Supporting Information

Preparation of hydrophobically modified associating multiblock copolymers via a one-pot aqueous RAFT polymerization

Claude St Thomas,*[a] Cesar Nadem Muñoz López,[b] Enrique Javier Jiménez Regalado,*[b] Marco Antonio de Jesús Tellez,[c,d] Grit Festag,[d, e] Ulrich S. Schubert,[d, e] Carlos Guerrero-Sánchez*[d, e]

a) CONACYT- Centro de Investigación de Química Aplicada (CIQA) Departamento de Procesos de Polimerización, Blvd. Enrique Reyna, 140, 25294, Saltillo, Coahuila, México,

b) Centro de Investigación de Química Aplicada (CIQA) Departamento de Procesos de Polimerización, Blvd. Enrique Reyna, 140, 25294, Saltillo, Coahuila, México.

c) Centro de Investigación y Estudios Avanzados (CINVESTAV), Unidad Mérida, km 6, antigua carretera Mérida-Progreso, 97310, Mérida, Yucatán, México.

d) Jena Center for Soft Matter (JCSM), Friedrich-Schiller-University Jena, Philosophenweg 7, 07743, Jena, Germany.

e) Laboratory of organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstrasse 10, 97743, Jena, Germany

Corresponding authors: claude.stthomas@ciqa.edumx, enrique.jimenez@ciqa.edu.mx, carlos.guerrero.sanchez@uni-jena.de

Materials

The hydrophobic monomer, *N, N'*-Dihexylacrylamide (DHAM) was prepared as reported elsewhere.[1] The RAFT chain transfer agent, S,S''-Bis (α, α'-dimethyl-α''-acetic acid) trithiocarbonate (DMAT) was synthesized as previously reported.[2] Methanol, chloroform-d ($CDCl_3$, 100%, 99.96 atom % D); dimethyl sulfoxide (DMSO-d_6, 100%, 99.96 atom % D); dehexylamine (97%), acryloyl chloride (97% contains 210 ppm MEHQ as stabilizer), triethylamine ((TEA), 99%) hydrochloric acid ((HCl) ACS, reagent, 37%), sodium chloride ((NaCl), anhydrous, 99%) hexane (anhydrous), diethyl ether (ACS reagent, anhydrous, 99% contains BHT as inhibitor), sodium bicarbonate (ACS reagent, anhydrous, 99.7%), silica gel (30 mesh) and 4, 4'-Azobis(4-cyanopentanoic acid (ACPA, ≥98.0% (T)) were purchased from Sigma Aldrich, USA and used as received. Water was deionized before use (Purelab classic UV, Elgalab water). All polymerizations were performed under mechanical agitation and argon atmosphere.

Synthesis of hydrophobic monomer DHAM.

In a three neck-bottom flask equipped with a condenser, an addition funnel and a septa for purging N_2 gas through the system, a solution of dihexylamine (29.7 g, 0.18 mol) dissolved in 100 mL of diethyl ether was added to triethylamine (TEA, 18.2 g, 0.18 mol). The mixture was kept under stirring agitation. Next, a solution of acryloyl chloride (16.3 g, 0.18 mol) dissolved in 100 mL of diethyl ether was added dropwise into the previous mixture while cooling the reactor at 0 ºC due to exothermic nature of this reaction. The reaction was kept under constant agitation for 24 h.

Afterwards, the reactor was opened to air and the mixture was filtered to remove the formed salt. Further, a diluted solution of HCl (150 mL with a concentration of 10 vol. %) was added into the reaction mixture to neutralize residual TEA with the aid of a separation funnel. The organic phase was washed with an aqueous solution of $NaHCO_3$ (200 mL, 10 wt%) until a neutral pH. Additionally, the organic phase was washed with a concentrated solution of NaCL. The purified monomer DHAM was recovered by distillation under vacuum and obtained as a yellowish liquid (7.2 g, 65%). DHAM was characterized by NMR and FTIR: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.65 (dd, 1H, vinyl proton), 6.22 (q, 1H, vinyl proton), 6.5 (dd, 1H, vinyl proton), 7.25-7.24 (m, 10H, aromatic). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 142.5, 128-126, 121, 118. FT-IR (cm^{-1}): 2940 (C-H), 1670 (C=O), 1640 (C=C), 1430 (C-N). The acquired ^{1}H, ^{13}C NMR and FTIR spectra are displayed in the **Figure S1 and S2**, respectively.

Synthesis of macroRAFT-PAM.

A typical synthesis of macroRAFT-PAM is as follows: acrylamide (201.2 g, 2.83 mol), DMAT (0.927 g, 3.3 mmol), ACPA (0.1185, 0.4 mmol) and water (400 g, 22.2 mol) were introduced into a jacketed reactor (500 mL) equipped with condenser, mechanical agitation and temperature control. The mixture was degassed under nitrogen bubbling for ca. 30 min and polymerization was performed at predetermined temperature (70°C). After 8 hours, the reaction was interrupted by cooling the system to room temperature. The acquired polymer was recovered by precipitation in methanol twice and dried under vacuum for 24 hours at 50°C.

