Electronic Supporting Information

Polymerizations

Polymerization of lauryl methacrylate mediated by CTA 7

Solution polymerization of lauryl methacrylate (LMA, 3.3 mL, 1.5×10^{-2} mol) was performed using AIBN (0.82 mg, 5×10^{-6} mol), **7** (47.2 mg, 5×10^{-5} mol), toluene (6.6 mL) and trioxane (127 mg, 1.4×10^{-3} mol) as an internal reference for the measurement of LMA consumption via ^{1}H NMR. A stock solution was transferred into Schlenk tubes which were thoroughly deoxygenated by five consecutive freeze-pump-thaw cycles. The tubes were subsequently placed in an oil bath thermostated at 60°C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into methanol in order to eliminate residual monomer and trioxane. The polymer was dried under vacuum and characterized by ^{1}H NMR and SEC. The molar mass of pure poly(lauryl methylacrylate) (HR-PLMA) was finally evaluated by ^{1}H NMR ($CDCl_3$) from relative integration of the protons of the PLMA backbone (-O-CH_2-CH_2-, 2nH, δ=3.86 ppm, with n being the degree of polymerization) and of characteristic protons of Hamilton wedge end-groups (-CH_2-CH_2-CH_3), 4H, δ=2.32 ppm).

Polymerization of styrene mediated by CTA 14

Solution polymerization of styrene was performed using 2,2'-azobisisobutyronitrile (AIBN) as initiator and **14** as chain transfer agent. Typically, the polymerization of styrene (2.3 mL, 2.0×10^{-2} mol) was carried out using AIBN (0.41 mg, 2.5×10^{-6} mol), **14** (27.3 mg, 5.0×10^{-5} mol), toluene (4.6 mL) and trioxane (127 mg, 1.4×10^{-3} mol) as an internal reference for the measurement of styrene consumption via ^{1}H NMR. A stock solution was transferred into Schlenk tubes which were thoroughly deoxygenated by five consecutive freeze-pump-thaw cycles. The tubes were subsequently placed in an oil bath thermostated at 80°C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into ethanol in order to eliminate residual monomer and trioxane. The polymer was dried under vacuum and characterized by ^{1}H NMR and SEC. The molar mass of barbiturate-functionalized polystyrene (Ba-PS) was finally evaluated by ^{1}H NMR (CD_2Cl_2) from relative integration of the aromatic protons of the PS backbone (5nH, δ=6.06-7.46 ppm, with n being the degree of polymerization) and of characteristic protons of the ester group (-(O=)C-O-CH_2-CH_2-, 2H, δ=4.03 ppm).

Polymerization of n-butyl acrylate (nBuA) mediated by CTA 14

Solution polymerization of *n*BuA was performed using 2,2'-azobisisobutyronitrile (AIBN) as initiator and **14** as chain transfer agent. Typically, the polymerization of *n*BuA (4.8 mL, 3.6×10^{-2} mol) was carried out using AIBN (0.60 mg, 3.6×10^{-6} mol), **14** (39.5 mg, 7.2×10^{-5} mol), toluene (9.2 mL) and trioxane (127 mg, 1.4×10^{-3} mol) as an internal reference for the measurement of *n*BuA consumption via ^{1}H NMR. A stock solution was transferred into Schlenk tubes which were thoroughly deoxygenated by five consecutive freeze-pump-thaw cycles. The tubes were subsequently placed in an oil bath thermostated at 70°C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into methanol/water (1/1, v/v) in order to eliminate residual monomer and trioxane. The polymer was dried under vacuum and characterized by ^{1}H NMR and SEC. The molar mass of barbiturate-functionalized poly(*n*-butyl acrylate) (P*n*BuA) was finally evaluated by ^{1}H NMR ($CDCl_3$) from relative integration of the protons of the P*n*BuA backbone (-O-CH_2-CH_2-, 2nH, δ=3.96 ppm, with n being the degree of polymerization) and of characteristic protons adjacent to the triazole cycle (=N-C(=CH)-CH_2-CH_2-, 2H, δ=2.68 ppm).

