Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Mild synthesis of poly(HEMA)-networks as well-defined nanoparticles in supercritical carbon dioxide

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Supporting Information

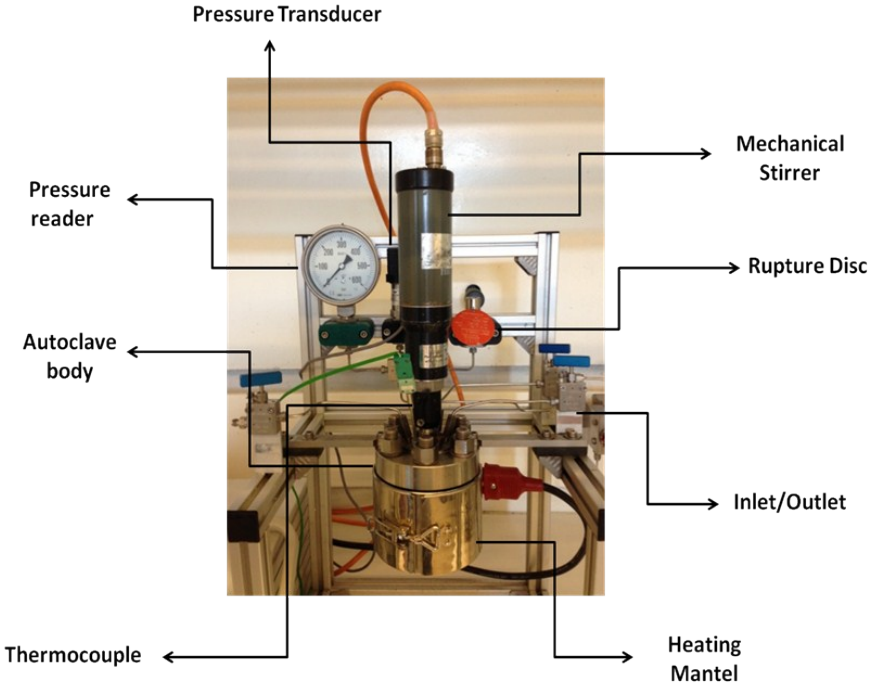


Figure S1: High pressure stainless steel cell (82mL, ToP Industrie) used for dispersion polymerisation of 2-hydroxyethyl methacrylate (HEMA). It is equipped with a mechanical stirrer, a pressure transducer, a rupture disc, and an internal thermocouple. 3 different interchangeable valves are used as inlet or outlet. The body of autoclave is bolted to the head of the reactor with 6 housings and a key is used to securely tighten the bolts. Internal parameters (temperature, pressure and stirring rate) are monitored by temperature control box containing an Auto-Adaptive PID controller. Carbon dioxide (I5122, CO_2 N27/N48, Air Liquide, Belgium) is transferred to cell via ISCO 260D model syringe pump which is designed to handle and transfer supercritical fluids for research purposes. The pump has 266 ml of CO_2 capacity

and can go up to pressures to 7500 psi (571 bar). As well as flow rate of the CO_2 can be adjusted in a wide range allowing constant desired flow of CO_2. The syringe is controlled by an LCD monitor attached to it. Syringe is connected and filled with CO_2 directly from the CO_2 tank with proper piping. The initial pressure on the syringe screen is equal to CO_2 bottle which is usually around 55 bar. Thereafter CO_2 is pressurised by the cylinder in the pump to the working pressures.

Figure S2: ISCO 260D® pump with one cylinder and LCD control unit.