Synthesis of subsequent multiblock copolymers

The chain extension polymerizations were carried out as follow: macroRAFT-PAM (30 g, 0.7 mmol) dissolved in water was placed in a jacketed reactor (500 mL), DHAM (0.4256 g, 1.6 mmol) and ACPA (0.0105 g, 0.03 mmol) were added to the reactor. Water concentration was adjusted to maintain the solid content ca 10 wt%. In the one-pot process corresponding to sequential addition of hydrophilic and hydrophobic monomer, the polymerization degree (DP) was calculated to reach a value of 780 for AM and 8 for DHAM considering 100% monomer conversion. The polymerization reaction was kept under constant stirring at 300 rpm and degassed by bubbling N_2 gas for ca. 30 min. The polymerization reaction was performed at 70°C. Before each new addition of monomer, a sample was withdrawn from the reactor using a syringe (10 mL). This procedure was repeated until five steps. The associating multiblock copolymers: macroRAFT-PAM, triblock copolymer (TBC), pentablock copolymer (PBC), heptablock copolymer (HBC) and nonablock copolymer (NBC) were recovered by precipitation in methanol twice and dried under vacuum for 24 hours at 50°C. Monomer consumption (conversion) was determined by gravimetry.

It is worth to highlight that additional experiments were carried out for preparing others PAM precursors with a DP of 600, 500 and 400. Attempts to incorporate the hydrophobic monomer DHAM to form a triblock copolymer (TBC) from these latter precursors via a chain extension reaction was unsuccessful. We unfortunately obtained a mild solution with no chain extended polymers. Herein, it is only discussed the case where the DP of PAM was 780.

Instrumentation.

Spectroscopic analyses. NMR spectra were recorded on a Bruker Advance III spectrometer (500 MHz) at room temperature. Hydrophobic monomer DHAM was dissolved in $CDCl_3$. Polymer samples were dissolved in a solvent mixture of D_2O/DMSO-d_6 (85-15 wt %). The chemical shifts (δ) are reported in ppm.

DOSY NMR analyses were performed on a Bruker Avance III spectrometer (500 MHz) at 30 ºC. Data are processed by Topspin 3.6 software and exhibited as 2D map: the ^{1}H NMR (chemical shift δ in ppm) is fixed on one axis and the diffusion coefficients in the other. Before carrying out the DOSY NMR experiments, acquisition parameters were carefully optimized[3] using the sequence "ledbpgp2s", pulse angle 90º. The measurement were performed in a BBOF 5 mm probe with a gradient amplifier, with a z-direction gradient strength set to 30 G cm^{-1} at 303 ºK. The employed proton pulse length employed was 4.66 µs, the gradient length (□) was set to 2 500 □s and the diffusion time (Δ) 0.645sec. The gradient strength was increased from 1.13 to 30.1 G cm^{-1} in 16 steps, scanning for 8 times. Gradient recovery delay time was set to 1 s at an acquisition time of 3 s.

ATR FTIR. Transmission and attenuated total reflectance (ATR) FTIR spectra were measured using a Thermo Scientific Nicolet 6700 FT-IR spectrometer using diamond crystal respectively. Data were collected between 500 and 4000 cm^{-1} using 50 scans.

SEC. The molar mass and molar mass distribution of copolymers were determined through size exclusion chromatography (SEC) using a HPLC instrument (Jasco Corporation, Tokyo, Japan) equipped with ultraviolet and refractive index detectors using a PSS SUPREMA 30 and 1000 Å columns in series (PSS, Mainz, Germany). Analyses were

conducted at a flow rate of 1.0 mL × min^{-1} at a temperature of 30ºC using a buffer solution of 0.08 M Na_2HPO_4 and 0.05% NaN_3 (pH 9). Before analysis, samples were filtered through a Nylon membrane with 0.45 µm pore size. Narrow distributed PEG standards (PSS, Mainz, Germany) were used for creating a calibrating curve at a MW range from 194-969,000 g × mol^{-1}.

DSC. Thermal analyses were carried out on a differential scanning calorimetry (DSC) instrument (TA instrument model Discovery Series) using N_2 gas at a flow of 50 mL/min, a scanning rate of 10 ºC/min and a temperature range from -80 to 250 ºC.

Rheology. Rheological analyses were performed in an Anton Paar Physics MCR-501 controlled stress rheometer equipped with a thermostated bath. The static measurements were carried out using a cone-plate geometry with an angle 2º and a diameter d =0.250 mm, a shear rate from 1 to 1000 s^{-1} at room temperature (25 ºC). The dynamic measurements were based on the Carreau-Yasuda model and conducted with a frequency range from 0.5 to 100 rad/s using similar conditions to the static state. Samples were prepared by dissolving of pre-determined amount of polymer in distilled water (one day) for obtaining predicted concentration.

Dynamic Light Scattering. DLS analyses were performed in a Zetasizer, Nanoseries instrument, Model Nano S90 (Malvern Instruments, USA). Polymers in a dilute solutions (1%, wt.) were measured at a scattering angle of θ = 90°and a room temperature (25 °C) using a polymethyl methacrylate (PMMA) cell (1.000 cm). Results were recorded using zetasizer software.

Table S1. Summary of the reaction conditions and results of the one-pot aqueous RAFT polymerization of hydrophobically modified associating multiblock copolymers performed at 70 ºC.

