Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Tailored Macroporous Hydrogel-Nanoparticle Nanocomposites for Monolithic Flow-Through Catalytic Reactors

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Experimental section

1.1 Materials

Ethylene propylene diene monomer (EPDM, Keltan 2070p) and poly(ε-caprolactone) (PCL, Capa™ 6500) were purveyed by Lanxess and Perstorp respectively in granular form. *N*-isopropylacrylamide (NIPAam, 99% purity), gold (III) chloride trihydrate ($HAuCl_4.3H_2O$, >99.9% purity), *N,N'*-methylenebis(acrylamide) (MBA, >98% purity), ammonium persulfate (APS, >98% purity), *N,N,N',N'*-tetramethylethylenediamine (TEMED, 99% purity), palladium (II) acetate (>99.9 % purity), sodium borohydride (>99% purity), 2-iodotoluene (99% purity), silver nitrate ($AgNO_3$, 99% purity) and *p*-Nitrophenol (>99% purity) were provided from Sigma-Aldrich. EpoFix resin was obtained from Struers. All products were used as received.

1.2 PCL molds preparation

1.2.1 Polymer blend melt processing

EPDM and PCL polymers (50/50 vol%, based on the densities at 180 °C) were melt-blended in a Plasti-Corder Digi-System internal mixer (C.W. Brabender Instrument Inc.) at 180 °C and 50 rpm for 7 min under a nitrogen flow. After mixing, the samples were quenched in cold water to freeze-in the morphology and subsequently annealed under quiescent conditions at 180 °C for t_{anneal} = 60 or 240 min using a hot press (model 3912 from Carver Inc.).

1.2.2 Polymer molds preparation and phase continuity measurement

The EPDM/PCL blends were trimmed into ≈ 1 cm^3 cubes and placed in cyclohexane for ≈ 14 days (the cyclohexane was changed daily) to selectively dissolve the EPDM polymer phase.

Subsequently, the continuity of the EPDM phase in the blends was evaluated by gravimetry, using **Equation 1** :

$$\text{EPDM continuity in the blend (\%)} = \frac{m_{s,ini} - m_{s,fin}}{m_{s,ini}} \times \frac{m_{blend}}{m_{EPDM\ in\ blend}} \times 100 \quad (1)$$

where $m_{s,ini}$ is the mass of the sample before extraction, $m_{s,fin}$ is the mass of the sample after extraction, m_{blend} is the mass of the original EPDM/PCL blend, and $m_{EPDM\ in\ blend}$ is the mass of EPDM in the original EPDM/PCL blend.

1.3 Porous hydrogels preparation and nanoparticles synthesis

PNIPAam hydrogels were prepared in three steps. First, 0.8 mol.l^{-1} NIPAam, 0.026 mol.l^{-1} MBA and 0.008 mol.l^{-1} APS were dissolved in 10 ml of cold distilled water. Then, the reactant solution was degassed with nitrogen for 15 min and 75 µl of TEMED were added. Finally, the mixture was injected into the porous PCL templates using an in-house system applying pressurized air-vacuum cycles. *In situ* polymerization was carried out at 10 °C for 48 h.

Porous PNIPAam hydrogels were obtained by selectively dissolving the PCL templates in toluene for ≈ 14 days (the toluene was changed daily). The obtained hydrogels were rinsed with methanol and distilled water, and stored in distilled water at 20 °C using a thermostatic bath. Non-porous PNIPAam hydrogels were prepared by pouring the monomer mixture into 1 cm^3 silicone molds covered by ≈ 1 ml of mineral oil.

Prior to nanoparticles synthesis, porous and non-porous PNIPAam hydrogels (equilibrated at 20 °C) were trimmed into ≈ 0.32 cm^3 cylinders (d = 0.82 cm, h = ≈ 0.6 cm). The samples were then individually placed into vials containing 4 ml of a 5 mM metal complex solution ($HAuCl_4$ or $AgNO_3$ dissolved in water, or $Pd(OAc)_2$ dissolved in acetone) at 22 °C for 15 h. Subsequently, the hydrogels were blotted to eliminate the excess of metal solution, and they were individually placed into vials containing 4 ml of a cold (≈ 5 °C) and freshly prepared 50 mM $NaBH_4$ aqueous solution for 30 min. The nanocomposite hydrogels were washed with Milli-Q water for 5-6 days, and stored in Milli-Q water at 20 °C using a thermostatic bath to maintain a constant temperature. Washing the monoliths with Milli-Q water allowed for gas bubbles elimination following nanoparticles synthesis. The reactant solutions were prepared with Milli-Q water, 18.2 MΩ.cm.

