Supplementary Information

Water dynamics and self-assembly of single-chain nanoparticles in concentrated solutions

Beatriz Robles-Hernández,[*ab] Edurne González,[b‡] José A. Pomposo,[abc] Juan Colmenero[abd] and Ángel Alegría[*ab]

[a] *Departamento de Polímeros y Materiales Avanzados: Física, Química y Tecnología, University of the Basque Country (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain*
[b] *Centro de Física de Materiales, Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain*
[c] *IKERBASQUE-Basque Foundation for Science, María Díaz de Haro 3, E-48013 Bilbao, Spain*
[d] *Donostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain*
‡ Present address: *POLYMAT, Kimika Aplikatua saila, Kimika Fakultatea, University of the Basque Country (UPV/EHU), Joxe Mari Korta Zentroa, Tolosa Hiribidea 72, 20018 San Sebastián, Spain*

1 Additional characterization techniques

1.1 Dynamic Light Scattering (DLS)

A Malvern Zetasizer Nano ZS apparatus was used to determine the hydrodynamic radius of the samples in deionized water. The "size distribution by number" plot was employed in this work.

1.2 Size-Exclusion Chromatography / Multi-Angle Laser Light Scattering (SEC/MALLS)

For the amphiphilic poly(OEGMA-*ran*-AEMA) and poly(OEGMA-*b*-AEMA) copolymers, SEC/MALLS measurements were performed at 30 ^{o}C on an Agilent 1200 system equipped with PLgel 5μm Guard and PLgel 5μm MIXED-C columns, a differential refractive index (RI) detector (Optilab Rex, Wyatt) and a multi-angle laser light scattering (MALLS) detector (MiniDawn Treos, Wyatt). Data analysis was performed with ASTRA Software from Wyatt (poly(OEGMA)-based polymers: dn/dc= 0.115, on-line determination). The same procedure was followed for poly(OEGMA). THF was used as eluent at a flow rate of 1 ml/min.

1.3 ^{1}H Nuclear Magnetic Resonance (^{1}H-RMN)

^{1}H-NMR spectra were recorded at room temperature on a Bruker spectrometer operating at 400 MHz using $CDCl_3$ as solvent.

2 Suporting data

2.1 Comparison of hydrodynamic sizes by DLS measurements

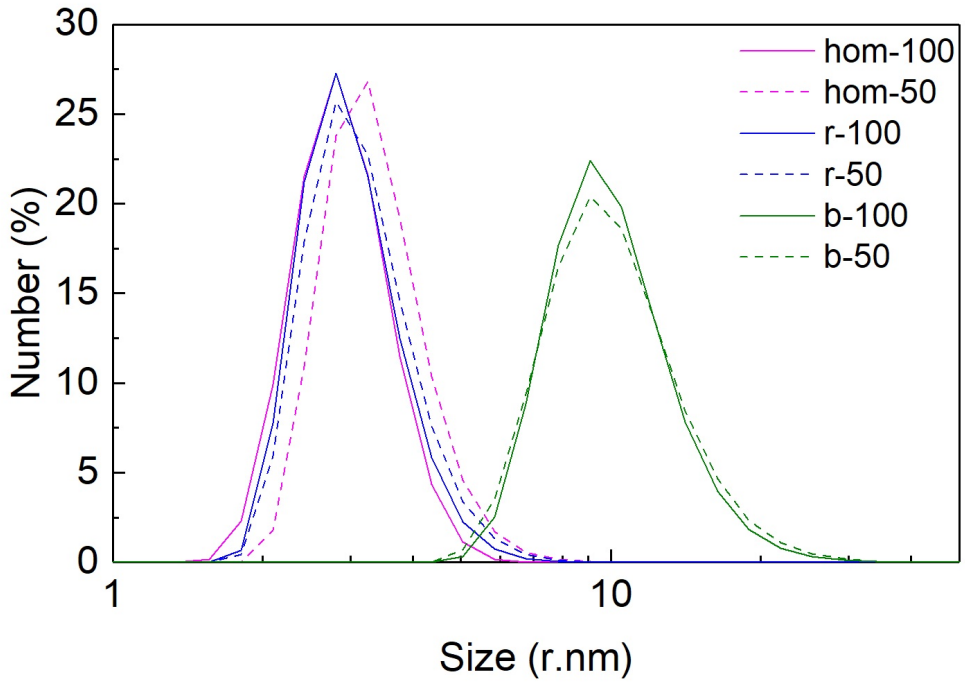


Figure 1 Hydrodynamic size distributions for a P(OEGMA) polymer (pink lines), an amphiphilic poly(OEGMA-*ran*-AEMA) random copolymer (blue lines) and an amphiphilic poly(OEGMA-*b*-AEMA) block copolymer (green lines) at 50 mg/mL (dashed lines) and 100 mg/mL (solid lines) in water, as determined by DLS.

Table 1 Hydrodynamic radius of the samples.

