

Electronic Supplementary Information (ESI).

Use of a Simple Surface-Active Initiator in Controlled/living Free-radical Miniemulsion Polymerization under AGET and ARGET ATRP Conditions

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Materials. 11'-(N,N,N-trimethylammonium bromide) undecyl-2-bromo-2-methyl propionate was prepared according to a procedure described in the literature.¹ Methyl methacrylate was distilled under vacuum before polymerization. Ascorbic acid (AA, 99.5+%, Fluka), hexadecane (99+%, Aldrich), copper(II) bromide (99+%, Acros), ethyl 2-bromoisobutyrate (EBiB, 98%, Alfa Aesar), cetyltrimethylammonium bromide (CTAB, 97+%, Acros) were used as received without purification. Bis(2-pyridylmethyl)octadecylamine (BPMODA) was synthesized following previously reported procedure.²

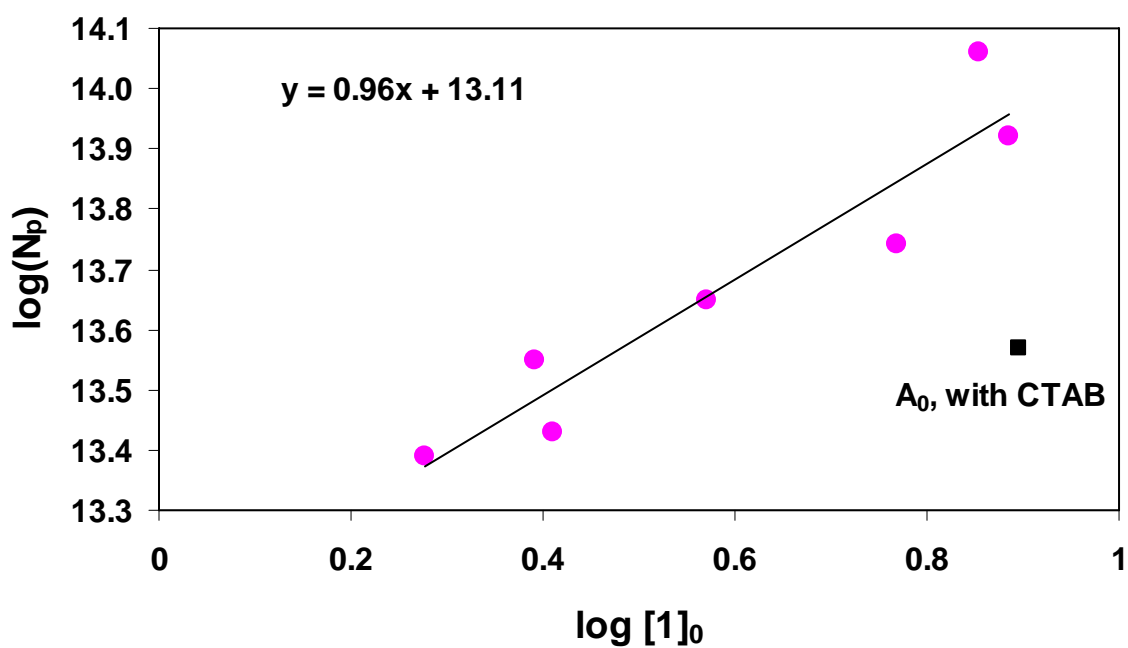
Instrumentation. Monomer conversion was determined by gravimetry. The number-average molar mass (M_n), the weight-average molar mass (M_w) and the molar mass distributions (M_w/M_n) were determined by size exclusion chromatography (SEC) in DMF (+ LiBr, 1 g/L) at 60°C and at a flow rate of 0.8 mL.min⁻¹. A differential refractive index detector (Viscotek, Dual 250) was used, and average molar masses were derived from a calibration curve based on poly(methyl methacrylate) standards from Polymer Standards Service. The z-average particle diameter (D_z) and polydispersity factor of the diluted aqueous dispersions were measured by dynamic light scattering (DLS) at 25 °C, with a Zetasizer Nano S90 from Malvern (90° angle, 5 mW He-Ne laser at 633 nm).

Surfactant-free miniemulsion polymerization of methyl methacrylate in the presence of 11'-(N,N,N-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate. In a typical recipe, the 11'-(N,N,N-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate initiator was dispersed in deionized water while CuBr₂, BPMODA ligand and hexadecane were dissolved in monomer. After the formation of the Cu(II) complex, the organic and water phases were mixed, cooled by iced water bath and subjected to ultrasonication (Branson 450 sonifier; power 7; 10 min). This led to a stabilized monomer-in-water emulsion, which was deoxygenated by argon bubbling for 30 min at room temperature and transferred into a Schlenk flask, immersed in an oil bath thermostated at 80°C. An aqueous solution of ascorbic acid (AA) was injected into the flask to reduce the copper (II) complex and initiate the reaction. Samples were periodically withdrawn to monitor the average particle diameter and to measure the conversion by gravimetry. After complete drying, the raw polymer from each sample was dissolved in DMF and the polymer solution was passed through a neutral aluminum oxide column to remove the copper catalyst before SEC analysis.

1 D. Wu, Y. Yang, X. Cheng, Li. Liu, J. Tian, and H. Zhao, *Macromolecules* 2006, **39**, 7513.

2 J. Xia and K. Matyjaszewski, *Macromolecules* 1999, **32**, 2434.

Figure 1. Dependence of the final number of particles, N_p , on the concentration of surface-active initiator (**1**) in the controlled miniemulsion polymerizations of methyl methacrylate.



Exp.	$[1]_0$	$\log(N_p)$	$\log([1]_0)$
A0	7.86 (CTAB)	13.57	0.90
A1	7.16	14.06	0.85
A2	3.73	13.65	0.57
A3	1.89	13.39	0.28
A4	5.87	13.74	0.77
A5	2.46	13.55	0.39
A1R	7.69	13.92	0.89
A2R	2.57	13.43	0.41