Entry	CTA[a]	Mon[b]	Conv[c] (%)	Molar Comp[d] [AM]/[DHAM]	$M\mathrm{w}_{\mathrm{th}}$ [e] g × mol^{-1}	$M\mathrm{w}_{\mathrm{SEC}}$ [f] g × mol^{-1}	$M\mathrm{n}_{\mathrm{SEC}}$ [f] g × mol^{-1}	$Đ$ [f]
MA	DMAT	AM	99	100/0	56,000	87,900	65,900	1.33
TBC	MA	DHAM	99	97/3	58,000	88,360	65,800	1.34
PBC	TBC	AM	99	98.6//1.4	114,000	211,600	142,500	1.48
HBC	PBC	DHAM	99	96.9/3.1	116,000	205,600	138,900	1.48
NBC	HBC	AM	99	98.8/1.2	172,000	500,000	258,100	1.93

a) MA = macroRAFT-PAM, TBC = triblock copolymer, PBC = pentablock copolymer, HBC = heptablock copolymer, NBC = nonablock copolymer, DMAT = S,S''-Bis (α, α'-dimethyl-α''-acetic acid) trithiocarbonate, b) AM = acrylamide, DHAM = *N,N'*-dihexylacrylamide, c) conversion was determined by gravimetry, d) chemical composition was calculated by ^{1}H NMR e) theoretical molar masses were determined following the equation: Mw = [Mon]/[CTA] × conversion × Mw of monomer + Mw CTA, f) the experimental molar masses: M_w, M_n and $Đ$ were determined by SEC.

The chemical composition of associating multiblock copolymers (TBC, PBC, HBC and NBC) was calculated using as reference the integral value (∫ = 3) of methyl protons of PDHAM detected at 1 ppm. Based on the ∫ of CH_3, we obtained the ∫ of methyne proton of backbone polymer appeared between 2.1 and 2.3 ppm.

