Use of a simple surface-active initiator in controlled/living free-radical miniemulsion polymerization under AGET and ARGET ATRP conditions†

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This communication describes the first example of the efficient use of a simple amphiphilic molecule as both a surfactant and an initiator in the miniemulsion polymerization of methyl methacrylate under AGET and ARGET ATRP conditions.

Controlled free radical polymerization (CRP) techniques,[1] and among them atom transfer radical polymerization[2–4] (ATRP) are of high academic and industrial interest to develop well-defined macromolecular architectures without the need of stringent purification conditions like in ionic polymerizations. Many CRP methods[5–7] and in particular ATRP with stable copper complexes were thoroughly studied in waterborne systems.[8] It was determined that the best suited process to develop ATRP in an aqueous dispersed system was the miniemulsion approach,[9] which efficiently locates the activator/deactivator complex and the propagating radicals within the polymerization loci, *i.e.* the monomer droplets formed upon high shearing.[10,11] Under miniemulsion conditions, well-defined polymers can be successfully synthesized using the simultaneous reverse and normal initiation (SR&NI)[12] or activator generated by electron transfer (AGET, a technique allowing the Cu(I) complex activator to be generated *in situ* by reaction between the more stable Cu(II) and a purposely added reducing agent),[13] both requiring the use of surfactants as stabilizers (mainly commercially available, nonionic and cationic low-molar-mass surfactants such as Brij 98[14] and cetyltrimethyl ammonium bromide (CTAB)[15]). Amphiphilic random, gradient or block copolymers can also be used as stabilizers for their advantages over commercially available surfactants in classical free-radical emulsion and miniemulsion polymerizations.[16–20] Hitherto, miniemulsion ATRP was mainly achieved in the presence of a hydrophobic alkyl halide initiator with non-reactive low-molar-mass surfactant. Our approach is to use, instead, a single molecule playing both roles (*i.e.* initiator and surfactant) simultaneously. This has the important advantage of reducing the number of components in the system, and in particular of avoiding the presence of free surfactant in the final latex, as the reactive molecule remains attached at the chain-end upon efficient initiation. Very recently, we reported this new approach, using a living, amphiphilic diblock copolymer to emulsify the monomer phase in water, stabilize the particles, and initiate the polymerization of a third monomer for the preparation of ABC triblock copolymer particles using AGET ATRP.[21] In this communication we now describe for the first time the straightforward atom transfer radical miniemulsion polymerization of methyl methacrylate (MMA), in the absence of additional surfactant and with a simple amphiphilic molecule, the 11′-(*N*,*N*,*N*-trimethylammonium bromide) undecyl-2-bromo-2-methyl propionate[22] (**1**, analogous to CTAB, Fig. 1) used as both a surfactant and an ATRP initiator. In that way, miniemulsion polymerizations of MMA in the presence of **1** were performed at 80 °C under two recent catalyst activation processes (AGET ATRP and activator regenerated by electron

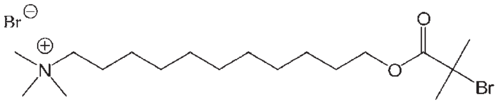

Fig. 1 Amphiphilic ATRP initiator (**1**).

Table 1 Atom transfer radical miniemulsion polymerization of MMA at 80 °C using 11′-(*N*,*N*,*N*-trimethylammonium bromide) undecyl-2-bromo-2-methyl propionate (**1**) as an initiator and a stabilizer and ascorbic acid (AA) as a reducing agent[a]

Exp.	MMA (wt%)	$[\mathbf{1}]_0$	$[\mathrm{EBiB}]_0$	$[\mathrm{CuBr_2}]_0$	$[\mathrm{MMA}]_0/[\mathrm{initiator}]_0$	$[\mathrm{AA}]_0$
A0[b]	25.4	0	10.7	8.75	216	1.30
A1	24.7	7.16	0	7.74	344	1.29
A2	25.2	3.73	0	4.40	699	0.65
A3	25.8	1.89	0	2.31	1353	0.33
A4	24.0	5.87	2.62	8.43	282	1.29
A5	23.8	2.46	6.56	8.38	263	1.28
A1R	23.6	7.69	0	0.76	304	1.29
A2R	24.0	2.57	6.22	0.87	271	1.29

[a] The amount of hexadecane used in each polymerization was 2.3 wt% based on the amount of monomer. The molar ratio of ligand BPMODA to $\mathrm{CuBr_2}$ was 1 : 1 for the AGET experiments (A0–A5) and 10 : 1 for the ARGET experiments[23,25] (A1R and A2R). Concentrations are given in mmol $\mathrm{L_{latex}}^{-1}$. [b] With [CTAB] = 7.86 mmol $\mathrm{L_{latex}}^{-1}$.

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transfer, ARGET ATRP, a technique similar to AGET, by which the amount of copper can be very significantly reduced)[23,24] at solid content as high as 23–26 wt% (Table 1).

