Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Synthesis and self-assembly of carbamoylmethylphosphonate acrylamide-based diblock copolymers: new valuable thermosensitive materials

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EXPERIMENTAL PROCEDURES

Nuclear Magnetic Resonance (NMR). Bruker Advance DRX 300 (300Hz) was used to record ^{1}H NMR spectra in DMSO-d_6 as deuterated solvent purchased from Eurisotop. The conversion rate of CPAAm6C was calculated comparing the relative intensity of the peak at 4 ppm (P-(O-CH_2-CH$_3$)$_2$ of monomer and polymer) to signals between 5.5 ppm and 6.3 ppm (acrylic protons of the monomer). For the P(AA) block, the relatives intensities of acid acrylic protons were compared to the relative intensities of phosphonate protons at 4.01 ppm of the P(CPAAm6C) block thus used as an internal probe.

Size Exclusion Chromatography (SEC). SEC was performed with a Varian 390-LC equipped with a refractive index detector. PolarGel M columns calibrated with poly(methyl methacrylate) (PMMA) standards were used at 60 °C with a flow rate of 0.8 mL.min^{-1}. Elution solvent was DMF (+ 0.1 %wt LiCl).

Cloud points measurements. Thermosensitivity of the polymers was estimated by a change in the transmittance through the polymer solution with temperature. The measurement of the transmittance was carried out of polymer aqueous solutions at a concentration equal to 5 g.L^{-1} with a Perkin Elmer Lambda 35 UV-Visible spectrometer equipped with a Peltier temperature programmer PTP-1+1. A wavelength of 500 nm was selected. The temperature ramp was 0.1 °C per minute. In the case of the copolymers, pH was adjusted at 8 with small quantity of 0.1N sodium hydroxide solution.

Static Light Scattering (SLS) measurements. Light scattering measurements were recorded on a Malvern Zetasizer Nano Series equipped with a He-Ne laser (λ = 632.8 nm). The samples were prepared by direct dissolution of copolymer in milli Q water, and were introduced into the cells (pathway: 10 mm) after filtration through 0.45 µm PTFE microfilters. Polymer concentration varied from 1.10^{-3} to 1 g.L^{-1}. pH was adjusted at 8 with a very small quantity of 0.1N sodium hydroxide aqueous solution.

Syntheses

Typical procedure for the RAFT polymerization of diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate (CPAAm6C). CPAAm6C monomer (1 g, 2.86 mmol), 2-cyano-2-propyl dodecyl trithiocarbonate (CTA) (39.4 mg, 0.11 mmol) and 2,2'-azobisisobutyronitrile (AIBN) (9 mg, 0.055 mmol) were dissolved in DMSO. The mixture was deoxygenated by five freeze pump thaw cycles and placed under nitrogen. The Schlenk tube was then immersed in a thermostated oil bath at 80 °C. The reaction was stopped after 240 minutes. The polymer was purified by cryodistillation to remove DMSO. Then a dialysis against water was performed with regenerated cellulose membrane with a cut off 2000 Da during three days to remove CPAAm6C monomer traces. The resulting aqueous solution was lyophilized leading to P(CPAAm6C) as a white solid.

^{1}H NMR (DMSO-d_6, 300MHz) δ (ppm): 0.86 (t, -CH_3 of CTA), 1.15-1.44 (m, -CH_2-CH-, -CH_2- of the CTA, and PO-CH$_2$-CH_3), 3.01-3.14 (m, HNCH_2 and CO-CH_2-PO), 3.97-4.06 (m, PO-CH_2-CH$_3$).

$M_{n,exp\ NMR}$ = 6700 g.mol^{-1}; $M_{n,\ exp\ SEC}$ = 5900 g.mol^{-1}; $Đ$ = 1.25.

*Typical procedure for the one-pot synthesis of poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate-*b*-acrylic acid) (P(CPAAm6C-*b*-AA)) diblock copolymer by RAFT polymerization.* The procedure described previously was used for the synthesis of the P(CPAAm6C) homopolymer. After 240 minutes, acrylic acid (0.26 mL, 3.82 mmol) previously degassed by a nitrogen flow was added. The reaction was stopped after a night at 80 °C. The polymer was purified by a cryodistillation to remove acrylic acid and DMSO. Then a dialysis against water was performed with regenerated cellulose membrane with a cut off 2000 Da during three days to remove CPAAm6C monomer. The resulting aqueous solution was lyophilized leading to P(CPAAm6C-*b*-AA) as a yellow solid.