1.4 Materials morphology characterization and analysis

1.4.1 Polymer molds

After melt-processing and quiescent annealing, 4 samples of each condition (t_{anneal} = 0, 60 or 240 min) were cryomicrotomed using a Leica RM2165 instrument. Once the EPDM phase extraction was completed, the obtained porous PCL samples were dried under vacuum and were coated with a gold−palladium layer by plasma sputtering (Polaron SC502 Sputter Coater, 18 mA and 0.04 mbar, 2 × 15 s, 10 nm Au−Pd film). Subsequently, the porous molds microstructure was analyzed by scanning electron microscopy (SEM) using a JEOL JSM-7600TFE field operated at 2 keV and 2.6 × 10^{-11} A.

The blends microstructural characteristics were quantified by image analysis. First, 6-10 micrographs were binarized using a digitizing table from Wacom and SigmaScan V.5 software, and

then, the interfacial perimeter *P* was obtained after calibration (see image treatment steps presented in a previous publication).[1] Using ImageJ software, the volume fraction of the pores (or PCL phase) was determined by dividing the number of corresponding pixels by the total number of image pixels. The interfacial area *S* was calculated using **Equation 2** :[2]

$$S = \frac{P}{A} \quad (2)$$

where A is the total area of the analyzed image.

The average pore size (or average PCL domain size) was calculated using **Equation 3** :[3]

$$d_{pores(PCL)} = \frac{4\varphi_{pores(PCL)}}{S} \quad (3)$$

where $\phi_{pores(PCL)}$ is the volume fraction of the pores (or PCL phase).

1.4.2 Porous hydrogels

Porous PNIPAam hydrogels were placed into vials containing a 30% solution of 2-iodotoluene (a radiocontrast agent) in toluene for 2 days. Then, the hydrogels microstructure was observed by X-ray microtomography using a Skyscan 1172 instrument from Brüker with the following parameters : 57 keV (source voltage), 173 µA (source current), 11.56 µm (image pixel size), 16 bits (depth) and 590 ms exposure time. Reconstructions of 2-D and 3-D images were performed with the CTAn and CTvol softwares, respectively.

The hydrogels microstructural parameters were determined with ImageJ software, following the procedure described in section 1.4.1 and using µtomography images (see image treatment steps presented in a previous publication).[1]

2. Nanoparticles characterization

2.1 Transmission electron microscopy (TEM)

Once AuNPs synthesis was completed, two nanocomposite hydrogels (G_{60}, ≈ 1 cm^3 cubes) were abundantly washed with Milli-Q water and placed into vials with Milli-Q water (18.2 MΩ.cm) for 12 h at 20 °C. Then, the gels were cut in smaller pieces and the samples obtained close to the surface (≈ 3 mm from the surface, in-between the gel surface and center) were dried in an oven at 55 °C for 3 h. Subsequently, the dried composite gels were immersed in epoxy resin for 20 h at ≈ 22 °C. Prior to microscope observations, the samples were microtomed at room temperature with a Leica UC7 instrument.

For AgNPs observations, once the synthesis was completed, two nanocomposite gels (G_{240}, ≈ 0.32 cm^3 cylinders) were abundantly washed with Milli-Q water and stored in Milli-Q water for 3 days. Then, the samples were individually placed into vials containing 10 ml of Milli-Q water and they were squashed using an ultrasonic homogenizer (Cole-Parmer, model CP505) at an amplitude of 50% for 1 h. Subsequently, one drop of the solution was placed onto a carbon grid and dried under ambient conditions.

Transmission electron microscopy observations were performed with a JEOL JEM-2100F field emission electron microscope operated at 200 kV.

