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Surfactant-Free, Controlled/Living Radical Emulsion Polymerization in Batch Conditions Using a Low Molar Mass, Surface-Active Reversible Addition-Fragmentation Chain-Transfer (RAFT) Agent

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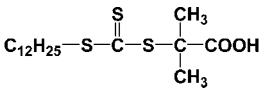
ABSTRACT: The purpose of this paper was to study the application of a surface-active trithiocarbonate RAFT agent, the 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid, sodium salt (TTCA) in surfactant-free, *ab initio*, batch emulsion polymerization. Because of the highly water-soluble character of the leaving group favoring exit from the micelles or the particles over reinitiation, the polymerization of styrene was completely inhibited. In contrast, the polymerization of *n*-butyl methacrylate was fast and led to small, stable particles, demonstrating the good stabilizing efficiency of TTCA. However, the control over molar mass was not effective, as homopolymers with high molar mass were formed. This was related to the inappropriate leaving/initiating group and low chain transfer constant of the RAFT agent in the free-radical polymerization of methacrylic esters and was also observed in bulk. This poor efficiency was overcome by copolymerizing *n*-butyl methacrylate with a low percentage of styrene or *n*-butyl acrylate. In this case, the bulk copolymerization led to controlled copolymers with predicted molar mass and narrow molar mass distribution and the chain transfer efficiency was similarly high in surfactant-free emulsion polymerization. The good colloidal characteristics of the latexes with the stabilizing group attached at the chain-end were maintained, leading to autostabilized latexes with small particle diameter, below 150 nm. This work is the first example of the direct and efficient use of a surface-active, low molar mass, RAFT agent in emulsifier-free, batch emulsion polymerization, leading simultaneously to a good control over molar mass and narrow molar mass distribution, together with good colloidal properties.

Introduction

The controlled free-radical polymerization[1] (CRP) methods (i.e., nitroxide-mediated polymerization (NMP),[2] atom transfer radical polymerization (ATRP),[3–5] reversible addition-fragmentation chain transfer (RAFT),[6] iodine atom transfer polymerization (ITP),[7] and the reverse ITP method developed in (mini)emulsion polymerization[8]) have become an intensively investigated area of research due to their ability to develop well-defined macromolecular architectures with a wide range of functional monomers. Among the available CRP techniques, the RAFT process is very promising because it works under classical experimental conditions.[9,10] It is quite a versatile method, thanks to the wide variety of reversible addition-fragmentation chain transfer agents (RAFT agents), such as dithioesters, trithiocarbonates, dithiocarbonates and dithiocarbamates, which allow the control over almost all monomers able to polymerize via free-radical chain growth method.[11,12]

In this work, 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid (TTCA, see Scheme 1)[13] was selected as a RAFT agent. The sodium salt of TTCA has the structure of a surfactant and makes it an excellent candidate for emulsion polymerization, as a surface-active RAFT agent. Moreover, it is easy to synthesize, it exhibits less unfavorable odor and color compared to most other RAFT agents and has proven to be very successful in controlled free-radical polymerization with a very wide range of monomers such as ethyl acrylate,[13] acrylic acid,[13] *N*-isopropylacrylamide,[14] *N*-(2-hydroxypropyl)methacrylamide,[15] styrene and substituted styrenes,[16,17] 4-vinylbenzaldehyde,[18] *N*-vinylpyrrolidone,[19] and isoprene,[20] to cite a few of them. A drawback however is the lack of control over the polymerization of methacrylate monomers. This can be assigned to the inappropriate leaving/initiating radical, i.e., 2-carboxy-2-propyl, which is a poor leaving group with respect to polymethacrylate-based propagating radical.[11,12,21]

Scheme 1. Structure of the 2-(Dodecylthiocarbonothioylthio)-2-methylpropanoic Acid (TTCA)



$$C_{12}H_{25}-S-\overset{\overset{\displaystyle S}{\|}}{C}-S-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-COOH$$

Reactive surfactants in emulsion polymerization are surfactants which are able to react in the free-radical polymerization process; they have been more particularly studied by Guyot et al.[22–24] Most often they bear a polymerizable group and then participate in the propagation step (they are usually called surfmers). They can also be initiators (the so-called inisurfs)[22] or chain transfer agents (the so-called transurfs).[25–27] Some papers reported the use of surface-active iniferters (sometimes called suriniferters) in emulsion photopolymerization (an iniferter[28] is a molecule which participates in initiation, chain transfer and termination and provides a partial control to the chain growth). Using this concept, Kwak et al.[29] described for the first time the synthesis of monofunctional carboxylated poly(methyl methacrylate) using a surface-active iniferter, 4-diethylthiocarbamoylsulfanylmethylbenzoic acid. Kim et al.