^{1}H NMR (DMSO-d_6, 300MHz) δ (ppm): 1.15-1.44 (m, -CH_2-CH- and -PO-CH$_2$-CH_3), 3.01-3.14 (m, HNCH_2 and CO-CH_2-PO), 3.97-4.06 (m, PO-CH_2-CH$_3$).

$M_{n,exp\ NMR}$ = 6700-1950 g.mol^{-1}.

CHARACTERIZATION BY SEC OF THE POLYMER SYNTHESIS

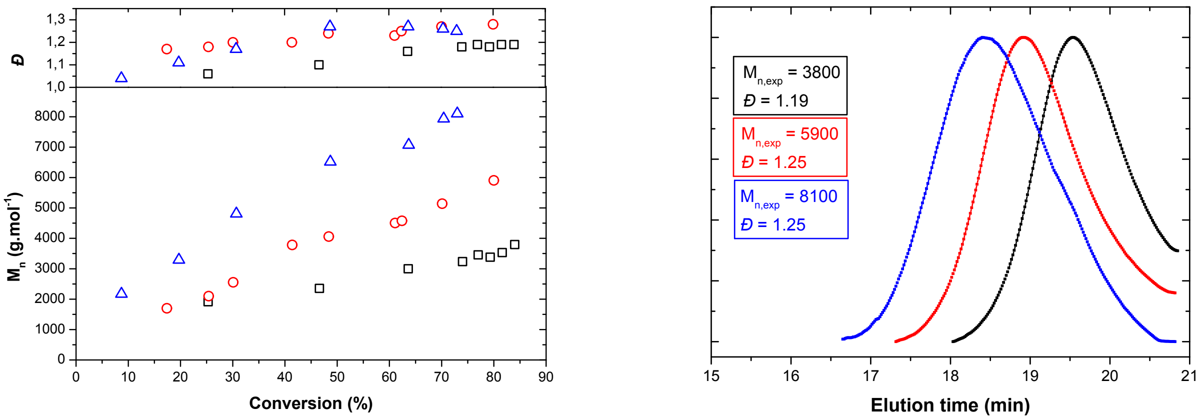

Fig. S1 left: Evolution of the molecular weight (M_n) and dispersity (*Đ*) *versus* conversion, and right: Size exclusion chromatograms, for the P(CPAAm6C)-CTA homopolymers prepared by RAFT controlled radical polymerization.

CHARACTERIZATION BY ^{1}H NMR OF THE POLYMER SYNTHESIS

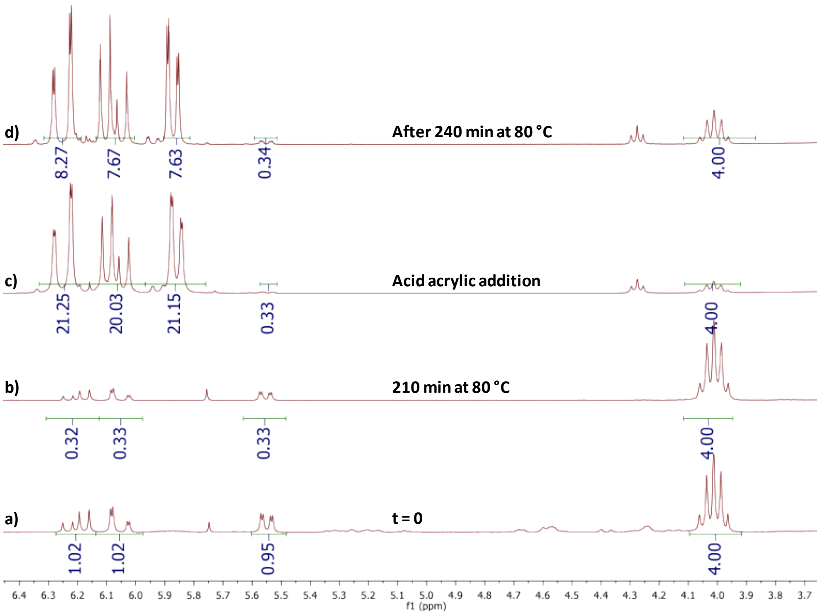

Fig. S2 ^{1}H NMR spectra in DMSO-d_6 during the one-pot synthesis of the P(CPAAm6C-*b*-AA)_2 copolymer: a) CPAAm6C monomer at t = 0, and b) after 210 min at 80 °C. Then, c) and d) were recorded just after and 240 min after the addition of acrylic acid, respectively.