2.2 Thermogravimetric analysis (TGA)

Thermogravimetric analyses were realized with a Q-500 instrument from TA Instruments. First, porous nanocomposite hydrogels (G_{60} and G_{240}, ≈ 0.32 cm^3 cylinders) were dried in an oven under vacuum at 85 °C for 3 days. Then, between 9-14 mg of each dried nanocomposite gel were heated to 800 °C under a constant nitrogen flow (60.0 $ml.min^{-1}$) at a heating rate of 10 °C.min^{-1}. Between 3-10 samples were analyzed for each gel type. The same procedure was followed to evaluate the residual quantity of hydrogel without NPs.

3. Catalytic reduction

PNIPAam nanocomposite gels trimmed into ≈ 0.32 cm^3 cylinders and equilibrated at 20 °C (section 1.3) were individually placed into chemical-resistant barbed tubes (internal diameter *d* = 0.8 cm) and equilibrated at 10 °C (to ensure hydrogel swelling inside the tube) for 24 h. Subsequently, the monoliths-charged tubes were fixed to a reactor system equipped with a syringe pump (Cole-Parmer, model 200, syringe volume = 140 ml) and a manometer. For each cycle, the syringe was filled with 60 ml of a 0.3 mM *p*-Nitrophenol aqueous solution and 60 ml of a 50 mM $NaBH_4$ aqueous solution (freshly prepared. Note that in the absence of catalytic nanoparticles, no reaction was observed up to 8 h (tests conducted during 8 h). The liquid flow rate was regulated by the syringe pump. The solution passing through the monolith was collected during 5 min into a new vial. For each flow rate value, the reactant solution was initially flowed through the monoliths during ≈ 15 min without taking measurements. At flow rates of 20 and 120 $ml.h^{-1}$, data points correspond to the average of 12 measurements taken at 5 min intervals. At flow rate of 80, 200 and 250 $ml.h^{-1}$, data points correspond to the average of 3 measurements taken at 5 min

intervals. Following the positioning of each monolith into the reactor system, the flow rate was regulated consecutively (from 20 to 250 ml.h^{-1}) for a total experiment duration of about 3 hrs. Spectra were obtained with a SFM-400 spectrometer from BioLogic and were recorded over 250 - 550 nm using a 1 cm path-length quartz cuvette.

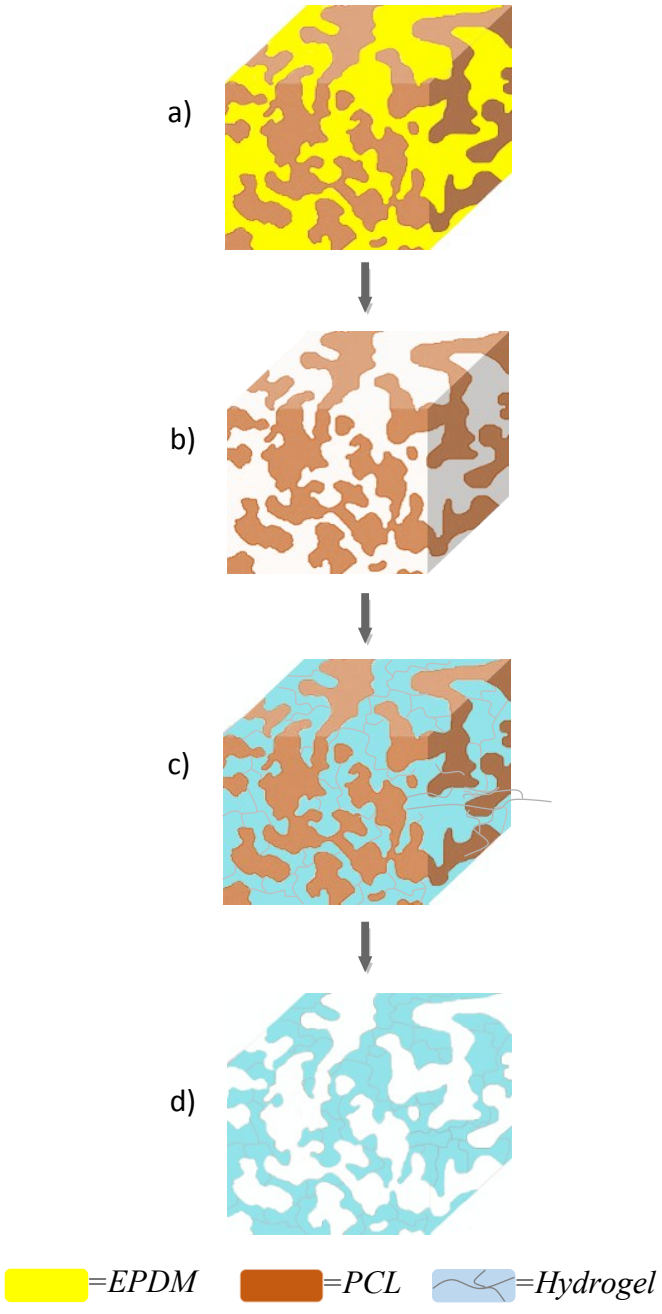
Table S1 : PCL molds microstructural characteristics as a function of the quiescent annealing time (t_{anneal}).[1]