Chain extension of α-Ba-functionalized PnBuA with styrene

Solution polymerization of styrene was performed using 2,2'-azobisisobutyronitrile (AIBN) as initiator and Ba-P*n*BuA ($M_{n\ SEC}$ = 24700 g.mol^{-1}, PDI = 1.09) as macromolecular CTA. Typically, the polymerization of styrene (2.6 mL, 2.3×10^{-2} mol) was carried out using AIBN (0.31 mg, 1.9×10^{-6} mol), Ba-P*n*BuA4 (1.0g, 3.8×10^{-5} mol), toluene (5.3 mL) and trioxane (127 mg, 1.4×10^{-3} mol) as an internal reference for the measurement of styrene consumption via ^{1}H NMR. A stock solution was transferred into Schlenk tubes which were thoroughly deoxygenated by five consecutive freeze-pump-thaw cycles. The tubes were subsequently placed in an oil bath thermostated at 80°C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into methanol in order to eliminate residual monomer and trioxane. The polymer was dried under vacuum and characterized by ^{1}H NMR and SEC. The molar mass of P*n*BuA-*b*-PS was finally evaluated by ^{1}H NMR (CD_2Cl_2) from relative integration of the aromatic protons of the PS backbone (5nH, δ=6.06-7.46 ppm, with n being the degree of polymerization) and of characteristic protons of P*n*BuA backbone (-O-CH_2-CH_2-, δ=3.95 ppm).

