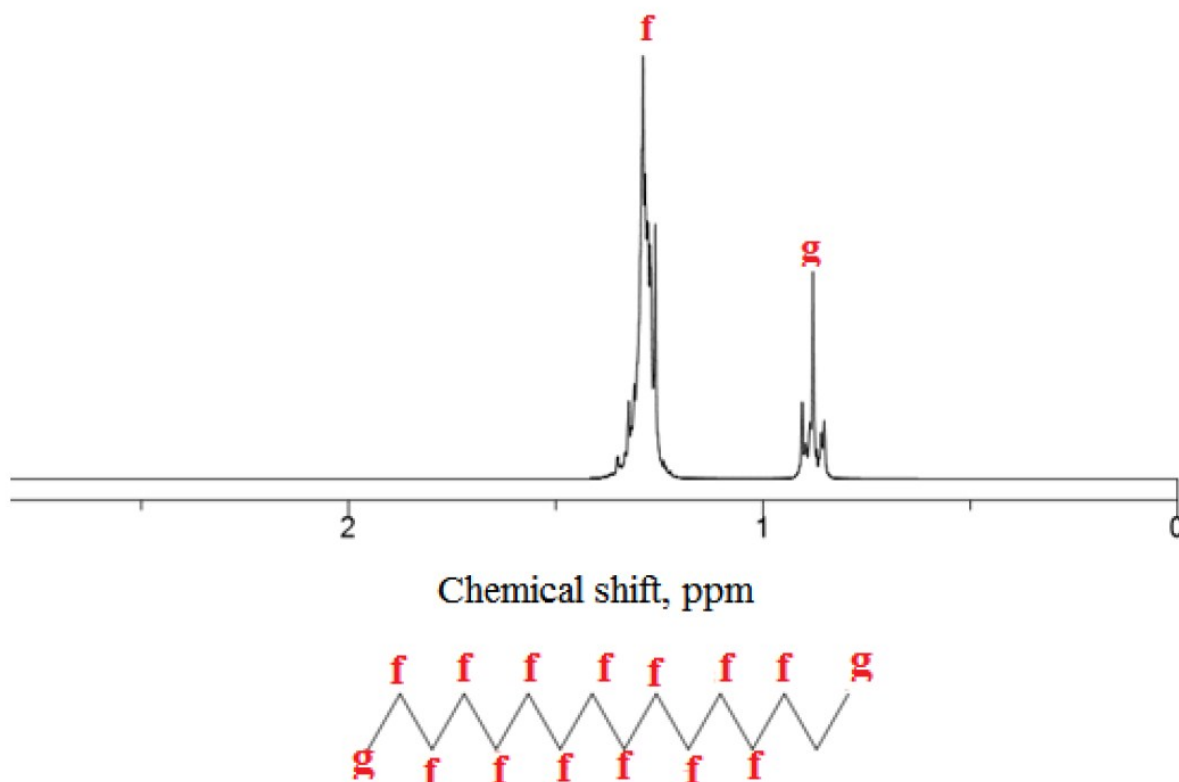
Equation S1

Furthermore, according to the Fourier-transformation of the graph  $I$  vs  $q$  [REF], it is possible to obtain the pair-distance distribution function (PDDF)<sup>3</sup>. The PDDF is used to predict the shape of the particles (globular, cylindrical, and lamellar) and understand if the particles have a core-shell structural arrangement. Details of how these PDDFs are calculated can be found in the literature<sup>4</sup>. In this work, the X'Pert PRO (PANalytical's, Netherlands) was used. In order to obtain the Guinier plot and PDDF from the graph  $I$  vs  $q$ , the software EasySAXS (PANalytical's, Netherlands) was employed.

SEM analyses were performed by using Scanning Electron Microscope (Zeiss Sigma, Germany). The samples were mounted on stubs by pressing them firmly onto carbon tape then sputter coated with gold for 20 s at 25 mA under argon to obtain a thin coating of approximately 10 nm thick.

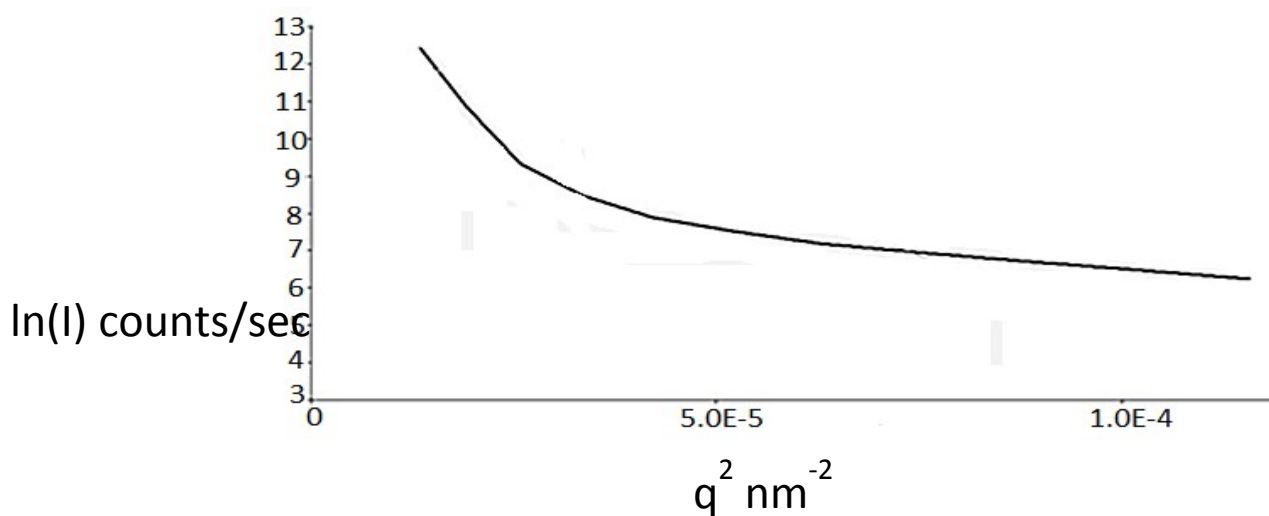
TEM analyses were performed by using JEOL 2000-FX TEM intermediate voltage (200 kV). Samples were mounted on 200 mesh Cu grids using a GO coating to literature procedure<sup>5</sup>.

Figure S2: <sup>1</sup>H-NMR spectra and assignment for hexadecane



Since the interfacial polymerization was performed in n-hexadecane, the <sup>1</sup>H-NMR of the solvent was recorded as a reference and it is reported in Figure S2. The <sup>1</sup>H-NMR spectra of the irradiated solution is reported in Figure 2.

Figure S3: Guinier plot obtained after SAXS analysis on the particles synthesized.



## References

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