In a typical recipe, the initiator (**1**) was dissolved in deionized water while $CuBr_2$, bis(2-pyridylmethyl)octadecylamine (BPMODA) ligand and hexadecane were dissolved in monomer. After the formation of the Cu(II) complex, the organic and water phases were mixed, cooled in an ice-water bath and subjected to ultrasonication. This led to a stabilized monomer-in-water emulsion, which was deoxygenated by argon bubbling for 30 min at room temperature and transferred to a Schlenk flask, immersed in an oil-bath thermostated at 80 °C. An aqueous solution of ascorbic acid (AA) was then injected into the flask to initiate the reaction. Detailed information on the experimental conditions of polymerization and on the characterization techniques can be found in the ESI.†

Table 2 Macromolecular and colloidal characteristics of the polymer latexes prepared *via* miniemulsion polymerizations of MMA in the presence of 11′-(*N*,*N*,*N*-trimethylammonium bromide)undecyl-2-bromo-2-methyl propionate as a surface-active initiator

Exp.	t/min	Conv. (%)	$M_{n,th}{}^{a}$/ g mol^{-1}	$M_{n,exp}$/ g mol^{-1}	PDI	$D_z{}^{b}$/nm; (poly)	log(N_p)^{c}
A0	20	13.7	3 145	5 200	1.28	—	
	38	30.3	6 745	8 000	1.26	—	
	80	53.5	11 740	11 700	1.22	—	
	120	70.3	15 380	14 300	1.34	197 (0.20)	13.6
A1	20	15.8	5 900	8 200	1.40	—	
	40	28.5	10 280	12 100	1.30	—	
	80	58.1	20 450	28 700	1.20	—	
	120	81.9	28 640	34 500	1.35	142 (0.12)	14.1
A2	20	6.9	5 080	7 700	1.16	—	
	40	17.7	12 350	14 500	1.26	—	
	79	43.6	29 650	37 850	1.24	—	
	168	88.3	59 652	69 400	1.63	200 (0.13)	13.7
A3	20	5.8	8 290	9 750	1.15	—	
	40	11.5	16 400	16 800	1.18	—	
	80	22.5	30 900	30 900	1.27	—	
	168	42.0	57 380	50 000	1.45	192 (0.08)	13.4
A4	20	10.8	3 425	5 400	1.27	—	
	40	24.9	7 410	9 100	1.27	—	
	70	49.2	14 290	15 900	1.22	—	
	100	70.9	20 410	24 900	1.21	—	
	210	96.9	27 765	31 700	1.38	188 (0.12)	13.7
A5	10	11.4	3 270	4 700	1.29	—	
	40	29.9	8 140	8 900	1.24	—	
	70	52.6	14 110	12 900	1.29	—	
	160	68.2	18 210	18 600	1.18	194 (0.15)	13.6
A1R	75	19.0	6 220	10 050	1.25	—	
	110	33.7	10 715	15 300	1.31	—	
	150	51.1	16 000	23 900	1.39	—	
	250	86.2	26 670	43 200	1.55	160 (0.20)	13.9
A2R	20	11.9	3 495	7 400	1.39	—	
	70	34.8	9 730	14 000	1.32	—	
	100	53.8	14 870	17 050	1.39	—	
	160	88.9	24 660	21 350	1.72	233 (0.14)	13.4

[a] Theoretical number-average molar mass at the experimentally determined conversion. [b] Intensity-average diameter D_z and polydispersity factor (poly) from dynamic light scattering analysis in dilute conditions (the lower the polydispersity factor, the narrower the particle size distribution). [c] Number of particles per g of latex calculated from gravimetry: $N_p = (6\tau)/(\pi D_z{}^3 \rho_p)$, with D_z, the average particle diameter, τ, the mass of polymer per gram of latex [g $g_{latex}{}^{-1}$] and ρ_p, the polymer density: PMMA = 1.19 g cm^{-3}.

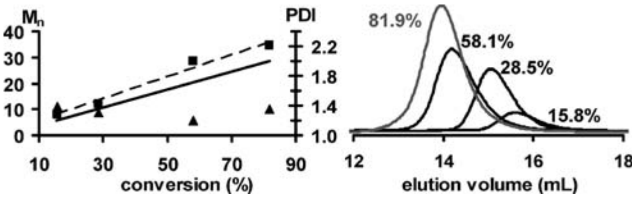

Fig. 2 Experiment A1: (Left) Number-average molar mass (M_n, kg mol^{-1}), and polydispersity index (PDI = M_w/M_n) *vs.* conversion determined by SEC (PMMA calibration); the straight line corresponds to the theoretical M_n values. (Right) Size exclusion chromatograms as a function of monomer conversion.

