Electronic Supplementary Material for :

All Poly(ionic liquid) Block Copolymer Nanoparticles from Antagonistic Isomeric Macromolecular Blocks via Aqueous RAFT Polymerization-Induced Self-Assembly

Jérémy Depoorter,[1] Xibo Yan,[1,3] Biao Zhang,[1,4] Guillaume Sudre,[2] Aurélia Charlot,[1] Etienne Fleury[1] and Julien Bernard[1]*

[1] : Univ Lyon, INSA Lyon, CNRS, IMP UMR 5223, F-69622, Villeurbanne, France

[2] : Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IMP UMR 5223, F-69621, Villeurbanne, France

[3]: School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.

[4]: Shaanxi Institute of Flexible Electronics (SIFE), Northwestern Polytechnical University (NPU), Xi'an, 710072 Shaanxi, China

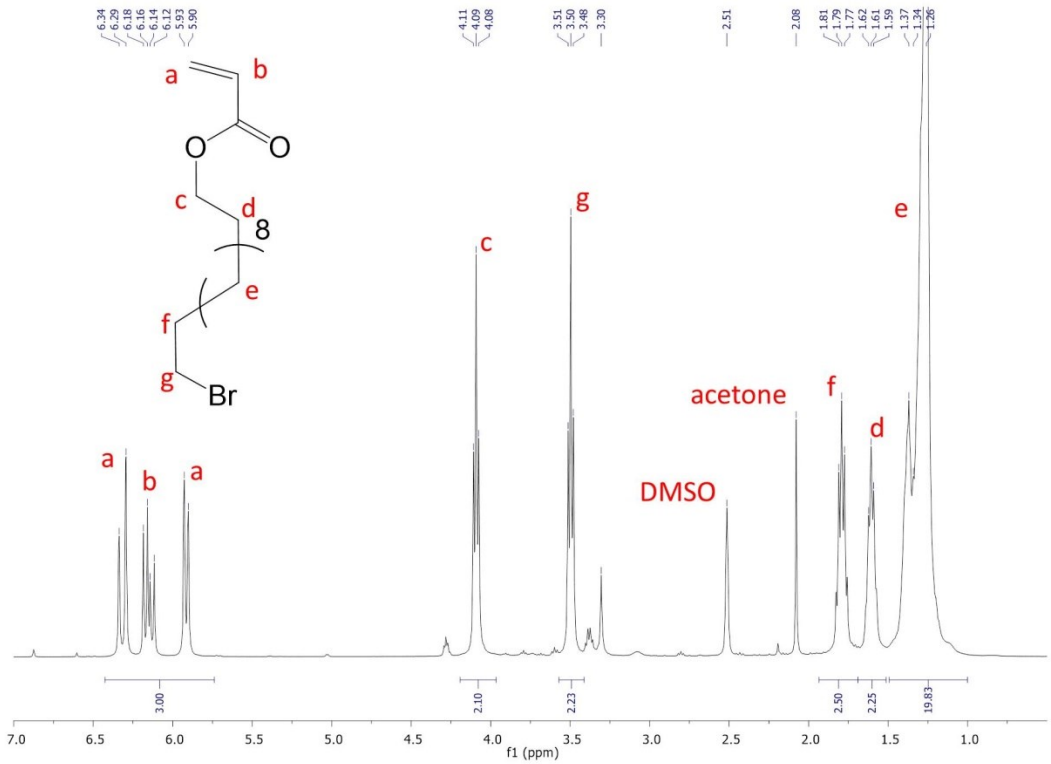

Figure S1: ^{1}H NMR of 2-Bromododecyl acrylate in DMSO-d^{6} at 298 K.

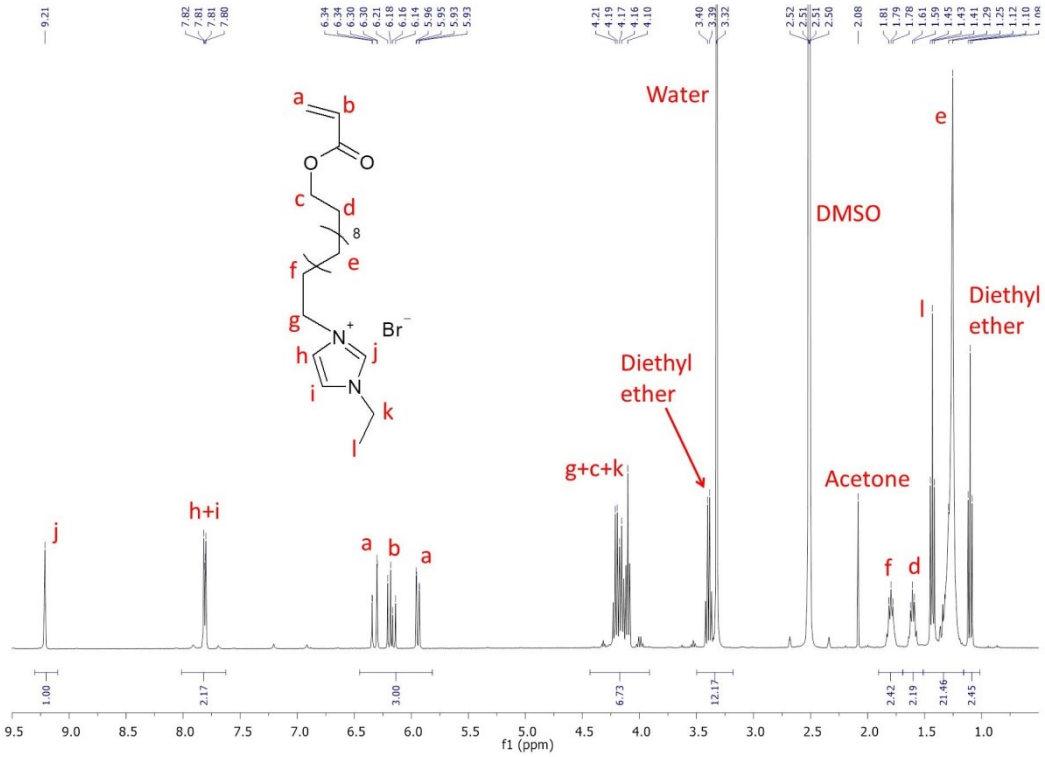

Figure S2:[1]H NMR of ADEIBr in DMSO-d[6] at 298 K.