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employed the same molecule for the emulsion polymerization of styrene,[30] of methyl methacrylate[31] and the formation of core−shell particles. The reactive surfactant has the advantage of being covalently bound to the polymer chain, which is beneficial for most of the applications, as it reduces migration. For instance, in coating applications, surfactant migration during drying of the latex leads to poor adhesion of the polymer film on the substrate and may induce high water sensitivity.

With the development of CRP, new reactive surfactants have been proposed such as surface-active alkoxyamines for NMP[32–35] and surface-active alkyl halides for ATRP,[36] both playing a role similar to that of the previously mentioned inisurfs. In some examples, the use of a water-soluble macromolecular alkoxyamine allowed an amphiphilic block copolymer stabilizer to be created in situ.[37,38] Besides stabilization of the latex particles, an additional feature of those reactive surfactants is to impart good control over polymer chain growth and to allow the creation of complex macromolecular architectures in waterborne systems.[39] Whereas hydrophobic RAFT agents have been extensively studied in miniemulsion and in emulsion polymerizations, very few works have actually been carried out using surface-active RAFT agents, in the presence or not of an additional surfactant.[39–41] In most instances, the low molar mass compounds did not allow a good control over molar mass and molar mass distribution simultaneously with good colloidal characteristics. In seeded emulsion polymerizations used as model experiments with classical RAFT agents, inhibitions and rate retardations were observed and assigned to favored desorption of the leaving/initiating radicals from the particles, followed by potential termination; those features were particularly enhanced when the leaving/initiating radical exhibited a certain degree of water solubility.[39,40,42,43] Uzulina et al.[44] and Kanagasabapathy et al.[45] studied the commercially available, water-soluble *S*-thiobenzoyl-thioglycolic acid, but they failed in achieving good macromolecular and colloidal characteristics at the same time. A series of dithiocarbamate RAFT agents with different water-solubility have been studied in detail for the emulsion polymerization of various monomers in the presence of surfactant: polymers with high polydispersity index and latexes with rather large particle size were obtained, the best results being observed with RAFT agents exhibiting the right balance of hydrophilicity−hydrophobicity (i.e., appropriate partition coefficient rather than surface-active character).[46] Shim et al.[47,48] described the surfactant-free emulsion photopolymerization of methyl methacrylate using a surface-active RAFT agent, 4-thiobenzoylsulfanylmethyl benzoate, in the absence of additional initiator. Molar mass of the polymers did not depend upon the RAFT agent concentration and were not so different from those expected in classical emulsion polymerization but the polydispersity indexes were rather low, typically below 2. In 2002, Hawkett's group[49–51] proposed a novel, very efficient, strategy to perform RAFT in surfactant-free emulsion polymerization. They used an amphipathic RAFT agent that was first chain extended in situ with sodium acrylate to form a short, water-soluble poly(sodium acrylate) macromolecular RAFT agent. Then, the emulsion polymerization was performed by adding a hydrophobic monomer under starved feed conditions and particles were generated by self-assembly of the so-formed amphiphilic diblock copolymers. Another similar work was later performed with a water-soluble, protonated poly(4-vinylpyridine) macromolecular RAFT agent.[52] More recently, Hawkett's group studied the application of amphiphilic, RAFT-capped, poly(acrylic acid)-*b*-polystyrene diblock copolymers as stabilizers in ab initio emulsion polymerization.[53] Fréal-Saison et al.[54] reported an emulsifier-free, controlled free-radical emulsion polymerization of styrene based on a spontaneous phase inversion mechanism, using dibenzyltrithiocarbonate as a chain transfer agent and acrylic acid as an ionogenic comonomer. More recently, we proposed the successful application of a nonionic poly(ethylene oxide)-based amphiphilic trithiocarbonate RAFT agent in surfactant-free *ab initio* batch emulsion polymerization of styrene and *n*-butyl acrylate.[55]

On the basis of this literature survey, and to the best of our knowledge, there is no successful example in the open literature of low molar mass, surface-active RAFT agent applied in emulsifier-free, *ab initio*, batch emulsion polymerization in a direct way, to effectively control the polymer chain growth together with the colloidal properties. In this work, the use of the sodium salt of 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid (TTCA, see Scheme 1) as a surface-active RAFT agent in the emulsifier-free, *ab initio*, batch emulsion polymerization of styrene and of *n*-butyl methacrylate was investigated. We first studied the conditions to polymerize a methacrylic ester with TTCA in a living way. Our special interest was then to find proper conditions to perform emulsifier-free, emulsion polymerization, with good understanding of the kinetic features and simultaneous production of stable particles and well-defined polymers with controlled molar mass and narrow molar mass distribution.