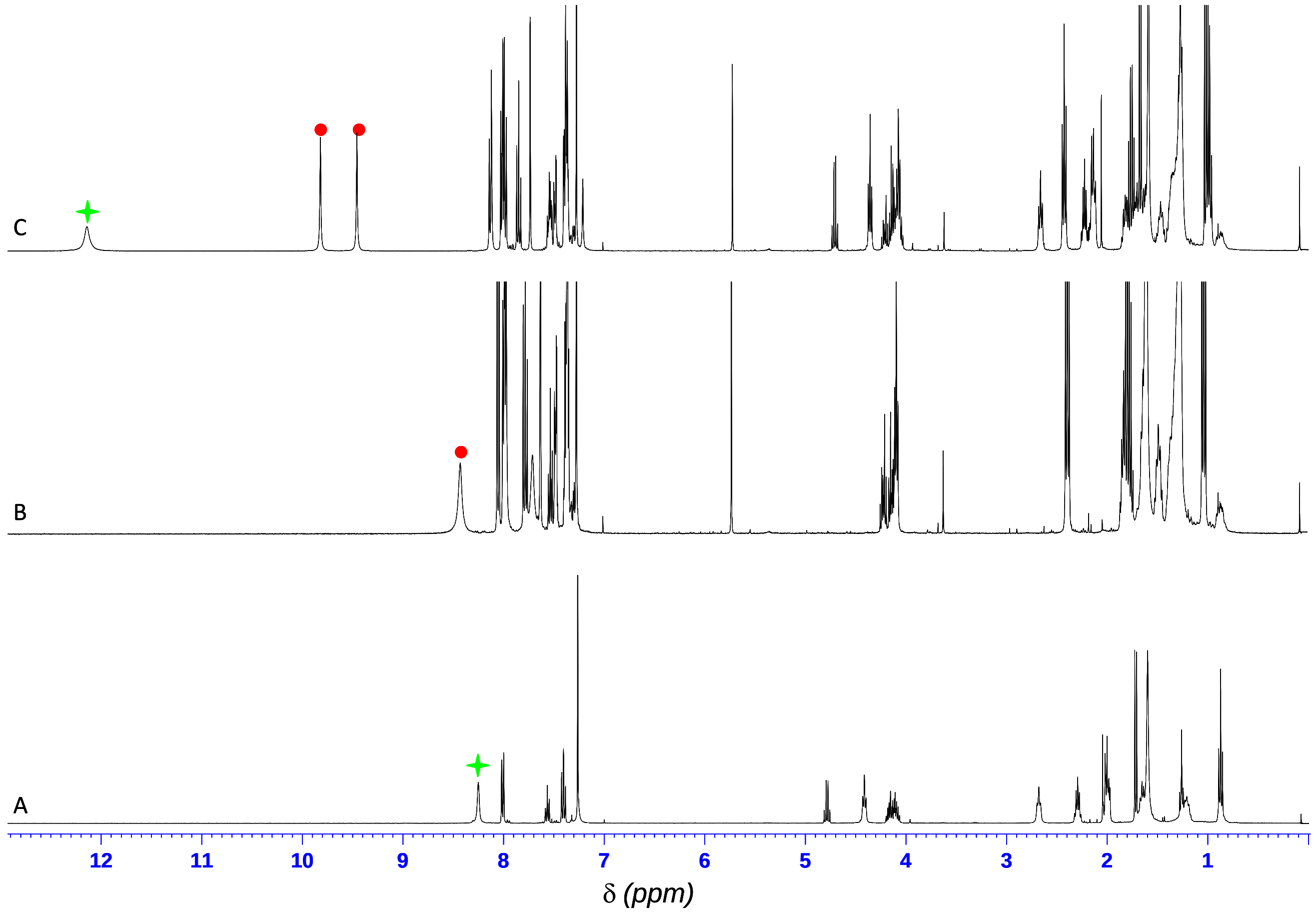

Figure S1: ^{1}H NMR spectra of CTA **14** (A), **7** (B) and a stoichiometric mixture of **14** and **7** (C), ([**14**] = [**7**] = 5 mM) at 25°C in $CDCl_3$**.** Green cross: barbiturate NH protons, red spot: Hamilton wedge NH protons (the second NH peak of HR is overlapping with the aromatic protons in spectrum B)**.**

