Electronic Supplementary Information

Facile Synthesis of Thermoresponsive Nanohybrids

Jose Ramos,*[a] Roque Hidalgo-Álvarez[b] and Jacqueline Forcada[a]

[a] *POLYMAT, Bionanoparticles Group, Departamento de Química Aplicada, UFI 11/56, Facultad de Ciencias Químicas, Universidad del País Vasco UPV/EHU, Apdo. 1072, 20080 Donostia-San Sebastián, Spain.*
E-mail: jose.ramos@ehu.es; Fax: +34 -943-015-270: Tel: +34-943-015-213

[b] *Grupo de Física de Fluidos y Biocoloides, Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain.*

Experimental Section

Materials

N-Vinylcaprolactam (VCL, Sigma-Aldrich), *N,N'*-methylenebisacrylamide (MBA, Sigma-Aldrich), 3-(Trimethoxysilyl)propyl methacrylate (TPM, Sigma-Aldrich), sodium dodecyl sulfate (SDS, Sigma-Aldrich), potassium persulfate (KPS Sigma-Aldrich), sodium bicarbonate ($NaHCO_3$, Sigma-Aldrich) tetraethyl orthosilicate (TEOS, Acros Organics), ammonia (Scharlau), benzene-1,3,5-tricarboxylic acid (BTC, Sigma-Aldrich). Double deionized (DDI) water was used throughout the work.

Synthesis of hybrid nanogels

Thermoresponsive hybrid nanogels were prepared by emulsion polymerization in a batch reactor. 2 g of VCL as the main monomer, 0.08 g of MBA as the cross-linker, 0.08 g of SDS as the emulsifier, and 0.02 g of $NaHCO_3$ as the buffer were dissolved in 190 g of DDI water and place into a 250 mL jacketed glass reactor, fitted with a reflux condenser, stainless steel stirrer, sample device, and nitrogen inlet tube reactor. The reaction was heated at 70ºC, stirred at 300 rpm and purged with nitrogen for 1 h before starting the polymerization reaction. Prior to the addition of the initiator, a shot of TPM (ranging from 0 to 1 g) was added. After adding the initiator (0.02 g of KPS), the polymerization reaction was allowed to continue with stirring for 5 h under nitrogen atmosphere at 70ºC. The reaction mixture was subsequently cooled to 25ºC and the final dispersion was filtered through glass wool. Prior to colloidal characterization nanogels were dialyzed against distilled water. In this way, six different PVCL-based nanogels were prepared: PVCL without TPM, PVCL-co-TPM5 with a 5 wt% of TPM, PVCL-co-TPM10 with a 10 wt% of TPM, PVCL-co-TPM20 with a 20 wt% of TPM, PVCL-co-TPM30 with a 30 wt% of TPM, and PVCL-co-TPM50 with a 50 wt% of TPM. In addition, using a 10 wt% of TPM, VCL was replaced by NIPAM preparing other nanogel named P(NIPAM-co-TPM10).

Silica growth inside hybrid nanogels

The growth of silica inside thermoresponsive nanohybrids was carried by an *in-situ* sol-gel process of TEOS in the presence of hybrid nanogel particles at room temperature. Typically, 40 g of the hybrid PVCL-based nanogel synthesized with 10 wt% of TPM was first diluted with 40 g of DDI water in a reaction glass-bottle. The pH value of the nanogel dispersion was adjusted with ammonia to be ~10.

Subsequently, 1.39 g of TEOS was slowly added dropwise into the stirred dispersion at room temperature and the reaction was left under stirring for 24 h. After the synthesis, the hybrid nanogels were purified by repeated centrifugation against DDI water.

Characterization

Quantitative proton Nuclear Magnetic Resonance (^{1}H NMR) was used to determine the evolution of the partial conversions of VCL, MBA and TPM in the reactions. Previous to the analysis of the samples by NMR, a calibration curve of each monomer (VCL, MBA, and TPM) was made. Sample preparation and the conditions used to record the NMR spectra were the same than those used in our previous work.[13] ^{1}H NMR spectra were recorded by using a 500 MHz Bruker AVANCE spectroscope at 300K. Benzene-1,3,5-tricarboxylic acid (BTC) was used as standard. By using the calibration curve, the amounts of residual monomers at each time were obtained from the initial and nonreacted amounts of VCL, MBA, and TPM.