Experimental Section

Materials. Styrene (S, Fluka ≥99%) *n*-butyl methacrylate (BMA, Fluka ≥99%) and *n*-butyl acrylate (BA, Aldrich >99%) were distilled under reduced pressure at room temperature before use. 4,4′-Azobis(4-cyanopentanoic acid) (ACPA, Fluka >98%) and sodium dodecylsulfate (SDS, Aldrich 98%) were used as received. 2-(Dodecylthiocarbonothioylthio)-2-methylpropanoic acid (TTCA) was synthesized as detailed by Lai et al.[13]

Bulk Polymerization. In a typical experiment (experiment **B1**, Table 1), a round-bottomed flask (100 mL) was charged with styrene (26 g, 0.25 mol), ACPA (32 mg, 0.11 mmol) and TTCA (0.32 g, 0.87 mmol). The mixture was deoxygenated by argon bubbling for 35 min at room temperature and was then immersed in an oil bath thermostatted at 70 °C. Samples were periodically withdrawn to measure the conversion by gravimetry. After complete drying, the raw polymer from each sample was dissolved in THF for size exclusion chromatography analysis.

Emulsion Polymerization. A typical recipe for the emulsion polymerization using TTCA as both a surfactant and a RAFT agent is the following. For experiment **E5** in Table 2, the RAFT agent (0.158 g, 0.435 mmol) was neutralized with 1 equiv of a NaOH solution (0.6 g, 1 $\mathrm{mol \cdot L^{-1}}$) and dissolved in a phosphate buffer aqueous solution (49.4 g, 0.6 mmol, pH = 8, $10^{-2}\ \mathrm{mol \cdot L^{-1}}$). The monomer (6.5 g, 45.8 mmol) and ACPA (0.0175 g, 0.062 mmol) were introduced and the mixture was deoxygenated by argon bubbling for 35 min at room temperature and then, was immersed in an oil bath thermostatted at 70 °C. Samples were periodically withdrawn to monitor the average particle diameter and to measure the conversion by gravimetry.

Characterizations. Size exclusion chromatography was performed at 40 °C with two columns (PSS SDV, linear MU, 8 mm × 300 mm; bead diameter, 5 μm; separation limits, 400 to 2×10^6 $\mathrm{g \cdot mol^{-1}}$). The eluent was tetrahydrofuran (THF) at a flow rate of 1 $\mathrm{mL.min^{-1}}$. A differential refractive index detector (LDC Analytical refractoMonitor IV) was used, and molar masses (M_n, the number-average molar mass, M_w the weight-average molar mass and PDI = M_w/M_n the polydispersity index) were derived from a calibration curve based on poly(methyl methacrylate) and polystyrene standards from Polymer Standards Service. In all curves showing the evolution of M_n with monomer conversion, the straight line corresponds to the expected evolution with the theoretical $M_{n,th}$ calculated by the ratio of the initial mass of monomer multiplied by the conversion over the initial number of moles of the RAFT agent (plus the molar mass of the RAFT agent that is almost negligible). The Z-average particle diameter (D_z) and polydispersity factor (σ) were measured by dynamic light scattering (DLS) at a temperature of 25 °C and an angle of 90°, with a Zetasizer Nano

Table 1. Experimental Conditions and Results for the Bulk Homopolymerizations of Styrene (S) and *n*-Butyl Methacrylate (BMA) and the Copolymerizations of BMA with Styrene or *n*-Butyl Acrylate (BA) Performed at 70 °C, in the Presence of 2-(Dodecylthiocarbonothioylthio)-2-methylpropanoic Acid (TTCA) as a Reversible Addition-Fragmentation Chain-Transfer (RAFT) Agent and 4,4′-Azobis(4-cyanopentanoic acid) (ACPA) as an Initiator

expt	monomer (g)	$[TTCA]_0$ ($mol \cdot L^{-1}$)	$[ACPA]_0/[TTCA]_0$	time (min)	convn (%)	$M_{n,th}$ ($g \cdot mol^{-1}$)	$M_{n,SEC}$[a] ($g \cdot mol^{-1}$)	PDI[b]
B1	S (26.0)	3.42×10^{-2}	0.13	123	3	1226		
				253	8	2653	2300	1.18
				373	15	4933	4100	1.13
				1152	30	9205	7400	1.09
B2	BMA (26.0)	3.07×10^{-2}	0.16	25	9	3083	26100	1.89
				62	22	7123	29600	1.72
				165	46	14332	30300	1.67
B3	BMA/S (23.2/2.6)	3.43×10^{-2}	0.13	32	4	1600	1650	2.00
				65	8	2780	2600	1.89
				98	13	4085	3850	1.74
				185	24	7550	6750	1.59
				275	33	10415	9450	1.44
B4	BMA/S (24.5/1.1)	3.27×10^{-2}	0.13	91	10	3385	3550	1.85
				177	33	9796	10400	1.57
				397	47	14537	14300	1.50
B5	BMA/BA (23.3/3.1)	3.41×10^{-2}	0.13	60	16	5245	7200	1.85
				127	32	10470	11550	1.66
				197	47	14970	13800	1.72
				273	59	18710	18250	1.53