Annealing time (min)	**EPDM continuity (%)**	**Φ_{pores} (%)**	**Φ_{PCL} (%)**	**Specific surface area S (cm^{-1})**	**Average pore diameter d_{pores} (µm)**	**Average PCL domain diameter d_{PCL} (µm)**
0	102 (± 1)	54 (± 4)	46 (± 4)	1180 (± 145)	19 (± 2)	16 (± 2)
60	102 (± 1)	51 (± 2)	49 (± 2)	187 (± 7)	109 (± 4)	105 (± 4)
240	104 (± 1)	51 (± 5)	49 (± 5)	65 (± 1)	310 (± 4)	298 (± 4)

Table S2 : PNIPAam hydrogels porosity characteristics as a function of the polymer blends quiescent annealing time (t_{anneal}).[1]

Annealing time (min)	Φ_{pores} (%)	Φ_{gel} (%)	Specific surface area S (cm^{-1})	Average pore diameter d_{pores} (µm)	Average gel domain diameter d_{gel} (µm)
0	40 (± 2)	60 (± 2)	850 (± 180)	23 (± 9)[a]	31 (± 15)
60	42 (± 1)	58 (± 1)	169 (± 7)	101 (± 6)[a]	135 (± 5)
240	49 (± 4)	51 (± 4)	77 (± 10)	262 (± 34)	280 (± 65)

[a] Value estimated with a digitizing table, between 12-15 measurements per image (6-7 µCT images).


a)
b)
c)
d)
=EPDM
=PCL
=Hydrogel

Scheme S1 : Macroporous hydrogels preparation using cocontinuous polymer blends : a) EPDM/PCL blend; b) porous PCL mold obtained after EPDM polymer phase extraction; c) PCL mold filled with hydrogel; d) porous hydrogel obtained after PCL phase extraction.[4]