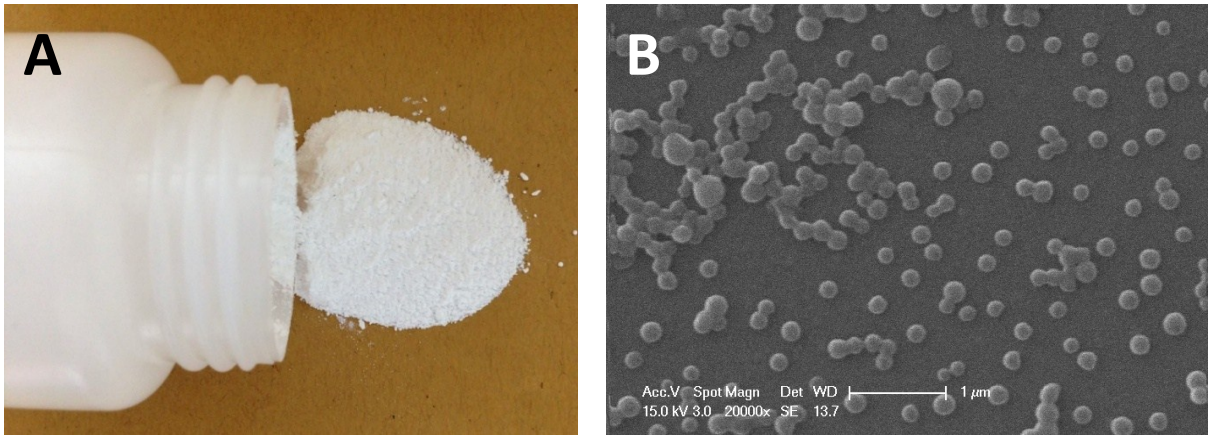
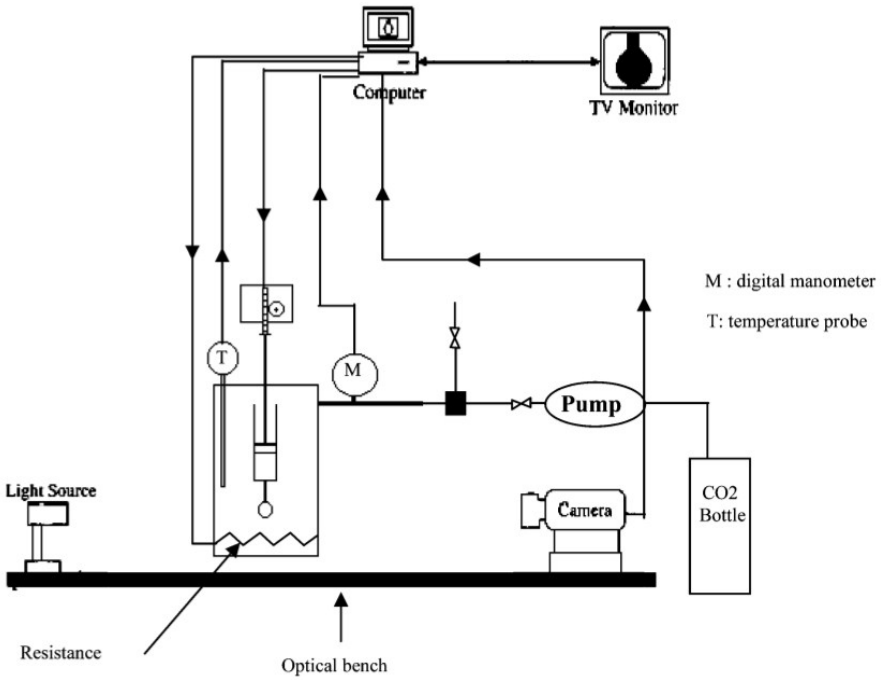


Figure S3: A) Representative photo of the free-flowing dry powder obtained by dispersion polymerisation in supercritical carbon dioxide in presence of a stabilizer as collected straight after polymerization from the high pressure reactor, i.e. without further treatment or purification (B) SEM image of the corresponding powder.

A)



B)

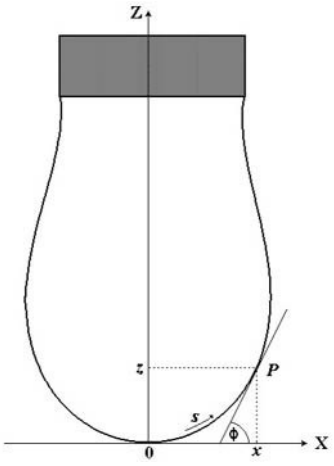


Figure S4: The interfacial tension is measured by first digitizing and analysing a drop of water pending in CO_2 containing the stabilizer by using a CCD camera coupled to a video image profile digitizer board connected to the computer (A). The drop profile (B) was processed according to the fundamental Laplace equation (eq 1):

$$\frac{1}{x}\frac{d}{dx}(x\,sin\Phi) = \frac{2}{S} - cz \quad (1)$$

where x and z are the Cartesian coordinates at any point of the drop profile, S is the radius of the curvature of the drop apex, and ϕ is the angle of the tangent to the drop profile. In addition, c is the capillarity constant, equal to "$(g\rho)/\gamma$", where ρ is the difference between the densities of the two liquids and g is the acceleration due to gravity. Five times per second, the computer calculates the characteristic parameters of the drop (area, volume, and interfacial tension). Data from at least three measurements were averaged for each polymer concentration and displayed a maximum variation lower than 2%.