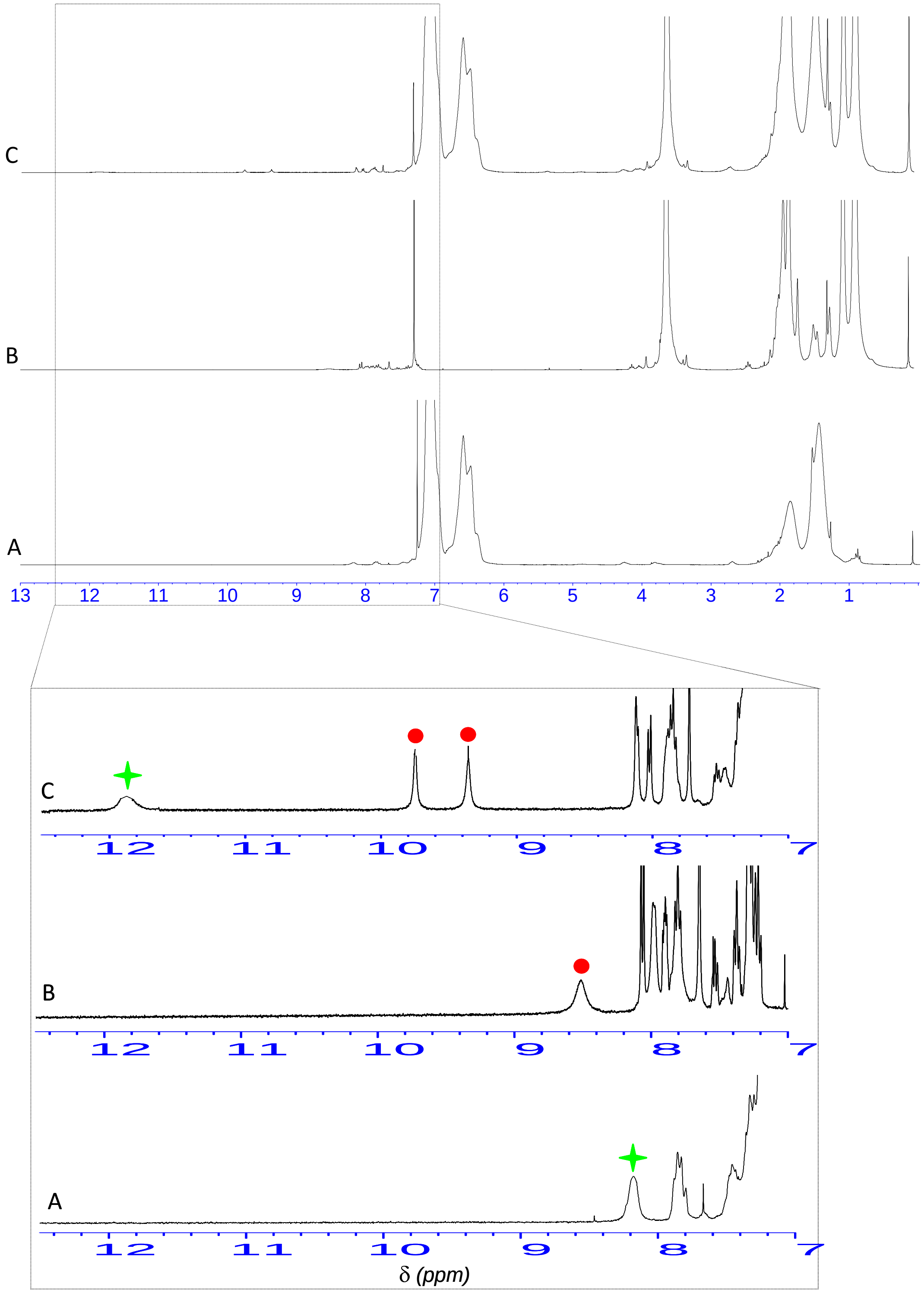

Figure S2: ^{1}H NMR spectra of Ba-PS3 (A), HR-PMMA3 (B) and of a stoichiometric mixture of HR-PMMA3 and Ba-PS3 (C) at 25°C in $CDCl_3$ ([Ba-PS3] = [HR-PMMA3] = 2 mM). Green cross: barbiturate NH protons, red spot: Hamilton wedge NH protons (the second NH peak of HR is overlapping with the aromatic protons in spectrum B).

