Supporting information for

High Molar Mass Polymers by Cationic Polymerisation in Emulsion and Miniemulsion

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Experimental part

Materials
Unless otherwise stated, all analytical grade products (purity superior to 99%) were purchased from Aldrich. Distilled water was checked by conductimetry prior use. \( p \)-methoxystyrene \((p\text{MOS})\) was purchased from various providers, but only the product from Acros was of sufficient purity (98%) and stability to be used further in these experiments. Ytterbium triflate \((\text{Yb(OTf)}_3, 6\text{H}_2\text{O})\) was kindly given by Rhodia Terres Rares; it was ensured by measuring the pH of a 1 M water solution that it did not contain traces of triflic acid (contrary to some commercial products). Ytterbium chloride \((\text{YbCl}_3, 6\text{H}_2\text{O}, \text{99.9\%})\) and pentachlorophenol (99%, caution: highly toxic product in contact with skin or inhalation) were used as received. Sodium polyoxyethylene (8) lauryl sulfate \((\text{C}_{12}\text{H}_{25}(\text{O-CH}_2-\text{CH}_2)_8\text{OSO}_3\text{Na}, \text{30\% water solution})\) is a generous gift of Cognis (sold under the brand Disponil Fes32is).

Methods
Molar mass measurements were performed using a SEC apparatus equipped with a Viscotek VE 5200 GPC autosampler, a Waters 515 HPLC pump, a LDC Analytical differential refractometer. Three 30cm columns from PSS (PSS SDV linear) were thermostated in a Croco-cilTM oven set at 40°C. Samples were diluted in THF at a concentration of 5 mg.mL\(^{-1}\) prior injection, and eluted at a flow rate of 1 mL.min\(^{-1}\) (the residual monomer was taken as an internal standard for flow corrections). Molar masses were calculated on the TriSec software from the Viscotek company, using a polystyrene calibration curve build with narrow standards of \( M_w = 2 \times 10^2 \text{ to } 10^6 \text{ g.mol}^{-1}\).

Particle sizes were measured on a MALVERN ZETA SIZER 4 apparatus. Samples were prepared by diluting one drop of the miniemulsion in a solution of surfactant (at a concentration below CMC, typically \( 10^{-4} \text{ M} \)) to maintain the droplets in suspension while carrying out the measurements. Transmission electron microscopy (TEM) was performed on a JEM100CXII UHR apparatus from GEOL, with an acceleration tension of 100kV. The sample
was first diluted, then a drop was deposited on a carbon grid. Scanning electron microscopy (SEM) was carried out on a S440 device from LEICA. The sample was directly diluted on a glass slide and sputtered with a thin layer of gold to favour the electron conduction.

$^1$H and $^{13}$C NMR spectroscopies were carried out on a Brücker AC200 (200 MHz frequency) and a Brücker ARX300 (300 MHz frequency), respectively. Samples were dissolved either in deuterated water (acid + surfactant complex analysis) or CDCl$_3$ (polymer analysis).

MALDI-TOF spectroscopy was performed on a PerSeptive Biosystems Voyager Elite spectrometer calibrated with polystyrene standards. 10 µL of a polymer solution (1 g.L$^{-1}$, THF) is mixed with 50µL the dithranol matrix solution (2 g.L$^{-1}$, THF) and 10 µL of a NaI solution (5 g.L$^{-1}$, THF) that promotes polymer cationisation. 1µL of the final solution is deposited on the target before accumulating the spectrogram (256 scans at a repetition rate of 3 Hz, acceleration tension of 20 kV).

(Mini)emulsion polymerisation procedure

Triflate ytterbium and surfactant were first diluted in water and mixed under a magnetic agitation until the solution became limpid. PCP was added straight in the monomer, but it was checked that no polymerisation occurred while preparing the emulsion. The two mixtures were poured together in a beaker, cooled in a ice bath while carrying out the sonication using a Sonifier 450 from Branson Ultrasonics Corporation (probe diameter: 13 mm; power: 55 W; time: 1½ min). The emulsion was then divided in several parts, poured in big test tubes thermostated in a water bath regulated at 60°C (magnetic agitation was ensured by a multiple rotor plate placed below the bath).

0.5 mL samples were withdrawn regularly and treated separately. First, reaction was stopped by pouring the sample in excess methanol and then in excess water, not to discard the monomer soluble in methanol. 1 mL of dichloromethane was added to ease the organic phase separation, particularly at high monomer conversion. After agitation during 15 min, the biphasic system was centrifuged during 30 mn on a bench centrifuge (4000 rpm). The organic phase was then dried on anhydrous MgSO$_4$ before evaporating CH$_2$Cl$_2$. Monomer and polymer conversion were determined by SEC, without correcting for the respective refractive indexes.

Two sets of conditions were tested, that we refer in the main text as “concentrated” and “diluted” conditions, in which cases whether an emulsion or a miniemulsion were obtained respectively. For the former, we used the following recipe: $[p$MOS$]= 2.2$ M; $[surfactant]= 0.25$ M; $[Yb(OTf)_3] = 0.21$ M; 60°C. Total volume =7 mL. In diluted conditions, the recipe
was as follows: \([p\text{MOS}]=1.5\text{M}; [\text{surfactant}]=0.17\text{M}; [\text{Yb(OTf)}_3]=0.15\text{M}; 60^\circ\text{C}\). Total volume = 10mL. Initiator conditions were varied, and concentrations are given in table 1 in the main text.

**Other polymerisation procedures**

Conventional cationic polymerisation of pMOS was performed in thoroughly purified dichloromethane (distilled twice, dried over CaH2), at 10°C, simply breaking an ampoule of triflic acid \(([\text{CF}_3\text{SO}_3\text{H}]=2.5\times10^{-4}\text{M})\) in the monomer solution \(([p\text{MOS}]=5.55\times10^{-2}\text{M})\). Polymerisation proceeded readily (in less than 10s, according to stop-flow kinetics experiments) until full conversion. The polymer was deactivated and purified by precipitation. 

\(M_n=17.5\ \text{kg.mol}^{-1}; M_n/M_n=2.5\) (trimodal distribution).

Free radical polymerisation of pMOS was performed in bulk, at 100°C, using persulfate potassium as an initiator \(([\text{K}_2\text{O}_8\text{S}_2]=2.2\times10^{-2}\text{M})\). Conversion after 1 hour was 74%. 

\(M_n=21500\ \text{kg.mol}^{-1}; M_n/M_n=2.1\).
Figure S1: $^1$H NMR spectrum of the surfactant alone (top) and complexed by ytterbium triflate (bottom).
**Figure S2** Evolutions of particle size (●) and size distribution (◇) with time for the model experiment (run 1, Table 1). Maximum polydispersity available on the apparatus is 1.41.
Figure S3 Monomer conversion versus time for different runs. (a) concentrated conditions (from bottom to top, runs 1,5-8); (b) diluted conditions (from bottom to top, runs 10-13).
Figure S4 Polymer (●); oligomer (▲) and total (□) conversions versus PCP concentrations (table 1, runs 1, 5-9).