[a] Number-average molar mass, M_n, determined by size exclusion chromatography using polystyrene standards for the experiment **B1** and poly(methyl methacrylate) standards for experiments **B2**−**B5**. [b] Polydispersity index, PDI = M_w/M_n (with M_w, the weight-average molar mass).

Table 2. *Ab Initio,* Batch Emulsion Homopolymerizations of Styrene (S) and *n*-Butyl Methacrylate (BMA) and Copolymerizations of BMA with Styrene and with *n*-Butyl Acrylate (BA) at 70 °C via RAFT (Reversible Addition-Fragmentation Chain Transfer) Using 2-(Dodecylthiocarbonothioylthio)-2-methylpropanoic Acid, Sodium Salt (TTCA), as both a RAFT Agent and a Stabilizer and 4,4′-Azobis(4-cyanopentanoic acid) (ACPA) as a Radical Initiator[a]

expt	monomers	monomers (wt %)	$[TTCA]_0$ ($mmol \cdot L_{aq}^{-1}$)	$[M]_0/[TTCA]_0$	$[SDS]_0$ ($mmol \cdot L_{aq}^{-1}$)	$[ACPA]_0/[TTCA]_0$	time (min)	convn (%)	$M_{n,th}$ ($g \cdot mol^{-1}$)	$M_{n,SEC}$ ($g \cdot mol^{-1}$)	PDI	D_z[b] (nm)	polydispersity factor (σ)[b]
E1	S	20.6	0		31		30	49		$>2.7 \times 10^{+6}$			
							60	87					
							92	94				103	0.02
E2	S	20.6	8.7	287	0	0.13	123	2					
							1130	3					
E3	S	20.6	8.8	284	31	0.12	390	2					
							1204	3					
E4	BMA	11.4	0		28		20	95		$>10^{+6}$		95	0.05
E5	BMA	11.5	8.7	105	0	0.14	20	14	2499	80150	1.98		
							42	62	9541	117500	1.52		
							90	93	14178	127400	1.54	50	0.06
E6	BMA	11.5	8.7	105	24	0.14	20	48	7516	111800	1.70		
							40	94	14351	103300	1.91	33	0.10
E7	95.0 wt % BMA + 5.0 wt % S	11.5	8.8	106	0	0.15	63	5	1080				
							134	11	2008	1550	1.76		
							196	58	8972	8550	1.96		
							262	83	12743	13500	1.98	39/290[d]	
E8	89.3 wt % BMA + 10.7 wt % S	14.8	8.7	147	0	0.15	120	4	1115				
							246	8	1900	1300	1.82		
							342	65	13520	13800	1.75		
							372	87	17780	21400	1.55	104	0.22
E9	79.8 wt % BMA + 20.2 wt % S	11.5	8.6	114	0	0.15	236	4	945				
							366	7	1437				
							430	32	5209				
							491	65	10245	9900	2.32	87/650[d]	
E10	89.4 wt % BMA + 10.6 wt % S	14.8	8.7	147	27	0.16	67	5	1341				
							203	41	8544				
							226	87	17744	13100	3.91[c]	41	0.20
E11	89.1 wt % BMA + 10.9 wt % S	15.0	4.5	285	0	0.16	175	4	2096				
							260	44	17422	23150	1.96		
							313	78	30782	51800	1.43	113	0.13
E12	89.3 wt % BMA + 10.7 wt % S	14.6	17.3	73	0	0.16	112	6	955				
							315	12	1572	1060	1.68		
							375	19	2222	1660	1.61		
							422	89	9201	11240	1.54	145	0.25
E13	87.2 wt % BMA + 12.8 wt % BA	14.6	8.4	145	0	0.17	60	6	1530				
							101	9	2330				
							147	16	3540	2450	4.11		
							164	37	7955	8880	1.64		
							213	90	18750	21360	1.36	49	0.19

[a] All emulsion polymerizations were conducted at 70 °C in the presence of phosphate buffer at pH = 8. [b] The average diameter, D_z, and the polydispersity factor σ (the closer to 0 indicating the narrower particle size distribution), were determined by dynamic light scattering analysis. [c] Bimodal molar mass distribution. [d] Bimodal particle size distribution.