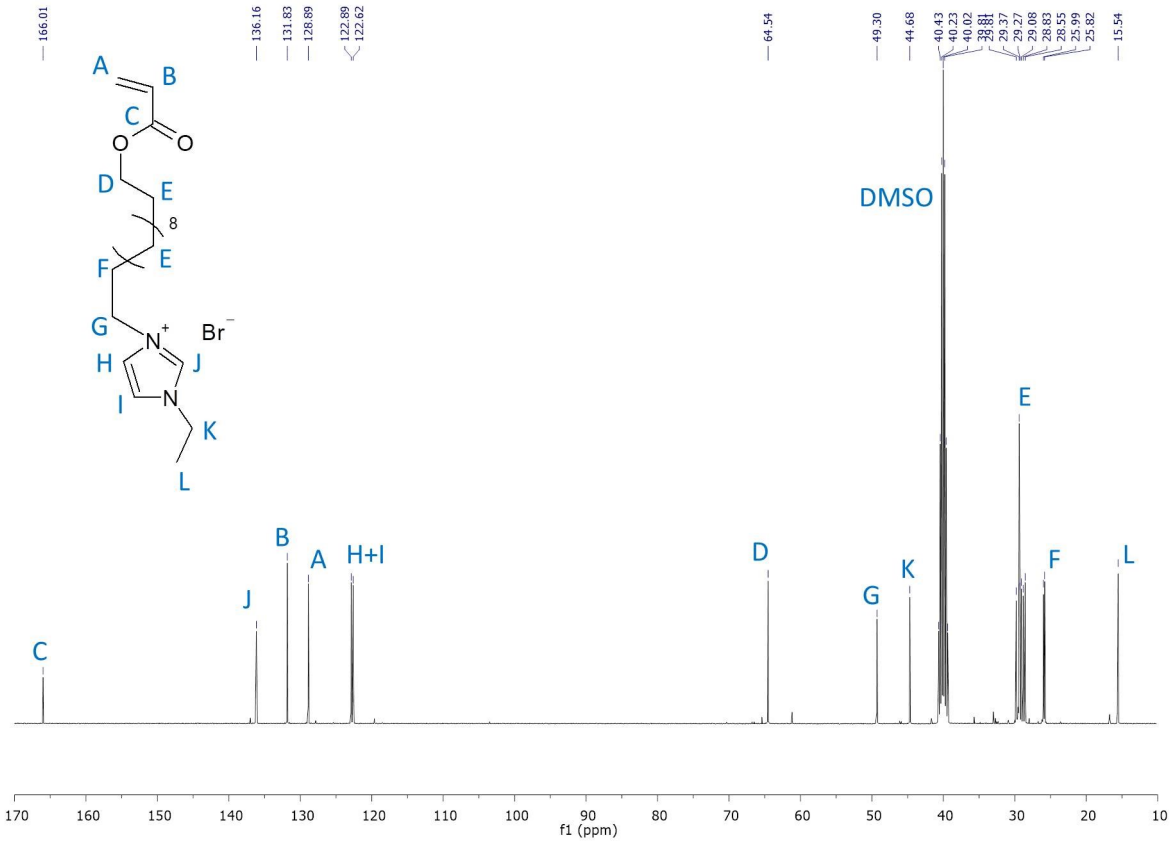

Figure S3: ^{13}C NMR of ADEIBr in DMSO-d^{6} at 298 K.

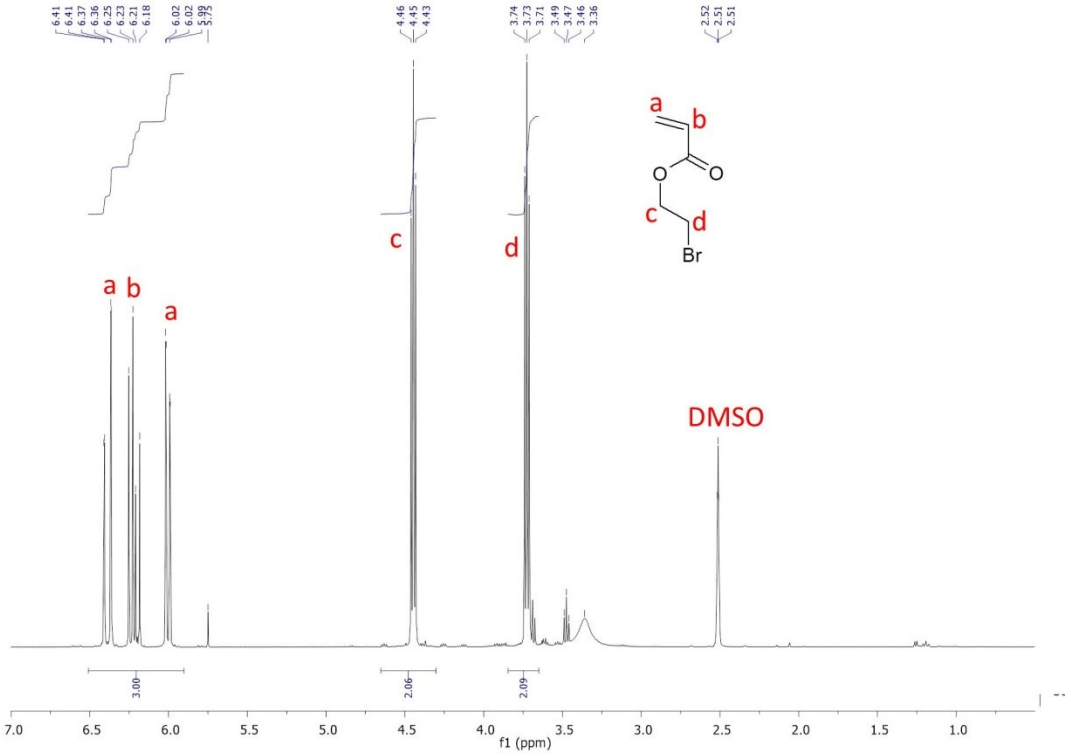

Figure S4:[1]H NMR of 2-bromoethyl acrylate in DMSO-d[6] at 298 K.