% PDHAM = 1 / ∫methyne × 100

% PAM = (∫methyne-1) / ∫methyne × 100

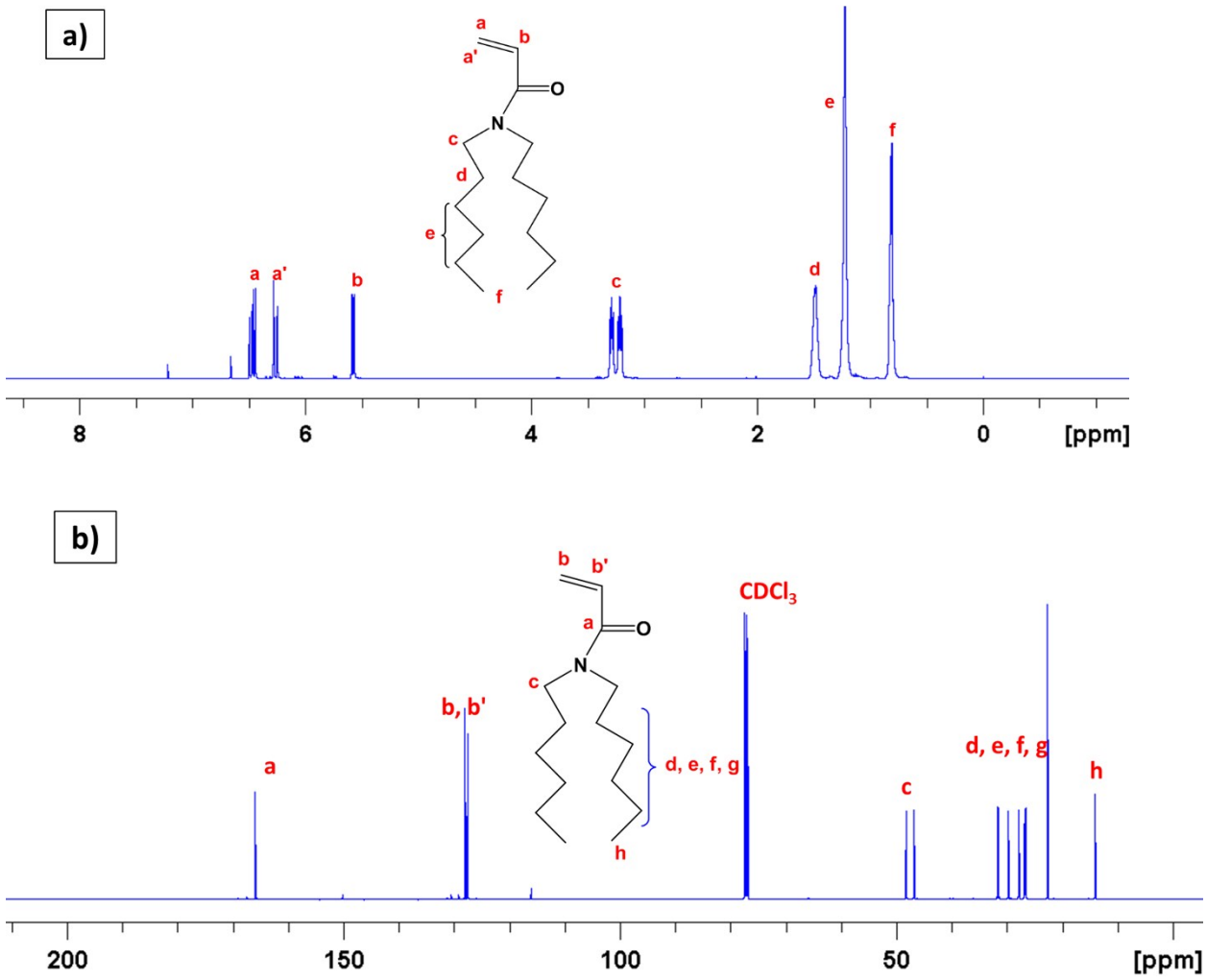


Figure S1. a) ^{1}H NMR and b) ^{13}C of hydrophobic monomer DHAM

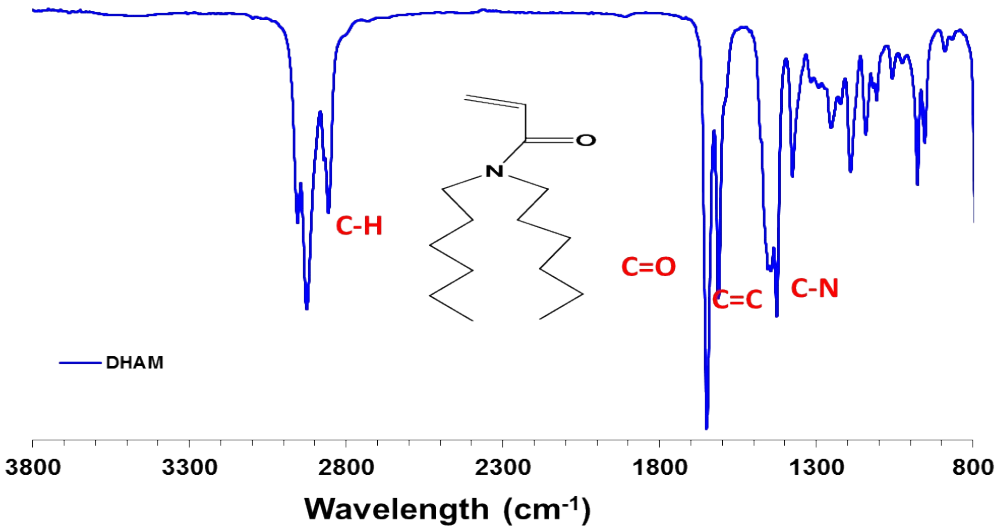


Figure S2. ATR FTIR of hydrophobic monomer DHAM

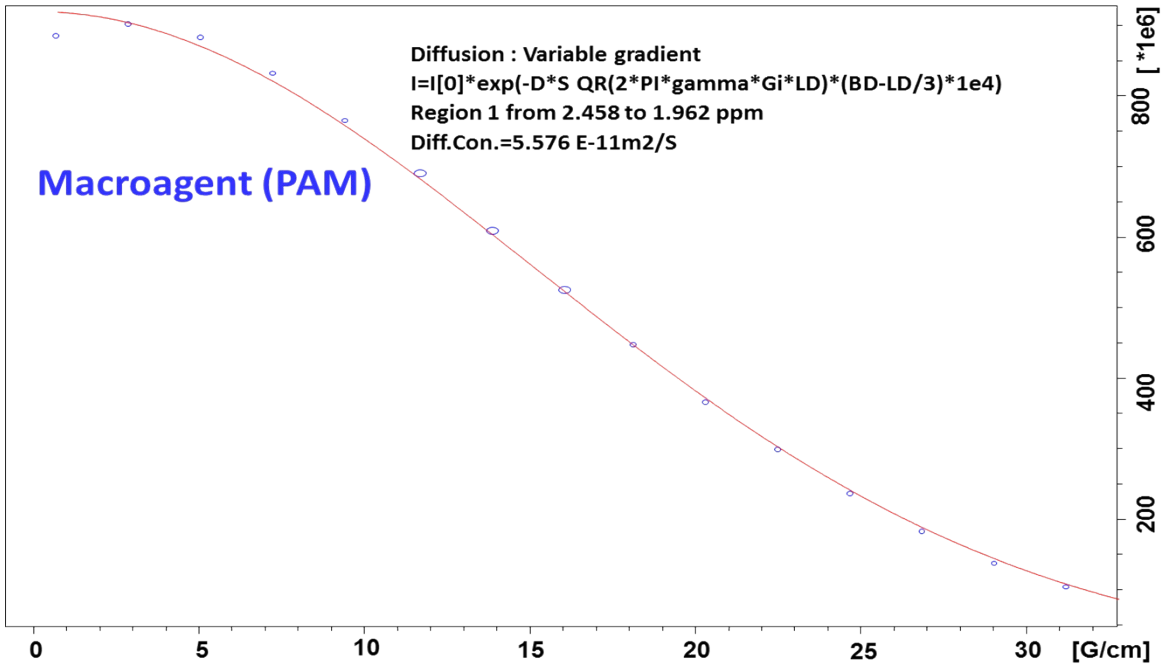


Figure S3. Diffusion coefficient optimization of macroRAFT-PAM

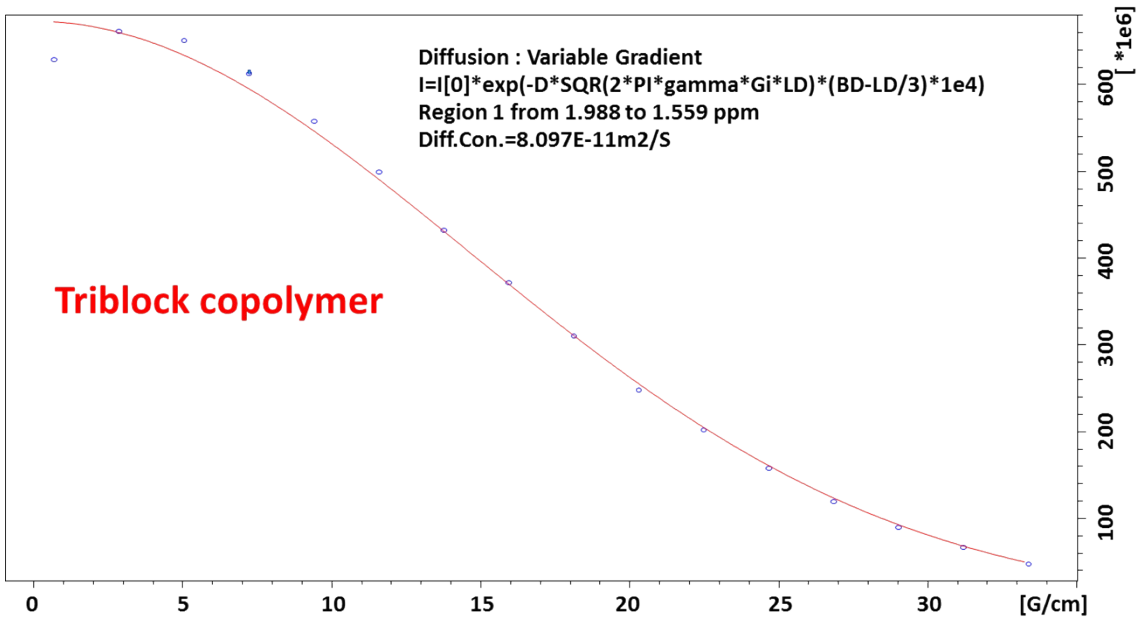