S90 from Malvern, using a 5 mW He−Ne laser at 633 nm. All measures were performed just after the polymerization and approximately 2 months later; a latex was claimed as stable when no change in the average particle diameter and the polydispersity factor was observed. The critical micelle concentration of TTCA was measured by conductimetry[27] at 21 °C with a Senteck-type conductivity cell. A stock solution of TTCA (9.7 mM, adjusted to pH = 8.0 with NaOH 1 $mol \cdot L^{-1}$) was diluted with an aqueous alkaline solution (deionized water adjusted to pH = 8 with NaOH) to obtain concentrations between 0.056 and 9.7 $mmol \cdot L^{-1}$.

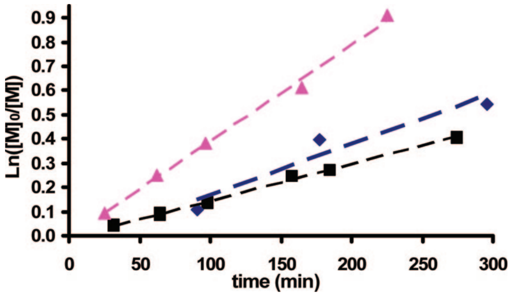

Figure 1. Semilogarithmic kinetic curves for the 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid (TTCA)-mediated bulk homopolymerization of n-butyl methacrylate (▲, experiment **B2**, in Table 1) and the TTCA-mediated bulk copolymerizations of n-butyl methacrylate with 4.3 wt % (5.8 mol %) of styrene (◆, experiment **B4** in Table 1) and 10.0 wt % (13.3 mol %) of styrene (■, experiment **B3** in Table 1).

Results and Discussion

Bulk Polymerization. Before testing the TTCA reversible addition-fragmentation chain transfer agent in emulsion polymerization conditions, we performed some preliminary tests in bulk, to find the proper conditions for the controlled polymerization of n-butyl methacrylate (Table 1).

As shown in Table 1, experiment **B1**, the RAFT homopolymerization of styrene was well-controlled as the recovered polystyrene exhibited a linear increase of M_n with monomer conversion and polydispersity indexes below 1.2, even in the early stage of the polymerization. However, the M_n values measured by SEC were lower than the theoretical values. The difference can be ascribed to nonnegligible contribution of the added initiator (ACPA), because the polymerization was particularly slow in the selected conditions (approximately 30% conversion within 20 h) and the long polymerization time was favorable to complete dissociation of ACPA. Such results are similar (15% conversion after 6 h with $[S]_0/[TTCA]_0 = 450$ instead of 288 in our case) to those obtained by Zhang et al.[17] under mild long-wave UV−visible irradiation at 30 °C in the presence of diphenylphosphine oxide as a photoinitiator and TTCA as a RAFT agent in bulk condition. The RAFT agent was also tested in its sodium salt form in 1,4-dioxane solution and the polymerization results confirmed its effectiveness (not shown here).

A complete literature study actually confirmed that TTCA is a very effective RAFT agent for a lot of monomers but does not yield poly(methacrylic ester)s with controlled molar mass and narrow molar mass distribution (see the introduction); this can be assigned to too low chain transfer constant.[56] It was confirmed with BMA monomer in the presence of TTCA in bulk conditions (experiment **B2** in Table 1): the observed molar masses were far above the predicted values, they did not change significantly with monomer conversion and the polydispersity indexes were rather large. All those results clearly indicate a lack of efficiency of the TTCA RAFT agent. To better control the polymerization of BMA, we decided to introduce a small percentage of styrene as a comonomer (10.0 wt %, i.e., 13.3 mol % in experiment **B3**; 4.3 wt %, i.e., 5.8 mol % in experiment **B4**; see Table 1) in a similar way as we previously did in NMP.[57] Under such conditions, the copolymerizations were slower than the homopolymerization of BMA as shown in Figure 1. The clear shift of the SEC traces toward higher molar masses with monomer conversion indicates that the chains were simultaneously extended to form copolymers with monomodal molar mass distribution (Figure 2). The plot of M_n and PDI dependence on conversion for the experiment **B3** is shown in Figure 2. The features of controlled free-radical polymerization were observed with a linear increase of M_n with respect to monomer conversion, a good agreement with the predicted values, and a significant decrease of the polydispersity indexes with conversion toward a value lower than 1.5 at 33% conversion. This indicates that the number of chains was governed by the RAFT agent concentration and remained constant throughout the polymerization in accord with a high apparent chain transfer constant to TTCA in the copolymerization system. As supported by the theoretical approach reported by Kubo et al.,[58] this can be explained by several favorable factors: (i) propagating radicals with a styrene terminal subunit undergo faster addition reaction to TTCA than the propagating radicals with a BMA terminal subunit; (ii) due to the absence of penultimate unit effect, fragmentation of the intermediate radical resulting from the addition of an oligomeric radical with styryl end-group to TTCA leads to efficient release of the 2-(hydroxycarbonyl)prop-2-yl radical. Consequently, the introduction of a small amount of styrene in the polymerization medium enhances the transfer reaction to TTCA and allows high transfer efficiency to be reached. A very similar result was achieved when styrene was replaced by 11.7 wt % (12.9 mol %) of n-butyl acrylate, as illustrated by the experiment **B5** (Table 1). The method is of high interest for the application of poorly adapted RAFT agents to the controlled synthesis of methacrylic ester-rich polymers. This approach, will be applied in an *ab initio,* batch emulsion polymerization of BMA in the presence and absence of free surfactant as shown below.