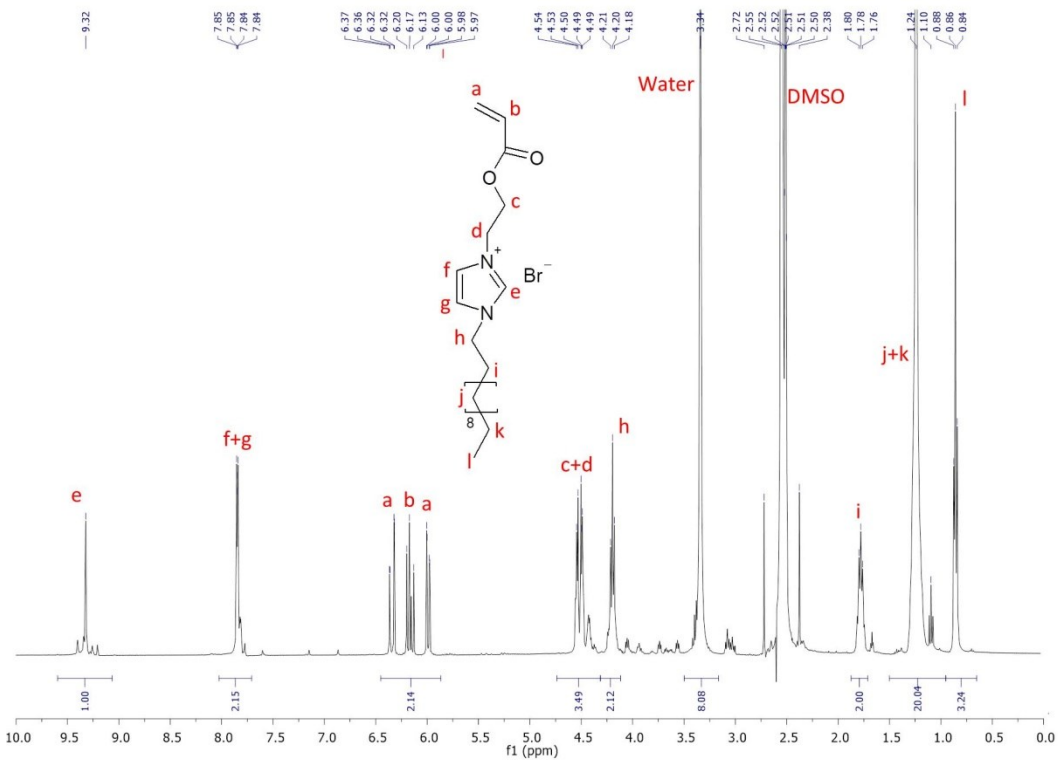

Figure S5: ^{1}H NMR of AEDIBr in DMSO-d^{6} at 298 K.