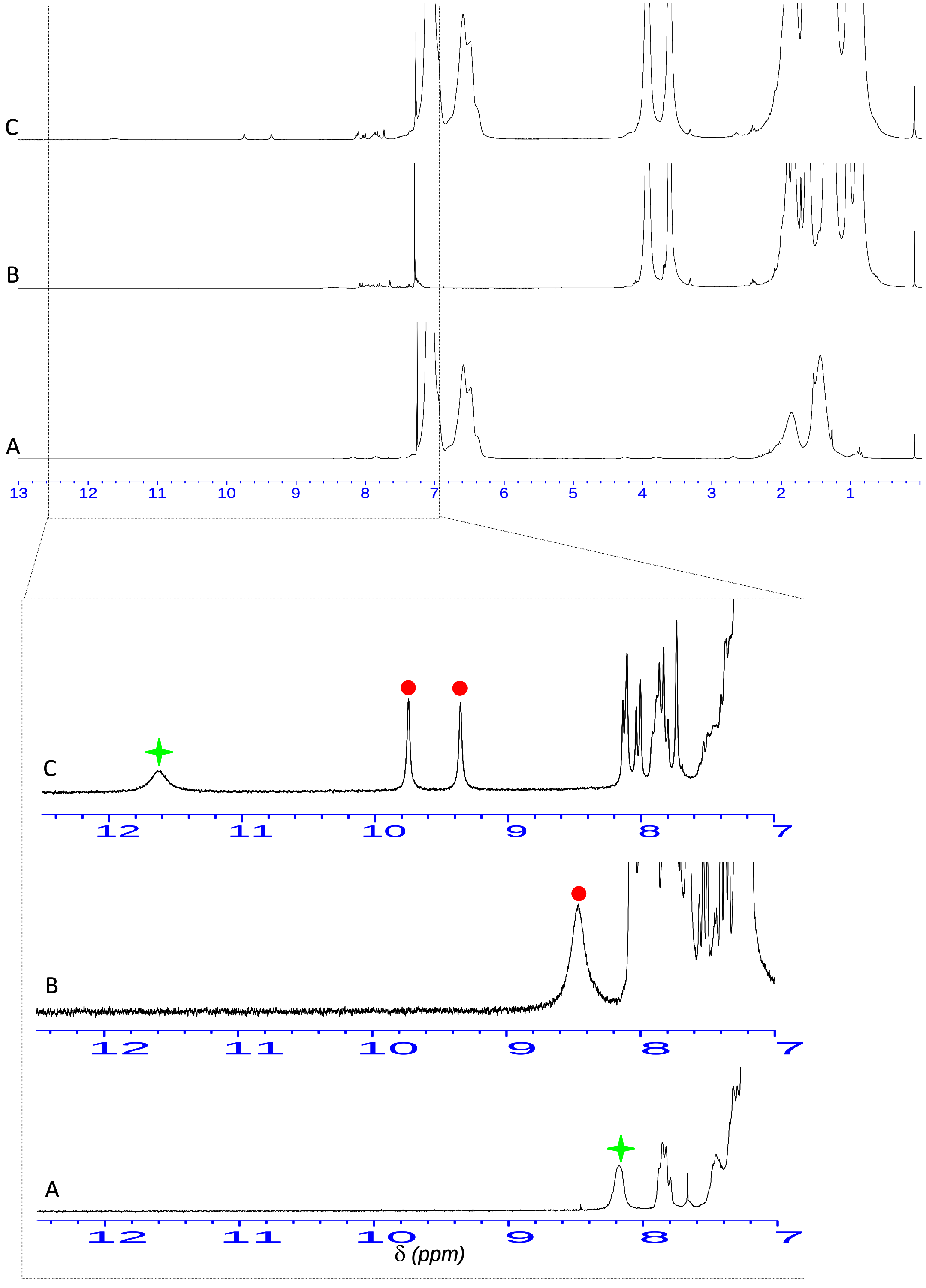

Figure S3: [1]H NMR spectra of Ba-PS3 (A), HR-PLMA-*b*-PMMA (B) and of a stoichiometric mixture of HR-PLMA-*b*-PMMA and Ba-PS3 (C) at 25°C in $CDCl_3$ ([Ba-PS3] = [HR-PLMA-*b*-PMMA] = 2 mM). Green cross: barbiturate NH protons, red spot: Hamilton wedge NH protons (the second NH peak of HR is overlapping with the aromatic protons in spectrum B).