Figure S4. Diffusion coefficient optimization of triblock copolymer (TBC)

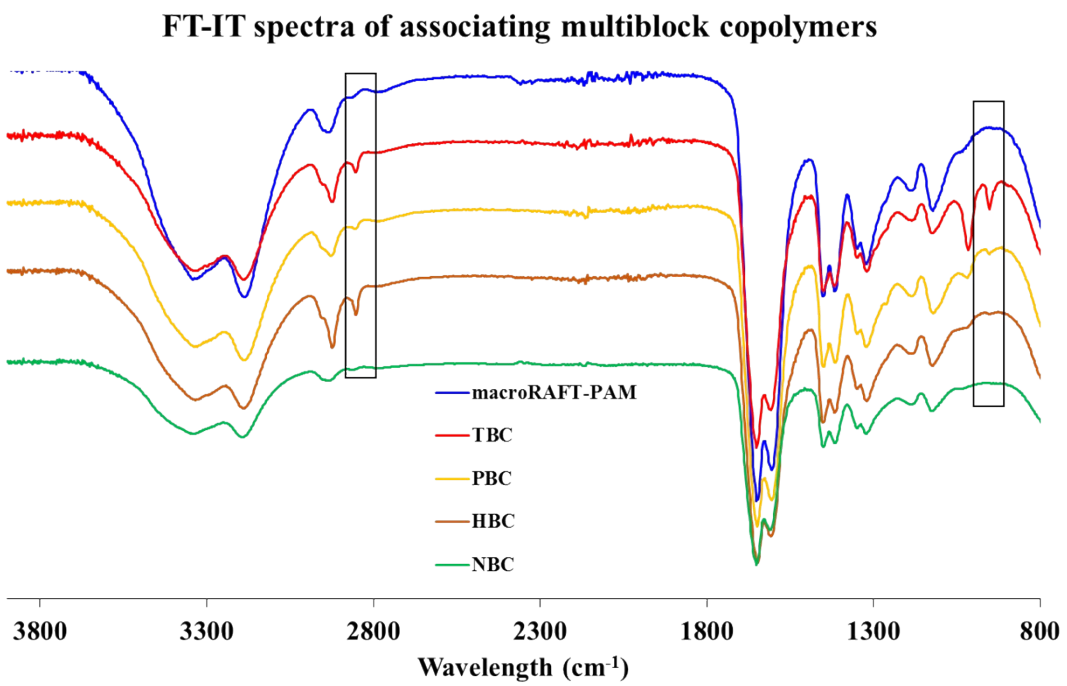
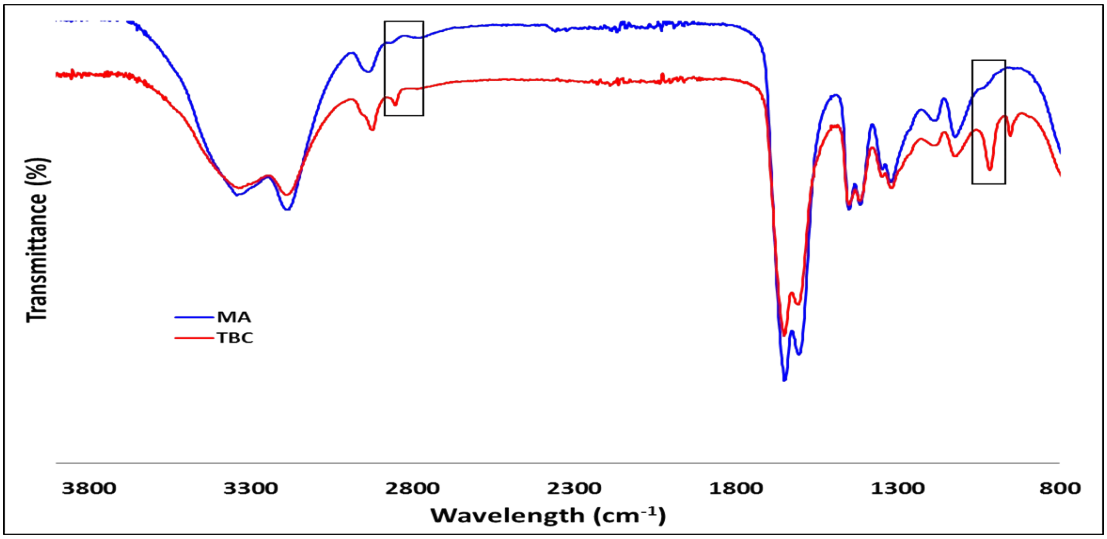


Figure S5. ATR FTIR of all associating multiblock copolymers obtained via a one-pot RAFT polymerization: macroRAFT-PAM (blue), TBC (red), PBC (orange), HBC (brown) and NBC (green)



ATR FTIR spectra of macroRAFT (blue) y triblock copolymer (red).