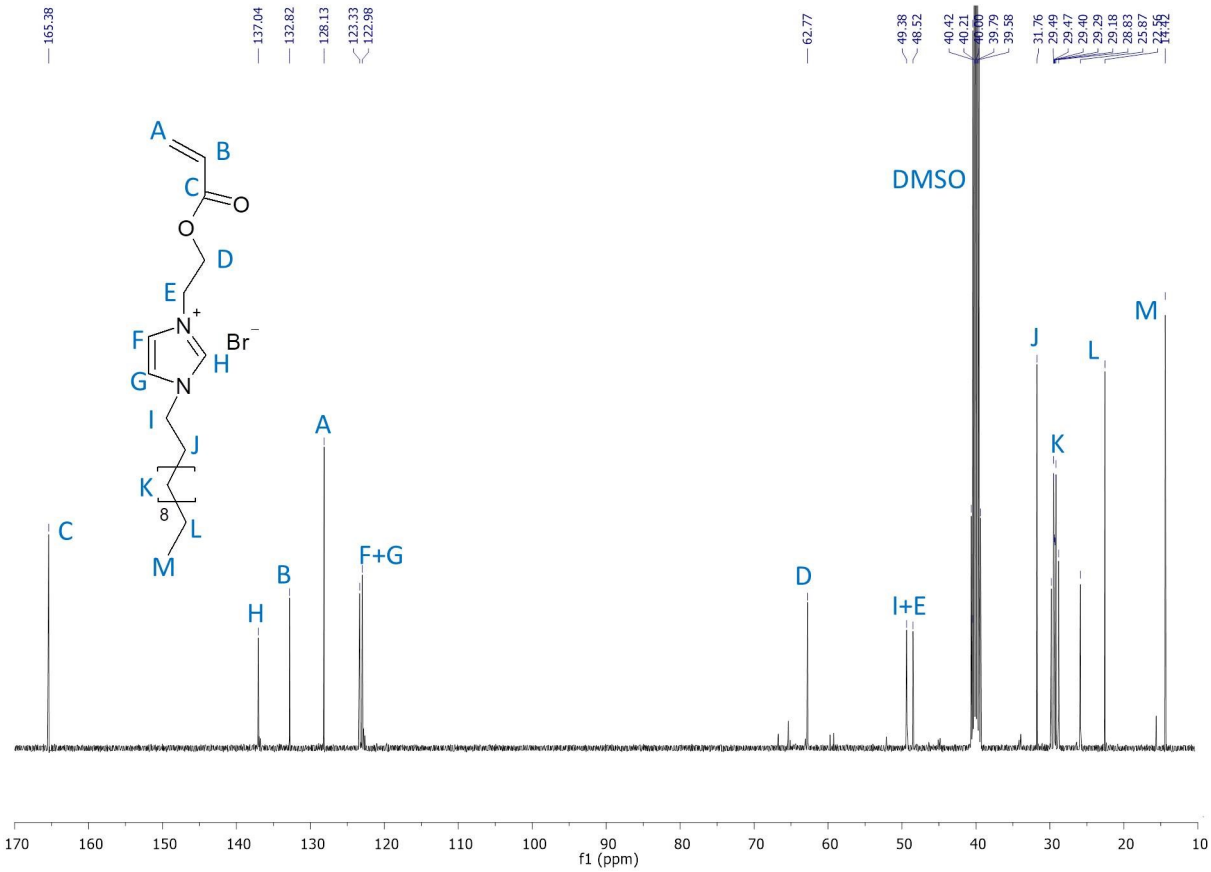

Figure S6: ^{13}C NMR of AEDIBr in DMSO-d^{6} at 298 K.

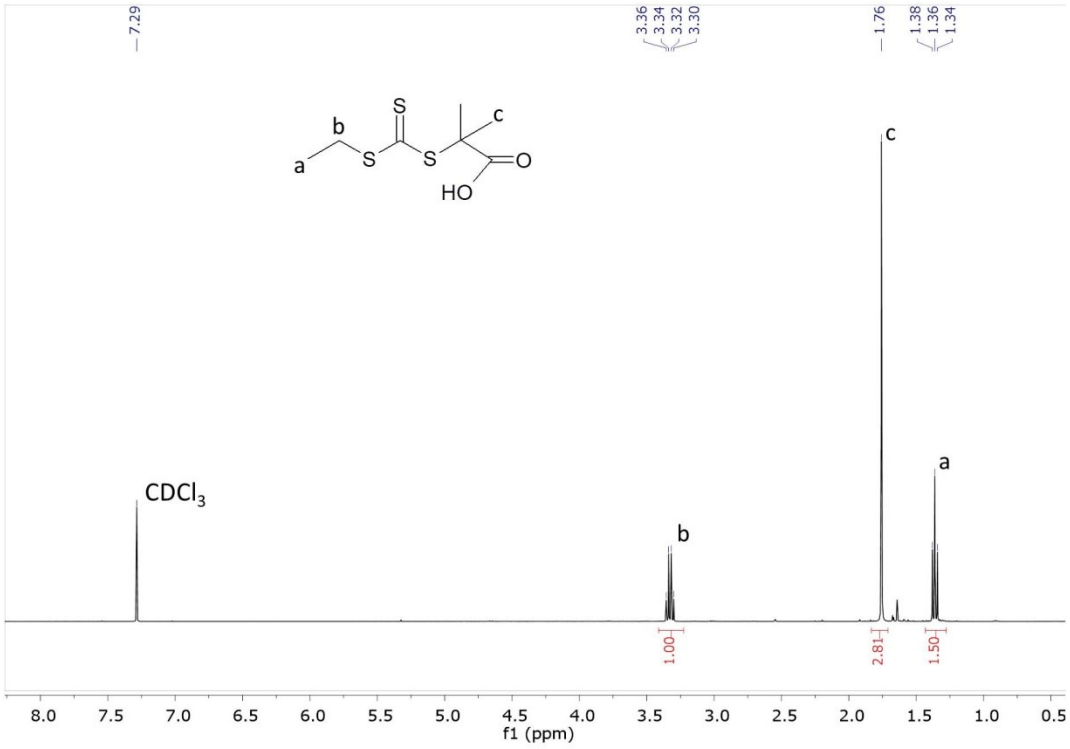

Figure S7: ^{1}H NMR of EMP in $CDCl_3$ at 298 K.