^{29}Si solid-state NMR spectra were obtained using a Bruker 400 WB Plus spectrometer. Spectra were collected by using a 4mm CP-MAS probe at a spinning of 6000Hz. CP-MAS ^{29}Si NMR spectra of solid samples were recorded for 16 h using the standard Bruker pulse sequence at 79.5 MHz, a time domain of 1K, a spectral width of 55 KHz, a contact time of 2 ms and an interpulse delay of 5s for ^{29}Si.

Photon Correlation Spectroscopy (PCS, Zetasizer NanoZS instrument, Malvern Instruments) was used to measure the average hydrodynamic particle diameters at different temperatures. Samples were prepared at a certain particle concentration in water. Measurements were carried out from 10 to 55 ºC taking measurements every 2 ºC except from 30 to 40 ºC carried out per grade. The stabilization time between measurements was 10 min. The swelling ratio was calculated following the next expression: $(dp_{10ºC}/dp_{55ºC})^3$, in which $dp_{10ºC}$ is the average hydrodynamic diameter at 10ºC and $dp_{55ºC}$ is the average hydrodynamic diameter at 55 ºC.

Transmission Electron Microscopy (TEM, TECNAI G^2 20 TWIN 200 kV LaB$_6$) was used for the direct observation of the morphology of the hybrid nanogels. The sample was prepared by dilution of nanogel dispersion at about 0.05 wt%. Then, a drop of the dilute sample was placed on copper grids covered with Formvar® (polyvinyl formal) and dried at room temperature.

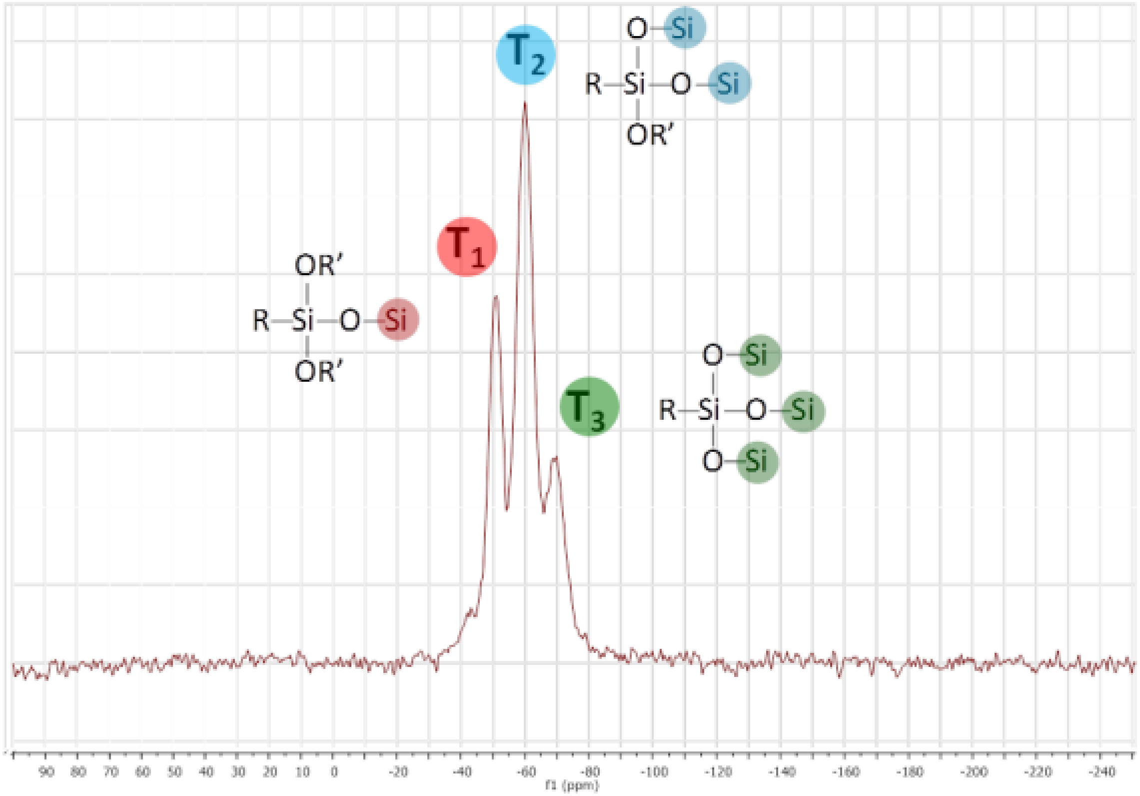

Figure S1. CP-MAS ^{29}Si NMR spectrum of PVCL-based nanogels with a 10 wt% of TPM synthesized at pH 7.