Sample	wt frac. water	wt frac. OEGMA	DLS R_H (nm)
ran-50	0.952	0.042	3.2
ran-100	0.909	0.079	3.1
hom-50	0.952	0.048	3.4
hom-100	0.909	0.091	2.9
b-50	0.952	0.018	10.5
b-100	0.909	0.033	10.3

2.2 SEC traces of the polymers synthesized in this work

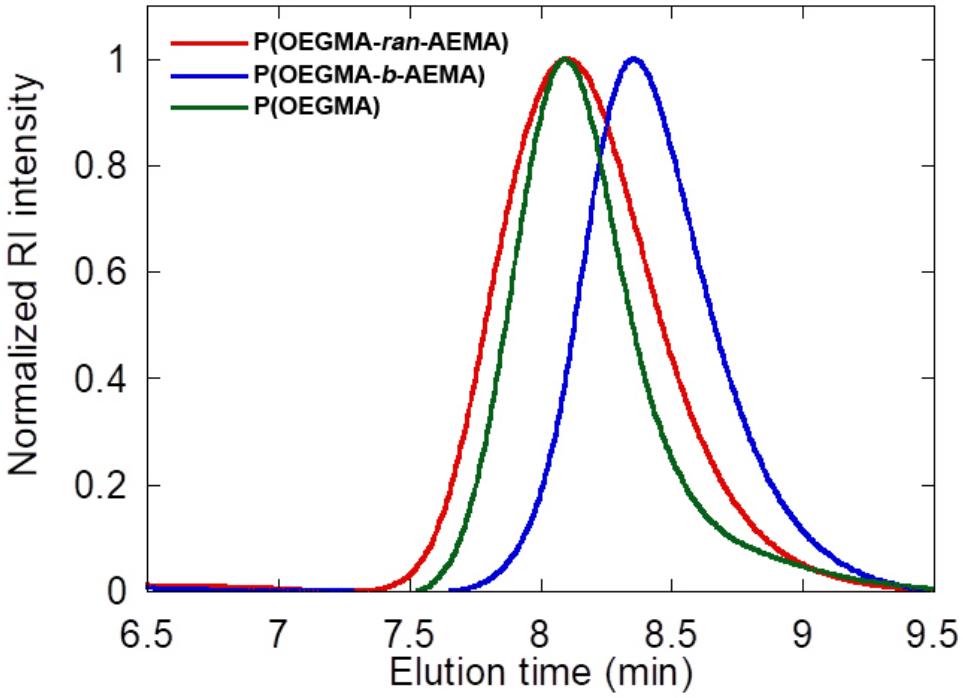
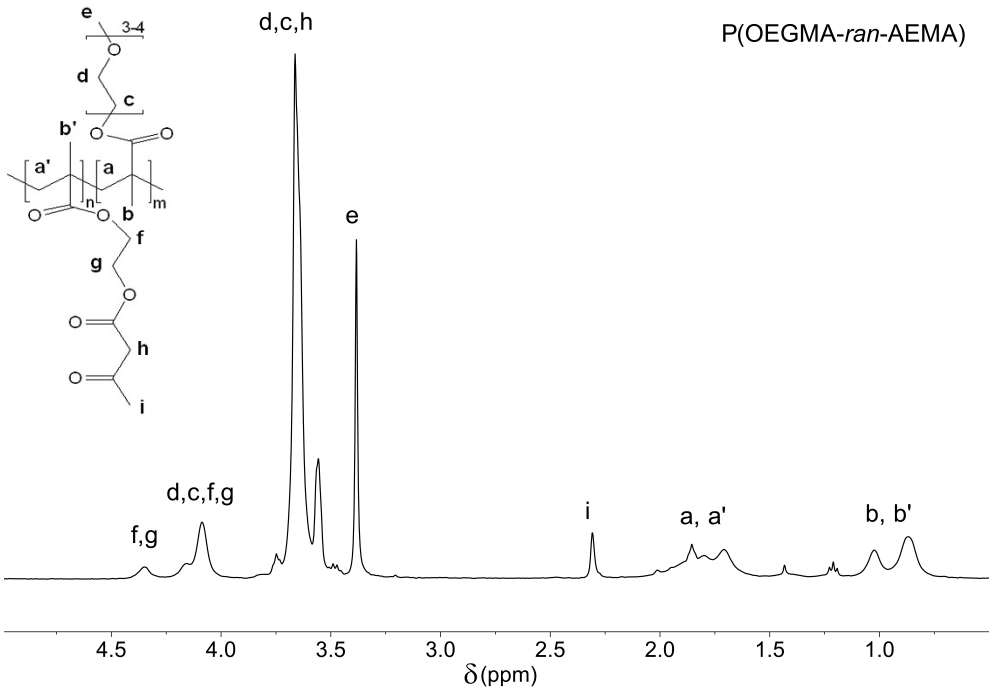
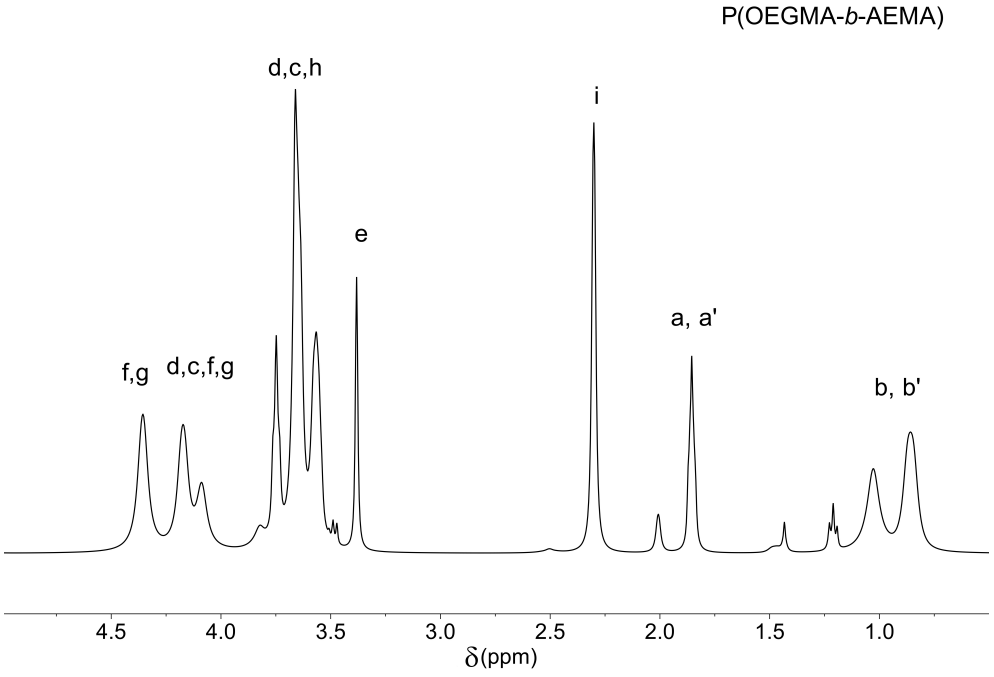