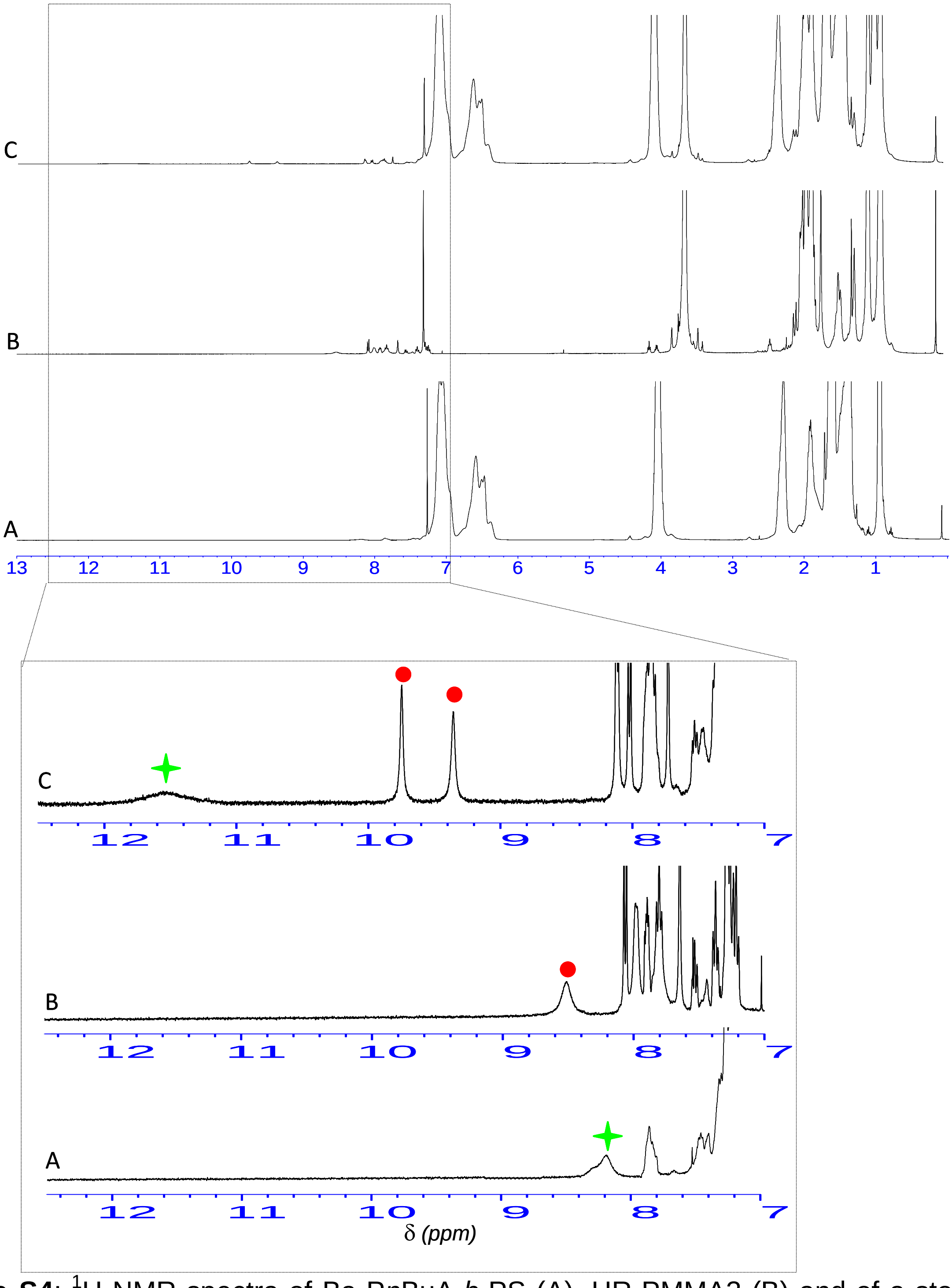

Figure S4: ^{1}H NMR spectra of Ba-P*n*BuA-*b*-PS (A), HR-PMMA3 (B) and of a stoichiometric mixture of HR-PMMA3 and Ba-P*n*BuA-*b*-PS (C) at 25°C in $CDCl_3$ ([Ba-P*n*BuA-*b*-PS] = [HR-PMMA] = 2mM). Green cross: barbiturate NH protons, red spot: Hamilton wedge NH protons (the second NH peak of HR is overlapping with the aromatic protons in spectrum B).