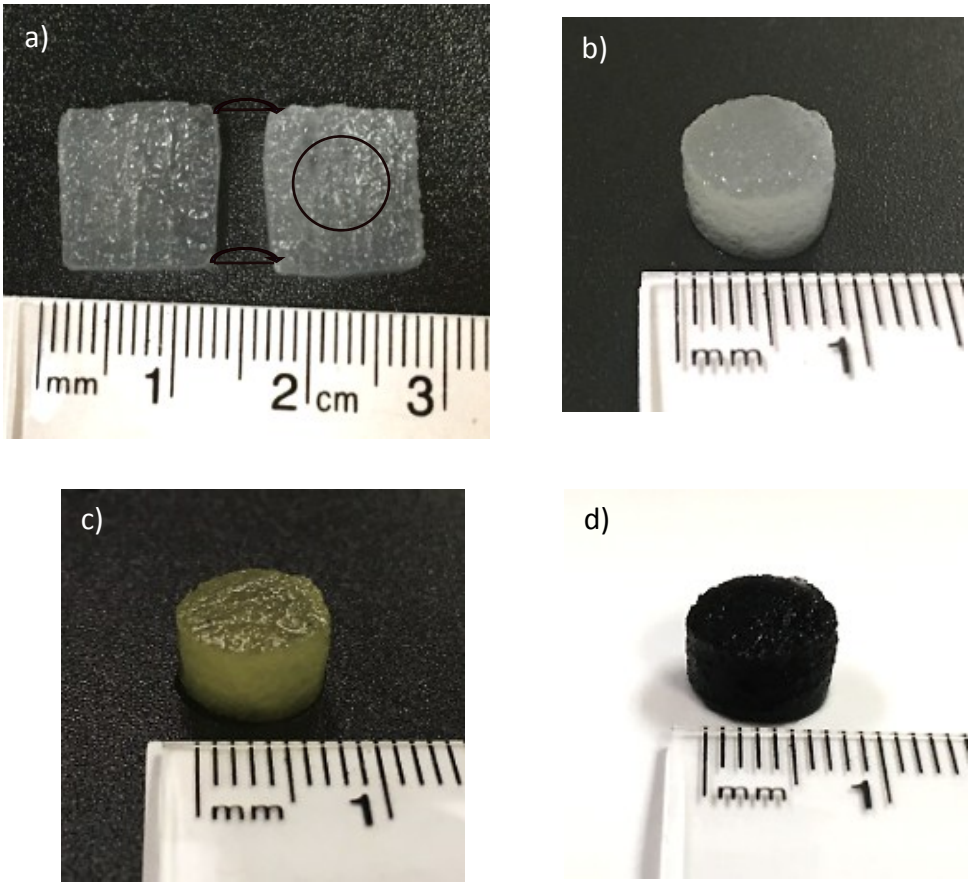


Figure S1 : Successive steps for the preparation of macroporous nanocomposite PNIPAam monoliths (illustrated for G_{240} gel) : a) porous hydrogel (≈ 1.2 cm^3 cube) trimmed in half ; b) porous monolith (≈ 0.32 cm^3) obtained after trimming one of the hydrogel halves; c) porous monolith loaded with gold ions; d) porous monolith embedded with AuNPs.

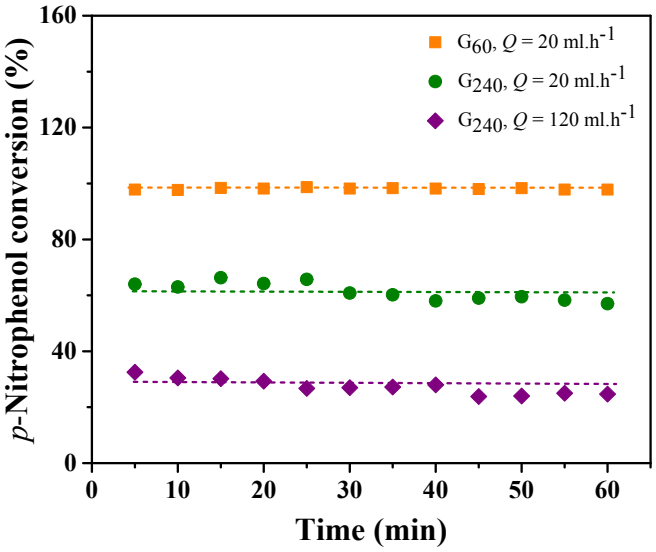


Figure S2 : *p*-Nitrophenol conversion as a function of time, flow rate (*Q*) and average pore size of PNIPAam monoliths loaded with AuNPs (the same monoliths samples were used at *Q* = 20 and 120 ml.h^{-1}, which maintained a constant catalytic activity for at least 3 h (between Q = 20 and 120 ml.h^{-1}, the measurements were conducted at Q = 80 ml.h^{-1} during 15 min. After each regulation of the flow rate, the reactant solution was flowed through the monolith for ≈ 15 min). Each data point corresponds to the average of 3 samples. Standard deviations are comprised in-between nearly 0% to 13% of the average value.

REFERENCES

1. T. Gancheva and N. Virgilio, *Macromolecules*, 2016, **49**, 5866-5876.

2. J. A. Galloway, M. D. Montminy and C. W. Macosko, *Polymer*, 2002, **43**, 4715-4722.

3. J. Li and B. Favis, *Polymer*, 2001, **42**, 5047-5053.

4. T. Gancheva and N. Virgilio, *ACS Applied Materials & Interfaces*, 2018, **10**, 21073-21078.