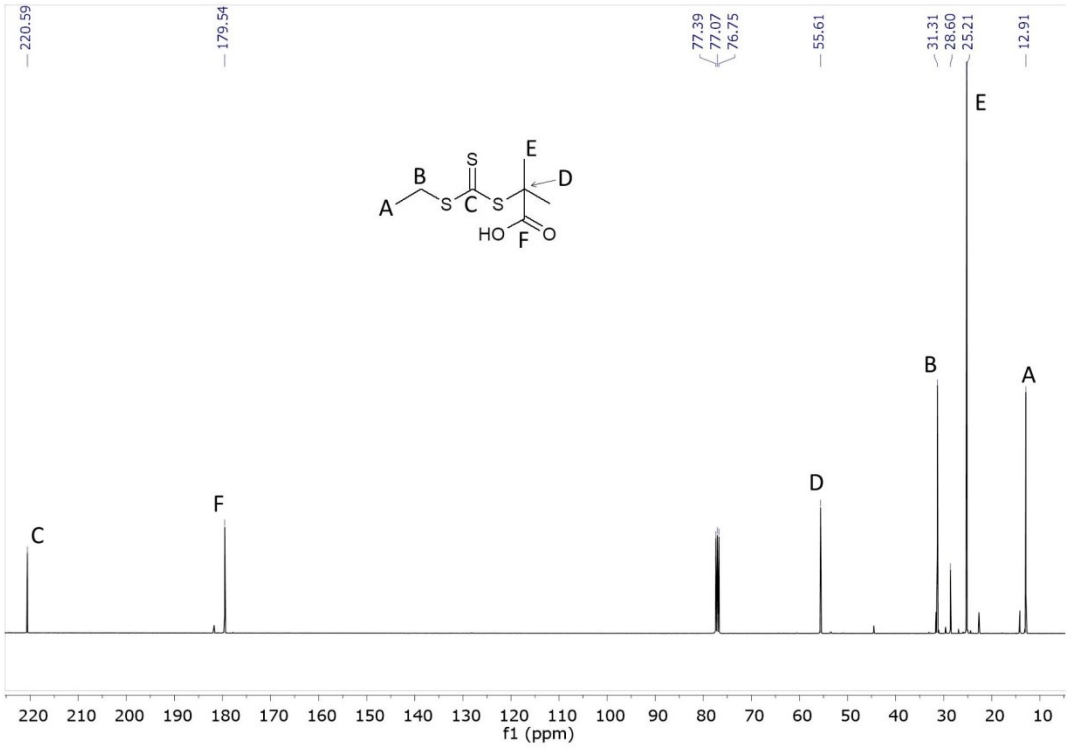

Figure S8 : ^{13}C NMR of EMP in $CDCl_3$ at 298 K.

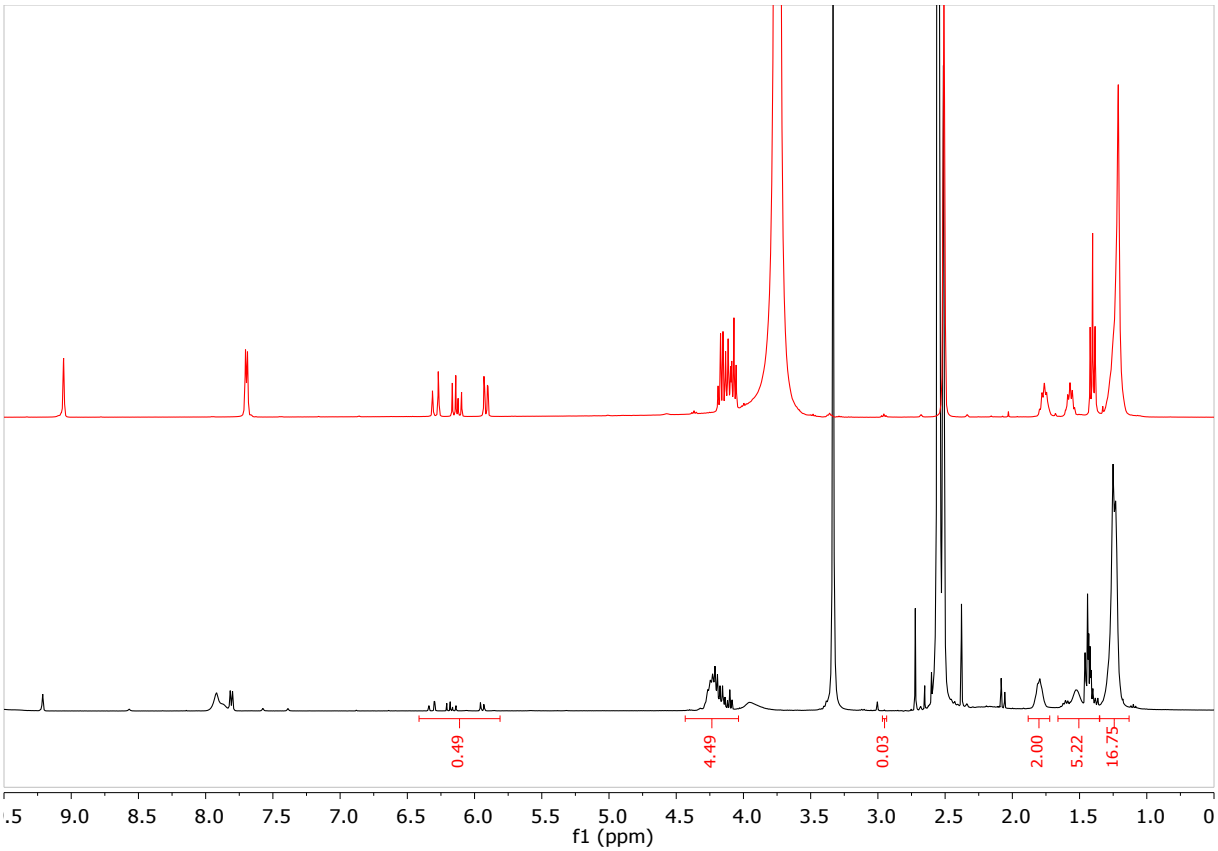

Figure S9: ^{1}H NMR of ADEIBr polymerization medium (in DMSO-d_6 at 298 K). using EMP as a CTA and ACPA as an initiator ([ADEIBr]:[EMP]:[ACPA] = 100:1:0.2) at t_0 (a) and t_f (83% of conversion) (b)