Figure 2 SEC traces in THF corresponding to a P(OEGMA) polymer (green line), an amphiphilic poly(OEGMA-*ran*-AEMA) random copolymer (red line), and an amphiphilic poly(OEGMA-*b*-AEMA) block copolymer (blue line).

2.3 ^{1}H-NMR spectra of the polymers synthesized in this work





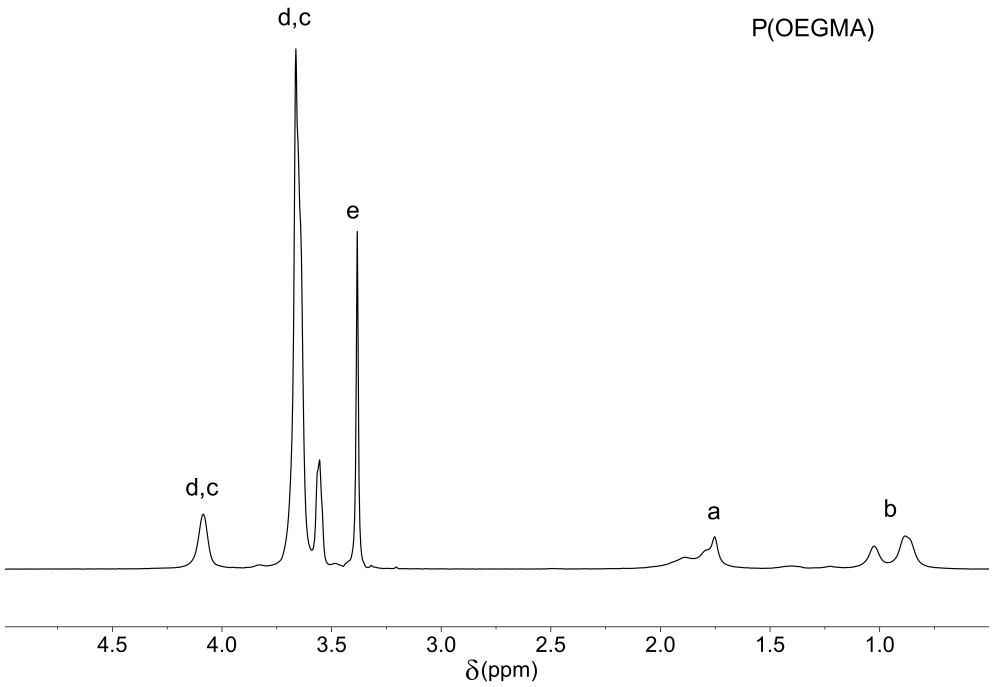


Figure 3 The ^{1}H-NMR spectrum of the amphiphilic poly(OEGMA-*ran*-AEMA) random copolymer, the amphiphilic poly(OEGMA-*b*-AEMA) block copolymer, and the P(OEGMA) homopolymer in $CDCl_3$ and the corresponding proton assignments.