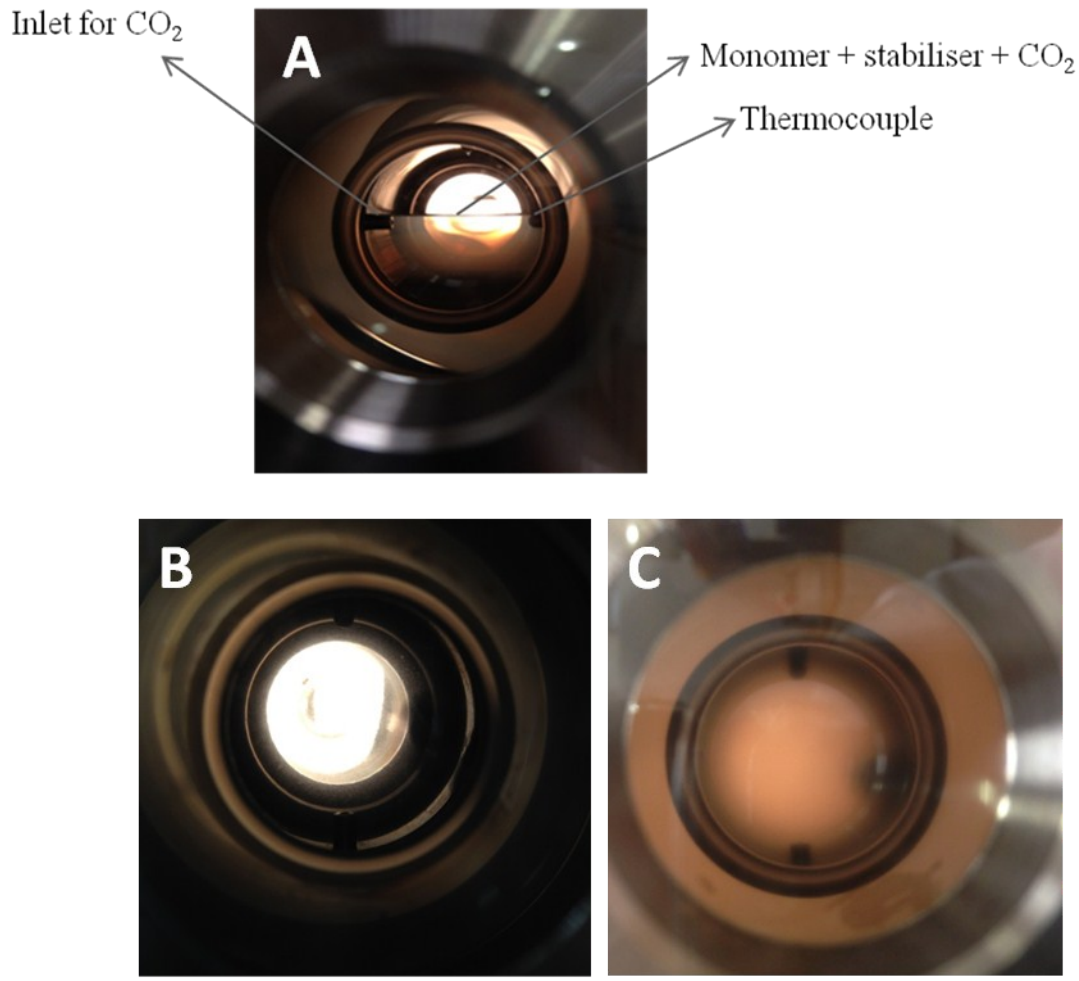


Figure S5: Photos of the view cell used for cloud point measurement. Image A shows the starting situation at room temperature and low pressure where CO_2 is liquid. At higher pressure and higher temperature, image B shows a condition where the stabiliser, monomer and CO_2 mixture is one phase indicating the full solubility in supercritical conditions, image C illustrates the turbidity observed while the mixture starts to be insoluble lowering the pressure.

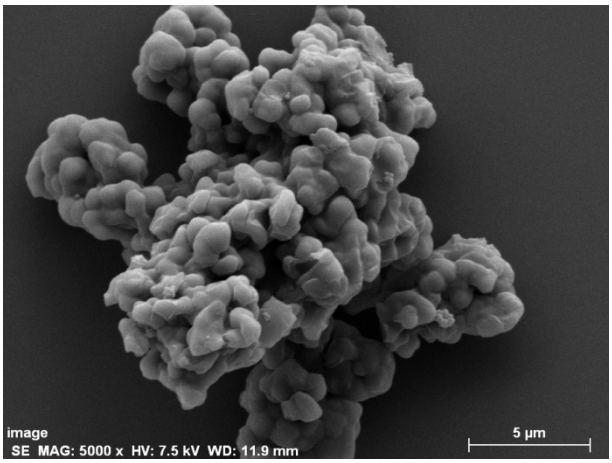


Figure S6: Scanning electron microscopy (SEM) image for the polyHEMA powder obtained when the polymerisation is performed in absence of stabiliser.