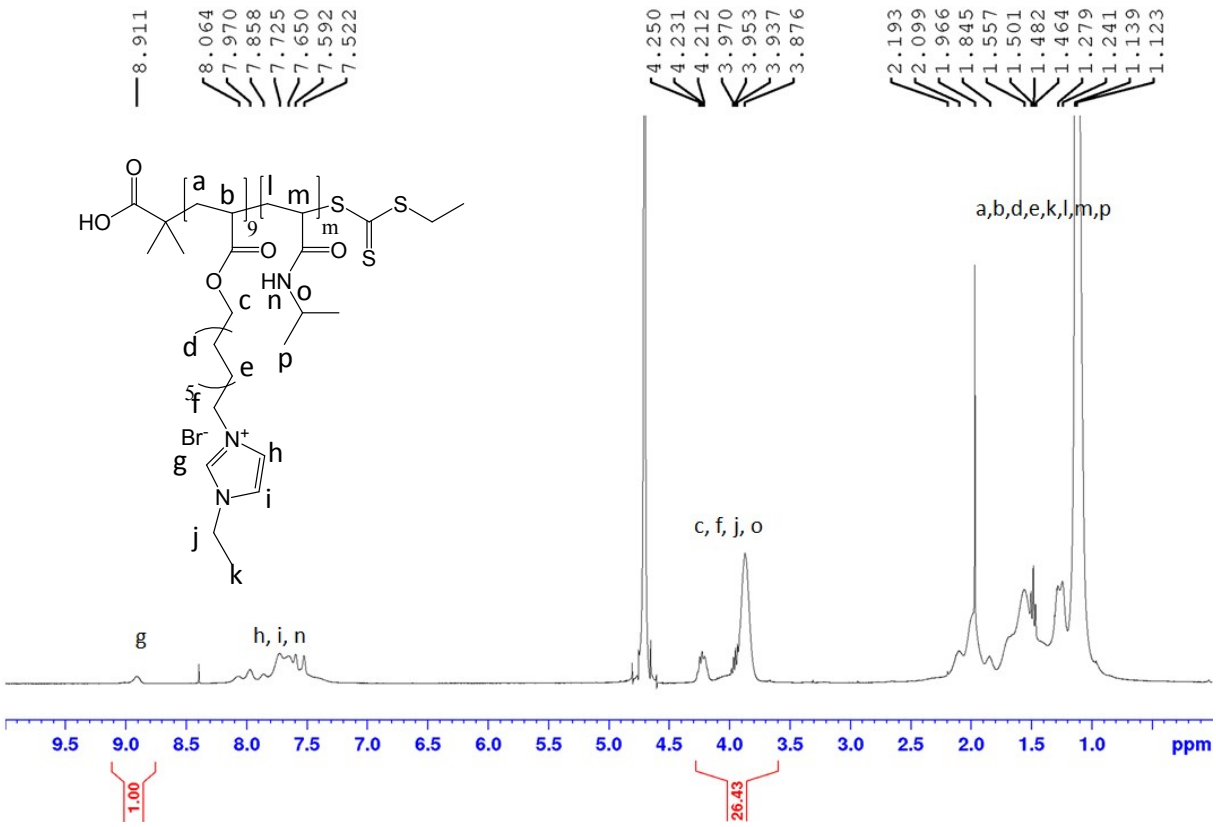

Figure S10: ^{1}H NMR of purified PADElBr$_9$-*b*-PNIPAAm$_{180}$ in D_2O at 298 °K ([NIPAAm]:[mCTA]:[ACPA] = 400:1:0.2 at 15 wt.%).

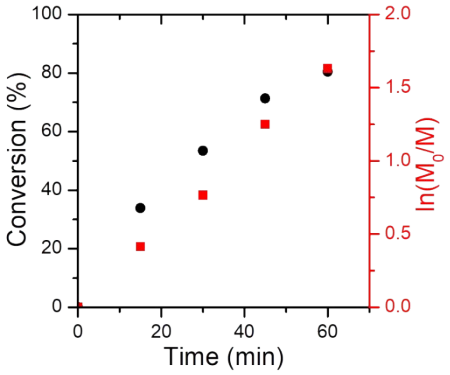

Figure S11: Monomer conversion *vs* time curve (black circles) obtained for the RAFT polymerization of AEDIBr 40 % w/w at 70 °C in DMF using EMP as a CTA and ACPA as an initiator ([AEDIBr]:[EMP] :[ACPA] = 100:1:0.2) and corresponding semilogarithmic plots (red squares)

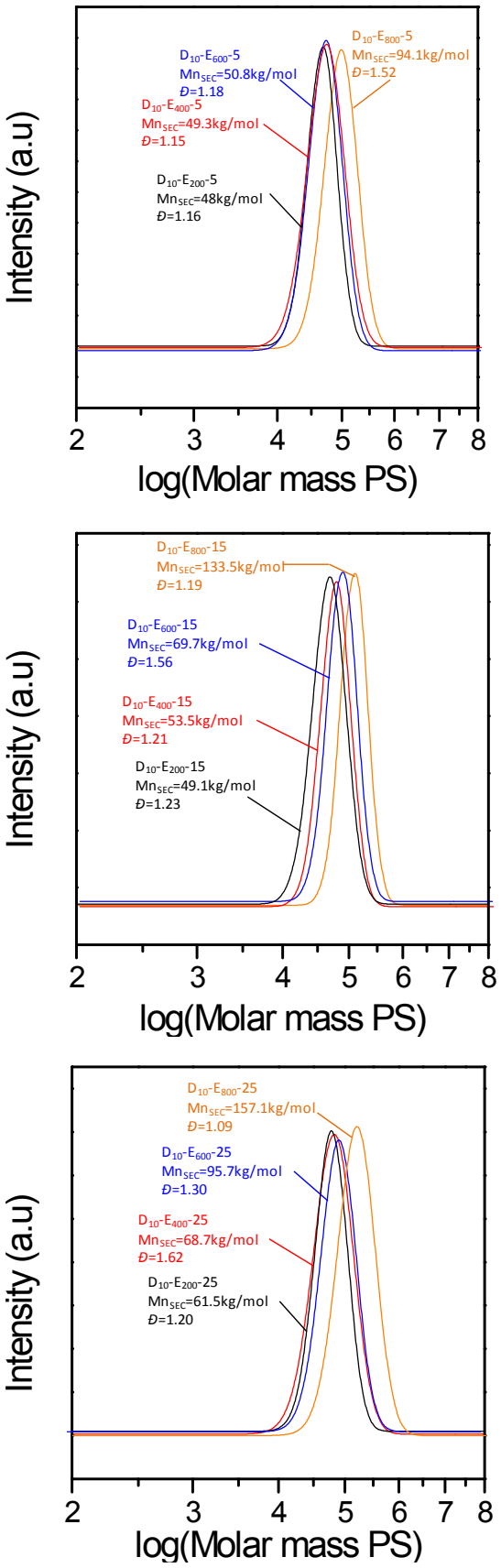

Figure S12: SEC traces evolution for D_{10}-E_{200}-5, D_9-E_{400}-5, D_9-E_{600}-5 and D_9-E_{800}-5 (first graph, up), D_9-E_{200}-15, D_9-E_{400}-15, D_9-E_{600}-15 and D_9-E_{800}-15 (second graph, middle), D_9-E_{200}-25, D_9-E_{400}-25, D_9-E_{600}-25 and D_9-E_{800}-25 (last graph). Analyses peformed in DMF/LiTFSI as eluent after ionic exchange of bromide anions by TFSI).