As depicted in Table 2, polymerizations under AGET and ARGET ATRP conditions proceeded rapidly and high monomer conversions were usually reached, which was not always the case previously when, for instance, an amphiphilic diblock copolymer was used as both a stabilizer and a macroinitiator.[21,26] In all cases, controlled polymerizations were achieved together with the formation of stable polymer colloids, with the average diameter in the 150–250 nm range and rather broad particle size distribution (a classical outcome for miniemulsion polymerization).[27] Throughout the polymerizations, the size exclusion chromatography (SEC) traces of the polymers were narrow and symmetric, and shifted towards higher molar masses with increasing monomer conversion (Fig. 2). The M_n values were close to the theoretical ones, indicating efficient initiation, and increased linearly with monomer conversion. The polydispersity indexes (PDI) were quite low (except in some cases, at the highest conversions), which is another feature for controlled radical polymerization. The good latex stability together with the high initiator efficiency indicate that (i) the amphiphilic molecule was mainly located at the droplet/particle surface and remained there after initiation to cover the surface with cationic charges and provide efficient electrostatic repulsion and (ii) no free surfactant was remaining at the end of the polymerization process.

Fig. 3 shows the conversion *vs.* time for the polymerizations of MMA under AGET ATRP conditions obtained with three different concentrations of initiator (**1**). Keeping the same

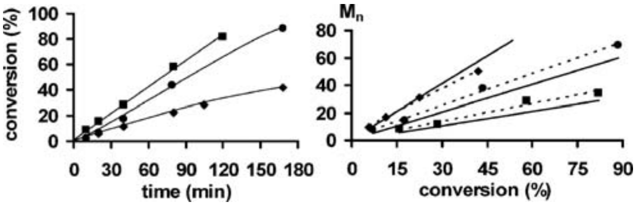

Fig. 3 (Left) Comparison of kinetics for miniemulsion polymerization of methyl methacrylate (80 °C) with three different concentrations of initiator **1**. ■: [**1**]$_0$ = 7.2 mM (experiment A1); ●: [**1**]$_0$ = 3.7 mM (experiment A2); ◆: [**1**]$_0$ = 1.9 mM (experiment A3). (Right) Number average molar mass (M_n; kg mol^{-1}; determined by SEC with PMMA calibration) *vs.* conversion (straight line = theoretical M_n; dashed line = experimental evolution).

$[\mathbf{1}]_0$: $[\mathrm{CuBr_2}]_0$: $[\mathrm{BPMODA}]_0$: $[\mathrm{AA}]_0$ ratio, the rate of polymerization increased when the concentration of initiator was increased, and, at a given conversion, the M_n values decreased accordingly. In parallel, the number of particles per g of latex, N_p, also increased with increasing concentration of **1** (Table 2). The trend was actually observed for all polymerizations, irrespective of the other experimental conditions. The surface-active initiator **1** was quite efficient as the variation of N_p was proportional to $[\mathbf{1}]_0^{0.96}$ and it was even more efficient than CTAB (lower number of particles N_p for the experiment A0 in comparison with A1 and A1R) (see Fig. 1 in ESI†).

The last two experiments (A1R and A2R in Table 2) are the first examples of miniemulsion polymerization in which the ARGET ATRP process has been successfully used, with very low copper concentration. Indeed the final amount of copper in the latex was reduced by a factor of ten (from 7.74 mmol $\mathrm{L_{latex}}^{-1}$ for the experiment A1 to 0.76 mmol $\mathrm{L_{latex}}^{-1}$ for the experiment A1R) compared to the AGET experiments with preservation of an acceptable control. The amount of ligand was however 10 times the amount of copper(II) in order to ensure the complex formation.[23,25] Investigations are now underway to optimize its concentration.

To decorrelate the surfactant concentration and targeted chain length, a second low molar mass, hydrophobic initiator, ethyl 2-bromoisobutyrate (EBiB) was used (in experiments A4, A5 and A2R) as proposed by Li *et al.* very recently (in conjunction with an amphiphilic diblock copolymer macroinitiator in the ATRP of *n*-butyl acrylate in miniemulsion).[26] Under AGET ATRP conditions, the molar ratio of EBiB to **1** was changed from 0 : 7.16 (experiment A1) to 6.56 : 2.46 (experiment A5) allowing the amount of chains initiated by EBiB to be gradually increased. All polymerizations were well controlled (with PDI values below 1.4 even at high conversion for A4 and A5) and stable polymer latexes were recovered. This approach is particularly interesting when a low molar mass polymer is targeted.

In summary, the 11′-(*N*,*N*,*N*-trimethylammonium bromide) undecyl-2-bromo-2-methyl propionate surface-active initiator was used in miniemulsion polymerization under AGET and ARGET ATRP control. This novel approach reduces the number of reagents and leads to surfactant-free living polymer latexes with submicron-size particles and solids contents as high as 25 wt%. Under ARGET ATRP conditions, it allows the copper amount in the final latex to be significantly reduced. The addition of a co-initiator (EBiB) permits the decrease of the amount of reactive surfactant, while targeting polymer with low molar mass. The extension of this promising approach to emulsion polymerization conditions and to the use of an anionically charged surface-active ATRP initiator are currently under investigation.

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