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 ¹H 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 ¹H NMR and SEC. The molar mass of pure poly(lauryl methacrylate) (HR-PLMA) was finally evaluated by ¹H NMR (CDCl₃) from relative integration of the protons of the PLMA backbone (-O-CH₂-CH₂-, 2H, δ=3.86 ppm, with n being the degree of polymerization) and of characteristic protons of Hamilton wedge endgroups (-CH₂-CH₂-, 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 ¹H 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 ¹H NMR and SEC. The molar mass of barbiturate-functionalized polystyrene (Ba-PS) was finally evaluated by ¹H NMR (CDCl₃) 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−CH₂−CH₂−, 2H, δ=4.03 ppm).

Polymerization of n-butyl acrylate (nBuA) mediated by CTA 14
Solution polymerization of nBuA was performed using 2,2′-azobisisobutyronitrile (AIBN) as initiator and 14 as chain transfer agent. Typically, the polymerization of nBuA (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 nBuA consumption via ¹H 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 ¹H NMR and SEC. The molar mass of barbiturate-functionalized poly(n-butyl acrylate) (PrBuA) was finally evaluated by ¹H NMR (CDCl₃) from relative integration of the protons of the PrBuA backbone (-O-CH₂-CH₂-, 2nH, δ=3.96 ppm, with n being the degree of polymerization) and of characteristic protons adjacent to the triazole cycle (=N-C(=CH)-CH₂-CH₂-, 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-PnBuA (Mₙ, 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-PnBuA (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 ¹H 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 ¹H NMR and SEC. The molar mass of PnBuA-b-PS was finally evaluated by ¹H NMR (CDCl₃) 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 PnBuA backbone (-O-CH₂-CH₂-, 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-PnBuA-b-PS (A), HR-PMMA3 (B) and of a stoichiometric mixture of HR-PMMA3 and Ba-PnBuA-b-PS (C) at 25°C in CDCl$_3$ ([Ba-PnBuA-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-PnBuA-b-PS (A), HR-PLMA-b-PMMA (B) and of a stoichiometric mixture of HR-PLMA-b-PMMA and Ba-PnBuA-b-PS (C) at 25°C in CDCl$_3$ ([Ba-PnBuA-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-PnBuA4
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)