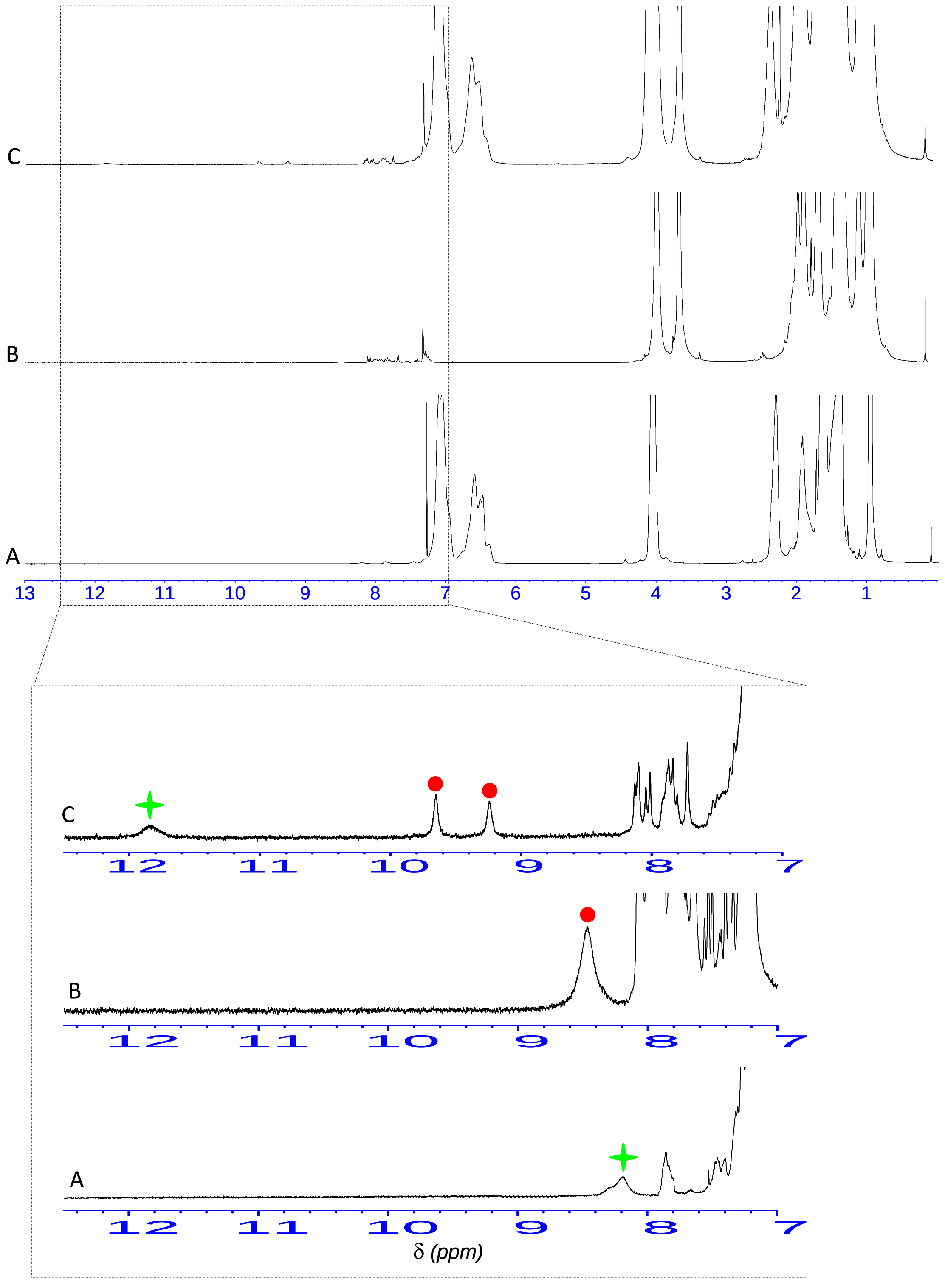

Figure S5: [1]H NMR spectra of Ba-P*n*BuA-*b*-PS (A), HR-PLMA-*b*-PMMA (B) and of a stoichiometric mixture of HR-PLMA-*b*-PMMA and Ba-P*n*BuA-*b*-PS (C) at 25°C in $CDCl_3$ ([Ba-P*n*BuA-*b*-PS] = [HR-PLMA-*b*-PMMA] = 2 mM). Green cross: barbiturate NH protons, red spot: Hamilton wedge NH protons (the second NH peak of HR is overlapping with the aromatic protons in spectrum B).