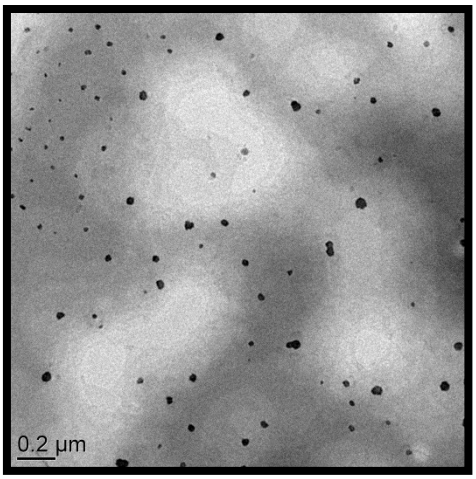

Figure S13: Representative TEM picture of PIL block copolymer spherical nanoparticles obtained at 5 wt% solid contents (E_9-D_{600}-5).

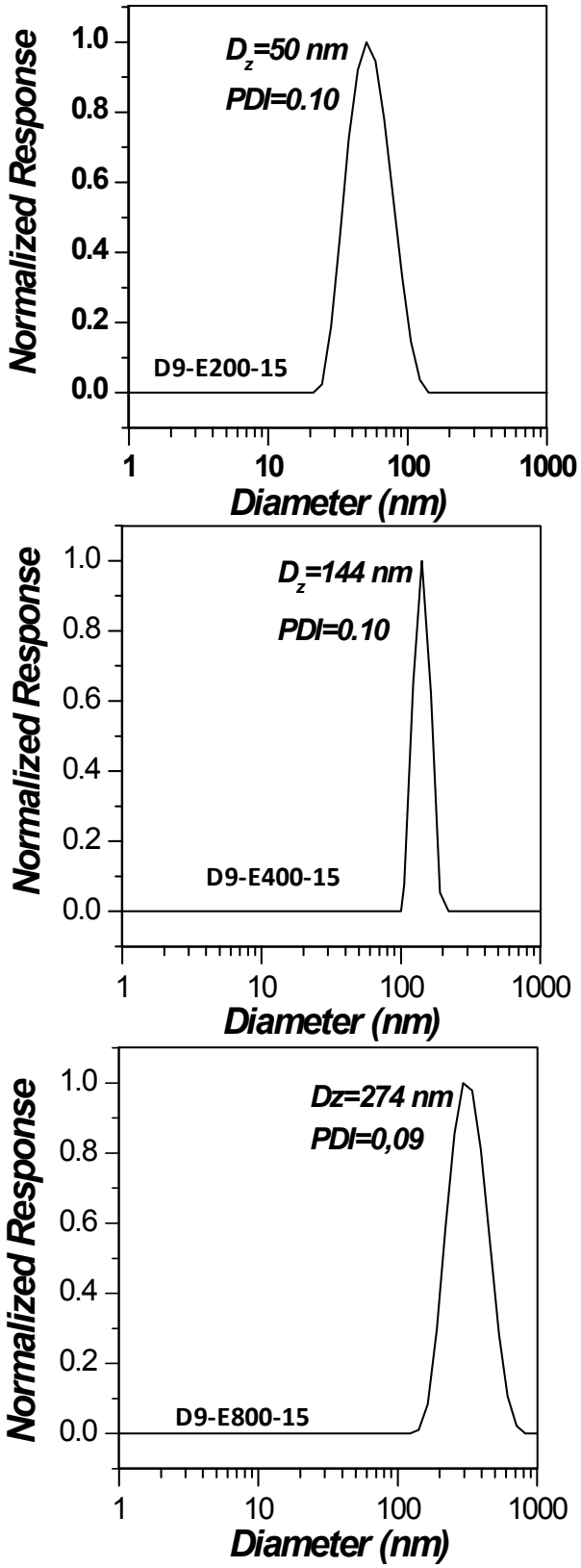

Figure S14: DLS in water of D9-E200-15, D9-E400-15 and D9-E800-15

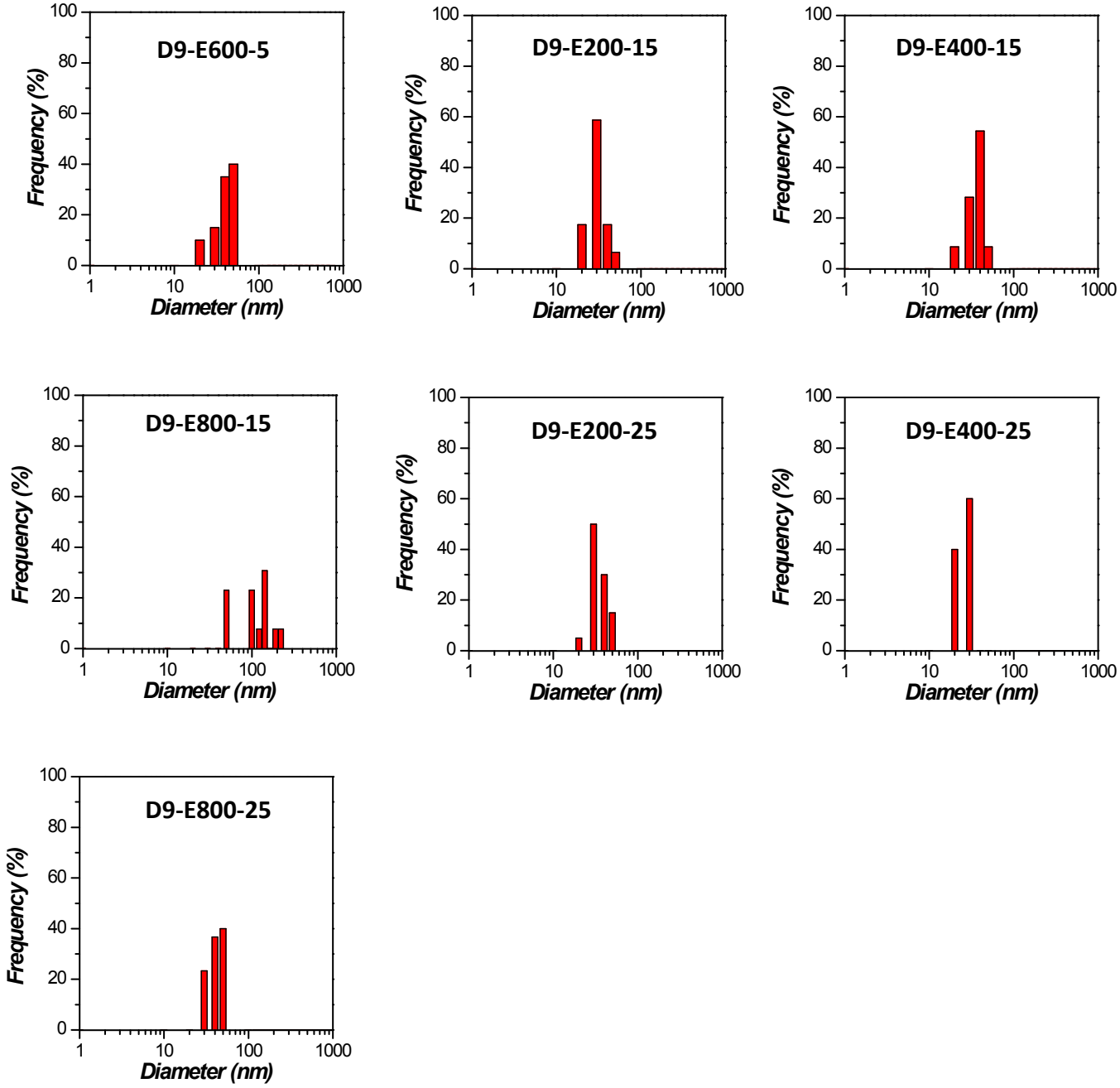

Figure S15: Histograms relative to TEM pictures of spherical particles

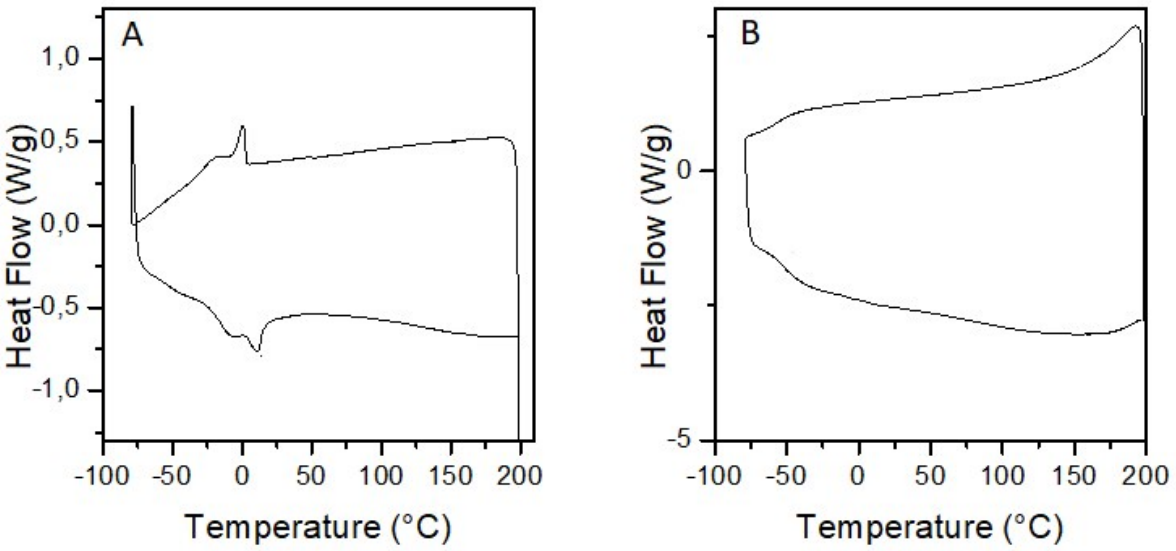

Figure S16: DSC s of PADEIBr and PAEDIBr (at 10°C/min).

Removal of the trithiocarbonate end-group from $PADEIBr_9$

50 mg of $PADEIBr_9$ (1.21×10^{-4} mol) were dissolved in 10 mL of DMSO. Then, addition of 70 mg of ethanolamine (1.21×10^{-3} mol, 10 molar eq.) in the solution provoked a change of the coloration. The solution was stirred for 30 min and 680 mg of NIPAAm (6.03×10^{-3} mol, 50 molar eq.) was subsequently added in the solution with the presence of 16.6 mg of dimethylphenylphosphine (1.21×10^{-4} mol, 1 molar eq.). The solution was reacted overnight at 25 °C and washed five times with a water/dichloromethane solution (5×25 mL) followed by dialysis (Mw cut off = 1000 Da) and freeze-drying. The obtained powder was analyzed by ^1H NMR in DMSO-d_6(Yield: 42 mg; 82 %).