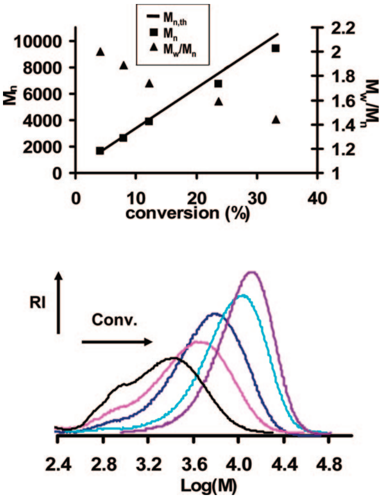

Figure 2. 2-(Dodecylthiocarbonothioylthio)-2-methylpropanoic acid (TTCA)-mediated bulk copolymerization of n-butyl methacrylate with 10.0 wt % (13.3 mol %) of styrene (experiment **B3** in Table 1). Top: Number average molar mass (M_n) and polydispersity index (PDI = M_w/M_n) dependence on conversion. Bottom: Evolution of the size exclusion chromatography traces with monomer conversion.

Ab Initio **Batch Emulsion Polymerization.** The trithiocarbonate TTCA (Scheme 1), composed of an aliphatic hydrophobic chain and a carboxylate hydrophilic moiety in alkaline conditions was applied to the RAFT emulsion polymerization of styrene and n-butyl methacrylate. Due to its structure, TTCA was first characterized in term of surface-activity, to check whether and to what extent it may be used as the sole stabilizer for the latex particles, in the absence of added surfactant. This would be of great interest, since in the final latex the RAFT agent should be covalently linked to the polymer chains, which would prevent deleterious migration of low molar mass surface-active material during application. The critical micelle concentration, determined by conductimetry at 21 °C, was actually 1.0 $\text{mmol}\cdot\text{L}^{-1}$, which is below the aqueous concentration used in this work, indicating the presence of micelles and hence the high probability for micellar nucleation.

*Homopolymerization of Styrene (Experiments **E1**−**E3**).* As reported in Table 2, experiments **E2** and **E3**, the TTCA RAFT

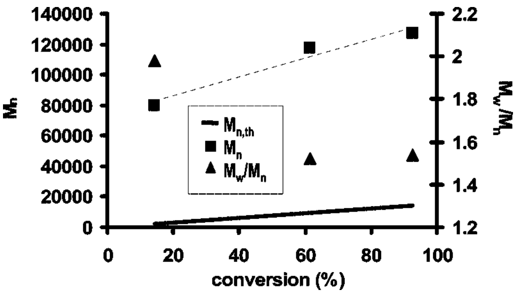

Figure 3. Surfactant-free, *ab initio*, batch emulsion homopolymerization of *n*-butyl methacrylate in the presence of 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid, sodium salt, as a RAFT agent: number average molar mass (M_n, ■) and polydispersity index (PDI = M_w/M_n, ▲) dependence on conversion (experiment **E5** in Table 2). (—) Theoretical M_n values.