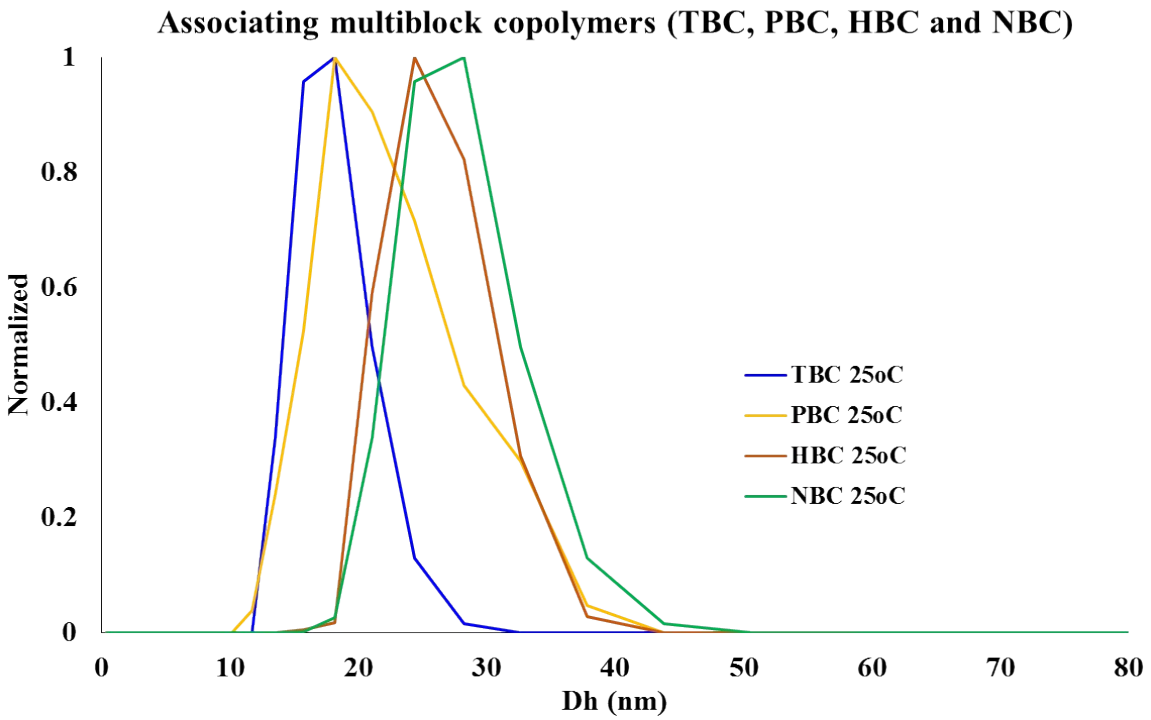


Figure S6. Hydrodynamic radius (R_h) of multiblock copolymer at a concentration of 1 wt. % in aqueous solution as determined by DLS: TBC (blue), PBC (orange), HBC (brown) and NBC (green)

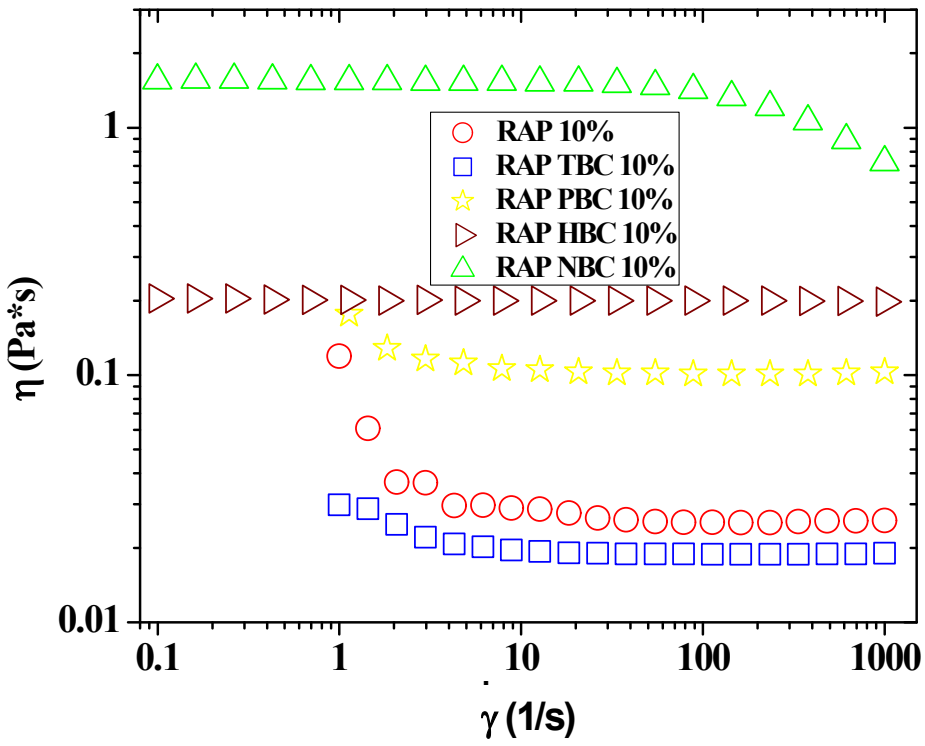


Figure S7. Log-log viscosity versus shear rate of copolymers hydro soluble associative obtained via a one-pot aqueous RAFT polymerization at a concentration of 10 wt. %.