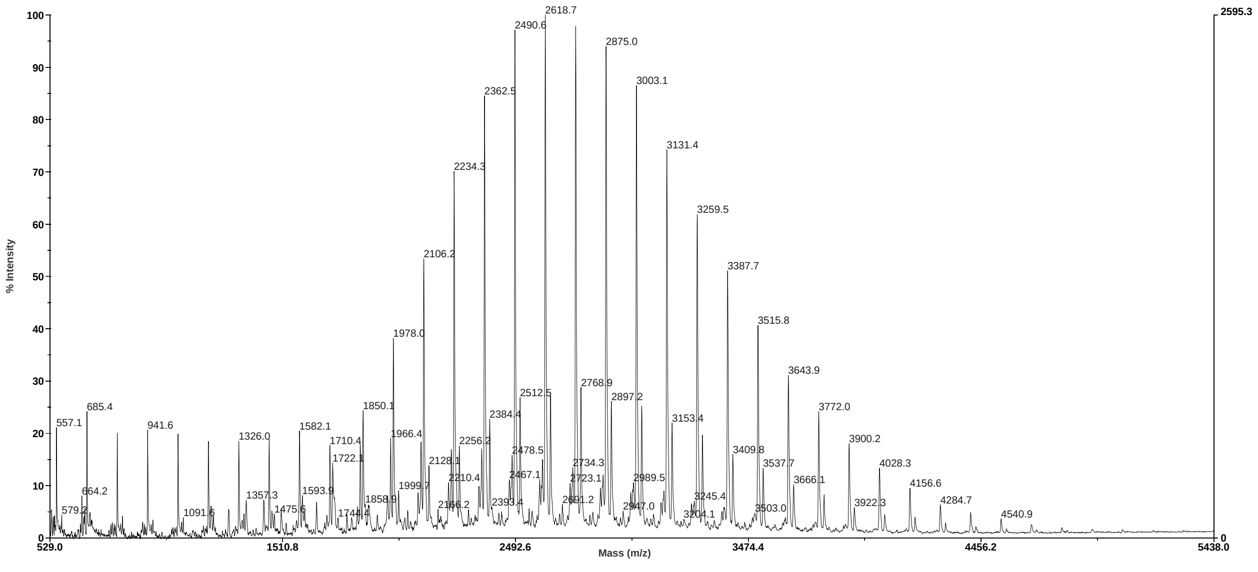

Figure S6: MALDI-TOF mass spectrum of Ba-P*n*BuA4

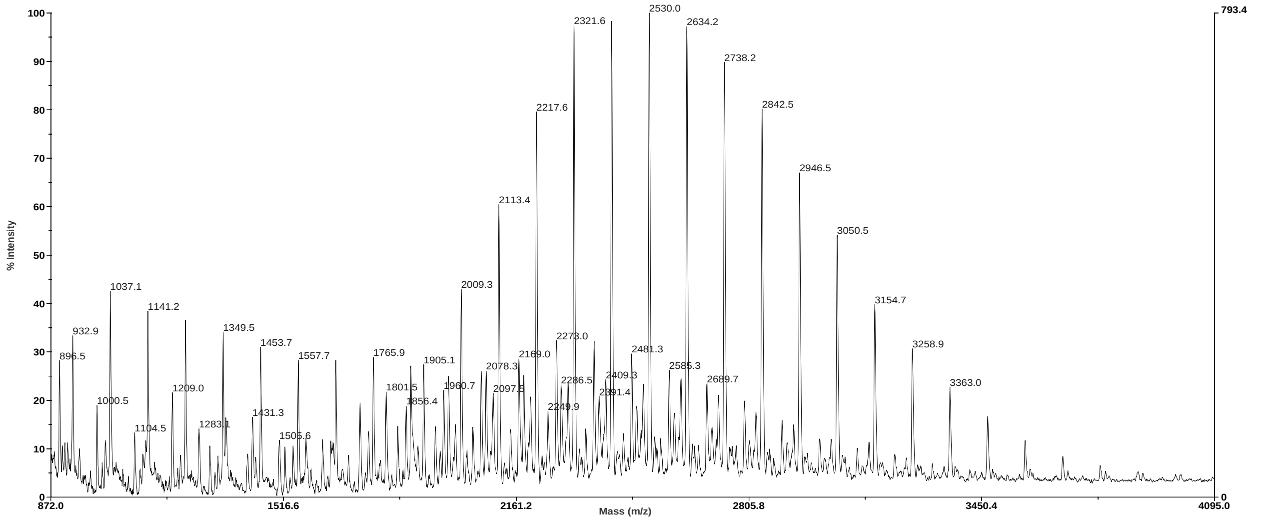

Figure S7: MALDI-TOF mass spectrum of HR-PS1

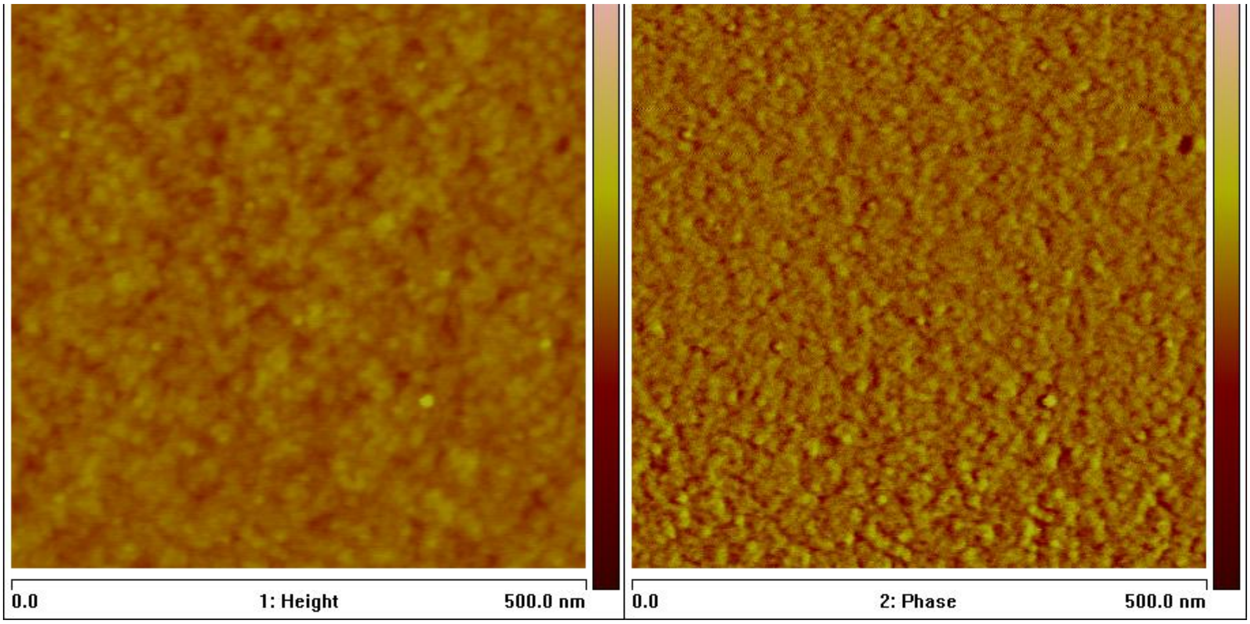

Figure S8: height and phase AFM images of Ba-PS3/HR-PMMA3 mixtures (2 g/L toluene)