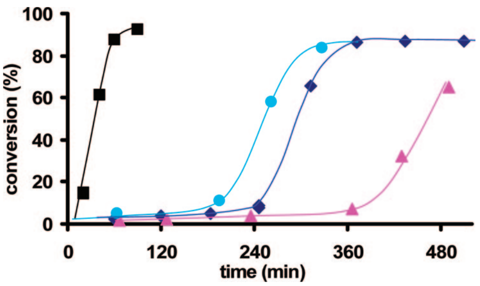

Figure 4. Conversion versus time for the surfactant-free, *ab initio*, batch emulsion polymerizations of *n*-butyl methacrylate in the presence of 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid, sodium salt, as a RAFT agent, with four different percentages of styrene: 0% (■, experiment **E5** in Table 2): 5.0 wt % (6.7 mol %, ●, experiment **E7** in Table 2); 10.7 wt % (14.2 mol %, ◆, experiment **E8** in Table 2); 20.2 wt % (25.7 mol %, ▲, experiment **E9** in Table 2).

agent inhibited almost completely the emulsion homopolymerization of styrene (in comparison with **E1**, performed without RAFT agent), in the presence and in the absence of added surfactant. Although the polymerization was rather slow in bulk, such an inhibition was not observed. There was consequently an additional effect of the dispersed state of the system to explain the experimental observations. This may be related to the highly water-soluble character of the 2-(hydroxycarbonyl)prop-2-yl sodium salt leaving/initiating radical. The entry of a polystyryl oligoradical into a TTCA micelle (or a TTCA/SDS mixed micelle) leads, upon fast transfer reaction, to the release of the initiating radical in the water phase, with very little chance of propagating in the monomer-swollen core of the micelle. Such an exited radical may either terminate in the aqueous phase or enter another micelle after addition of a few styrene units and then undergo the same transfer/exit fate. Under experimental conditions with low initiator/RAFT agent ratio the polymerization may never start. Different observations were made when the RAFT agent was turned into the corresponding poly(ethylene oxide) ester: with styrene, the polymerization was slow but the control over the chain growth was good. This may be ascribed to a lower solubility and a lower diffusivity of the poly(ethylene oxide)-based initiating radical in water, and hence to a higher probability of reinitiation over exit upon transfer.[55]

*Homopolymerization of n-Butyl Methacrylate (Experiments **E4**−**E6**).* In all cases (experiments **E4**−**E6** in Table 2), the emulsion homopolymerization of BMA was fast, i.e., much less than 2 h were required for more than 90% monomer conversion. In contrast to the homopolymerization of styrene, in the presence of the RAFT agent no inhibition was observed, but only a slight rate retardation. The evolution with monomer conversion of the number-average molar masses, M_n, and the polydispersity indexes, PDI = M_w/M_n, of poly(*n*-butyl methacrylate) (PBMA) prepared with 8.7 mmol·L_{aq}^{-1} TTCA (experiment **E5** in Table 2) at 70 °C in the absence of SDS are displayed in Figure 3. It can clearly be seen that the experimental M_n values increased continuously but were far above the theoretical ones. In the presence of SDS (experiment **E6**), the results followed the same trend with however slightly higher molar masses and broader molar mass distribution. In the absence of RAFT agent but in the presence of SDS surfactant (28 mmol·L_{aq}^{-1}, experiment **E4**) the molar masses were about 1 order of magnitude higher.

Those results indicate a low (but nonnegligible) contribution of the RAFT agent during the polymerization process. In contrast to the homopolymerization of styrene, the entry of oligoradicals into TTCA-rich micelles does not lead to efficient transfer reaction; their propagation is favored, hence leading to high conversion within relatively short polymerization times. Upon transfer to TTCA, the water-soluble 2-(hydroxycarbonyl)prop-2-yl sodium salt radical is formed, which may exit toward the water phase and undergo possible irreversible termination (which induces the observed rate retardation effect) or re-enter (after addition of a few monomer units in the aqueous phase) into another micelle/particle where propagation can take place. At complete monomer conversion, only part of the TTCA molecules has reacted, as supported by the large difference of experimental and theoretical M_n values discussed above (approximately 11% efficiency for the experiment **E5**, with calculation based on the final M_n).

The PBMA latexes obtained with and without the RAFT agent, in the presence or not of free surfactant (experiments **E4**, **E5**, and **E6** in Table 2) exhibited actually very good stability with average particle diameter below 100 nm. In the presence of TTCA and without any added surfactant (experiment **E5**, Table 2), the average particle diameter was 50 nm with very narrow particle size distribution, corroborating the surface-active character of the RAFT agent and its location at the particle surface.

*Copolymerization of n-Butyl Methacrylate with Various Amounts of Styrene (Experiments **E5** and **E7**−**E12**).* The aforementioned approach to control the polymerization of BMA in bulk was applied here to the surfactant-free, *ab initio*, batch emulsion polymerization in the presence of various percentages of styrene (Figure 4). While the homopolymerization of BMA was fast, the presence of styrene led to an inhibition period, the duration of which increased when the percentage of styrene was increased (experiments **E5**, **E7**, **E8**, and **E9** in Table 2). After the inhibition period, the polymerization rate was however particularly high, similar to that observed in the homopolymerization reaction. A too large proportion of styrene provided the copolymerization with the characteristics of the homopolymerization of styrene, i.e. long induction period tending to complete inhibition. In contrast, in the presence of a small percentage of styrene, like already observed in bulk, the features of controlled radical polymerization were actually observed with a linear increase of M_n with respect to monomer conversion and relatively low polydispersity indexes. The plot of M_n and PDI dependence on conversion for the polymerization with 10.7 wt % (14.2 mol %) of styrene (experiment **E8** in Table 2) is shown in Figure 5. The M_n values were close to the theoretical ones indicating a complete consumption of the RAFT agent. For all polymerizations in the presence of the styrene comonomer, the same features were observed, but the polydispersity indexes were rather dependent on the amount of styrene, 10.7 wt % (14.2 mol %) corresponding to the optimal conditions.