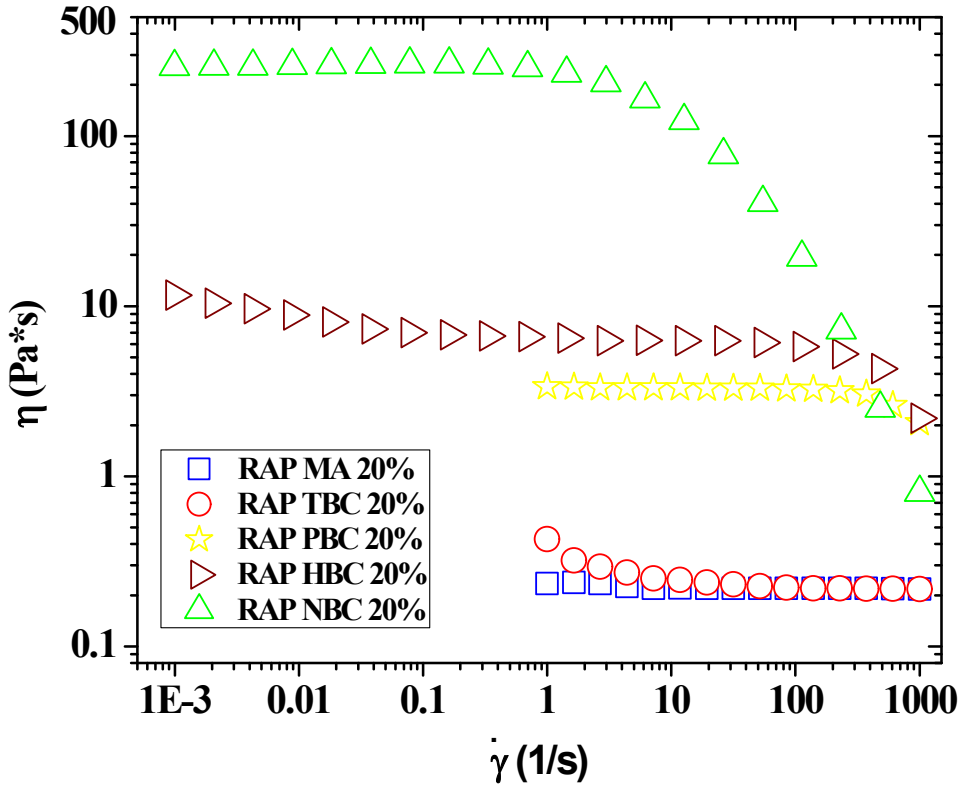


Figure S8. Log-log viscosity *versus* shear rate of associating multiblock copolymers obtained via a one-pot aqueous RAFT polymerization: at a concentration of 20 wt. %.

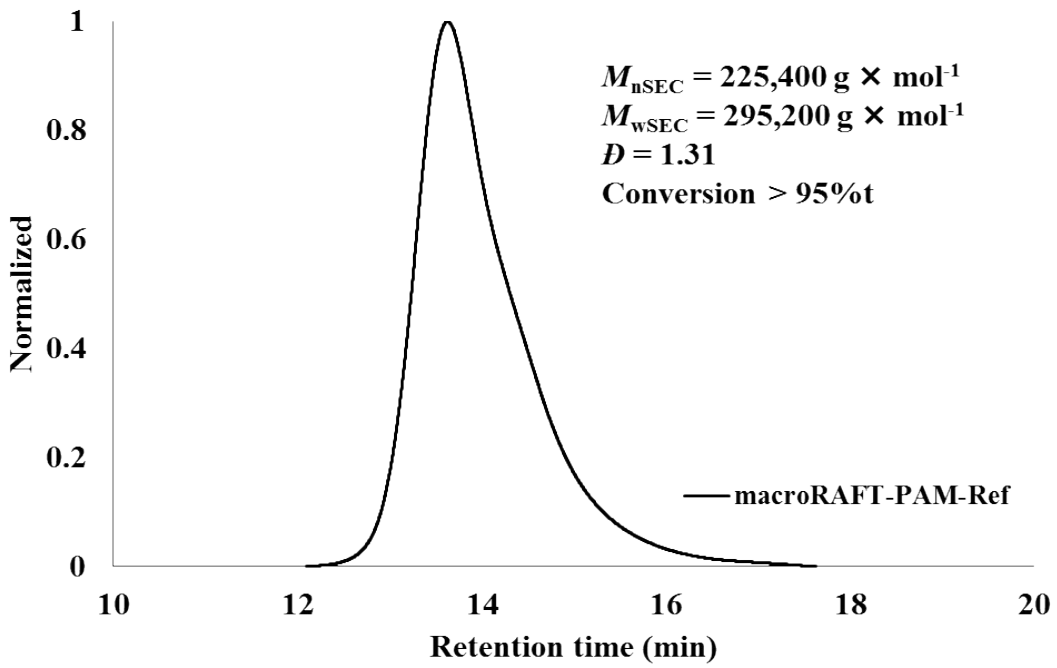


Figure S9. SEC traces of reference polyacrylamide obtained via an aqueous RAFT polymerization.

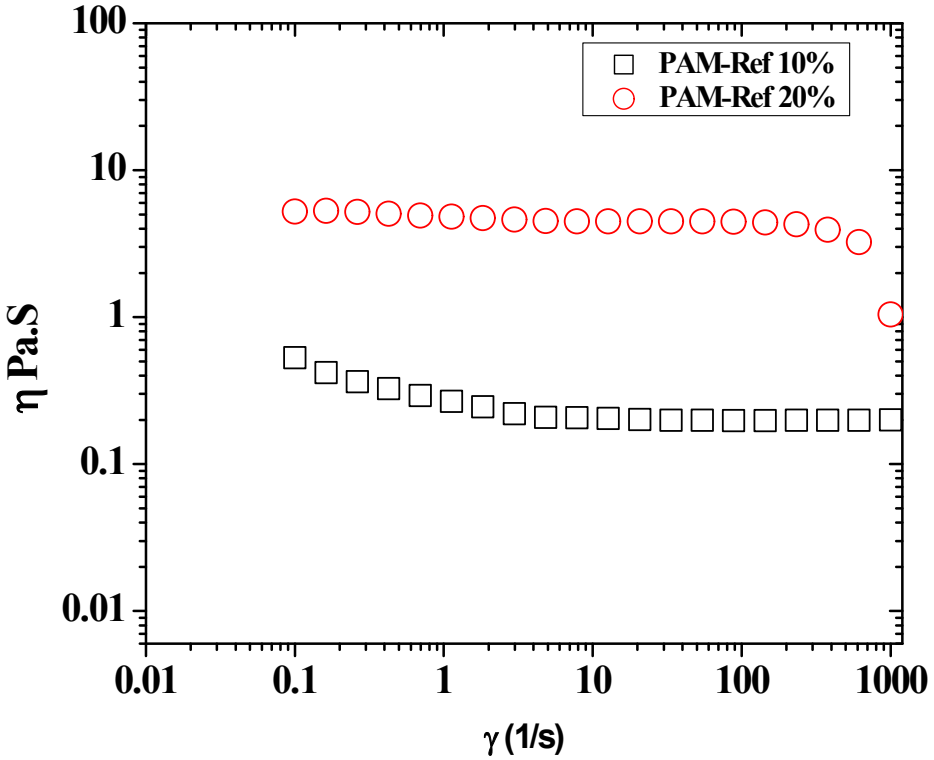


Figure S10. Log-log viscosity *versus* shear rate of reference polyacrylamide obtained via an aqueous RAFT polymerization: at both concentration: 10 and 20 wt. %.

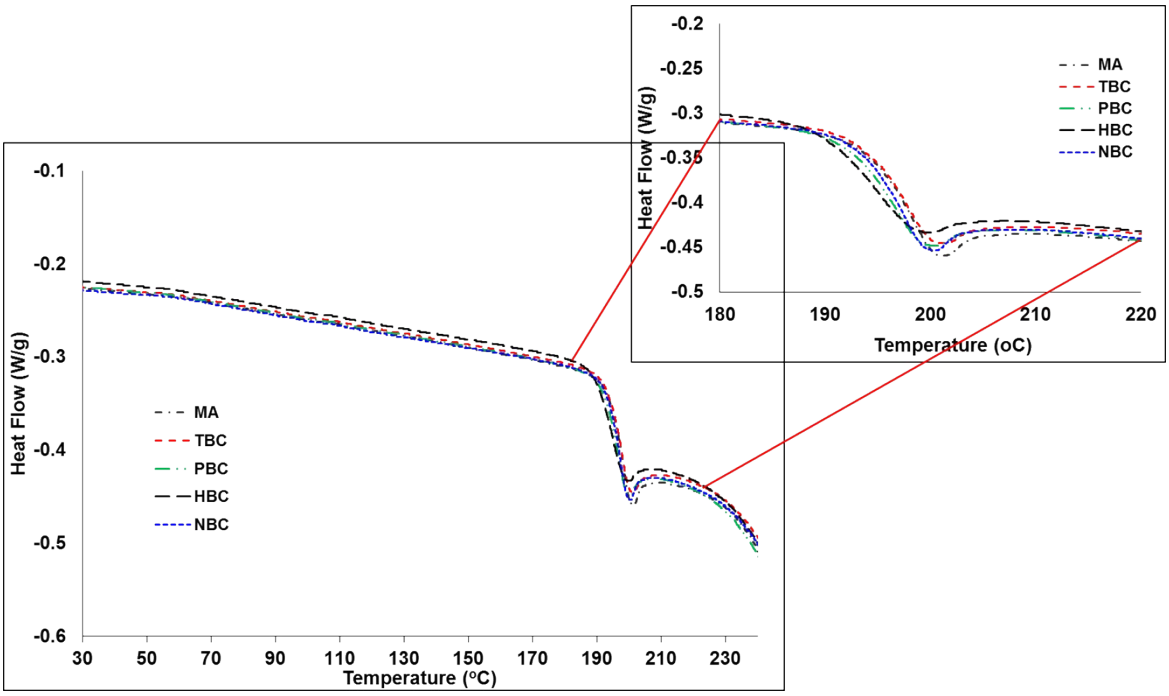


Figure S11. DSC diagrams of associating multiblock copolymers composed of PAM and PDHAM obtained via a one-pot aqueous RAFT polymerization.

References

[1] Lara-Ceniceros, T., Cadenas-Pliego, G., Díaz de León-Gómez, R., Rivera-Vallejo, C., A. Coronado, A., Jiménez-Regalado, E. J., *J. Polym Res.,* **2014**, 21, 511-522.

[2] Lai, J. T., Filla, D., Shea, R., *Macromolecules*, **2002**, 35, 6754-6756.

[3] Delsuc, M. A., Malliavin, T. E., *Anal. Chem*., **1998**, 70, 2146-2148.