In the copolymerization of BMA with 10.7 wt % (14.2 mol %) of styrene (experiment **E8**), the surface-active RAFT agent was sufficient to stabilize effectively the latex particles, since the average diameter was 104 nm and the latex was stable. However, the particle size distribution was slightly broader in

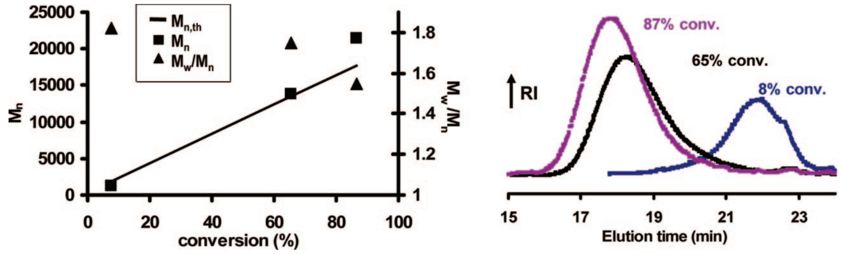

Figure 5. Surfactant-free, *ab initio*, batch emulsion polymerization of *n*-butyl methacrylate with 10.7 wt % (14.2 mol %) of styrene in presence of the 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid, sodium salt, RAFT agent at 70 °C (experiment **E8** in Table 2). Left: Number-average molar mass (M_n) versus conversion (■); theoretical M_n (—) and PDI = M_w/M_n (▲). Right: Evolution of the size exclusion chromatography traces with monomer conversion.

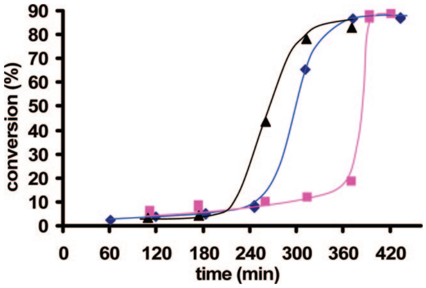

Figure 6. Conversion versus time for the surfactant-free, *ab initio*, batch emulsion copolymerizations of *n*-butyl methacrylate (70 °C) with 10 wt % of styrene, in the presence of various concentrations of the 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid RAFT agent (TTCA) sodium salt: $[\text{TTCA}]_0 = 4.5\ \text{mmol}\cdot\text{L}^{-1}$ (▲ experiment **E11**); $[\text{TTCA}]_0 = 8.7\ \text{mmol}\cdot\text{L}^{-1}$ (◆, experiment **E8**); $[\text{TTCA}]_0 = 17.3\ \text{mmol}\cdot\text{L}^{-1}$ (■, experiment **E12**). See Table 2 for the experimental conditions.

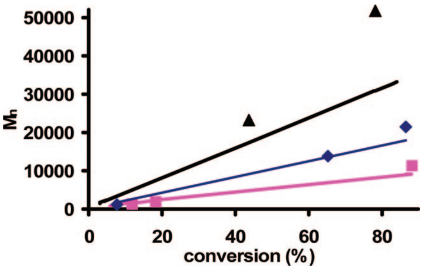

Figure 7. Number-average molar mass (M_n) versus conversion for the surfactant-free, *ab initio*, batch emulsion polymerizations of *n*-butyl methacrylate with 10 wt % of styrene in the presence of various concentrations of the 2-(dodecylthiocarbonothioylthio)-2-methyl propanoic acid RAFT agent (TTCA), sodium salt: $[\text{TTCA}]_0 = 4.5\ \text{mmol}\cdot\text{L}^{-1}$ (▲, experiment **E11**); $[\text{TTCA}]_0 = 8.7\ \text{mmol}\cdot\text{L}^{-1}$ (◆, experiment **E8**); $[\text{TTCA}]_0 = 17.3\ \text{mmol}\cdot\text{L}^{-1}$ (■, experiment **E12**). Theoretical M_n (—). See Table 2 for the experimental conditions.

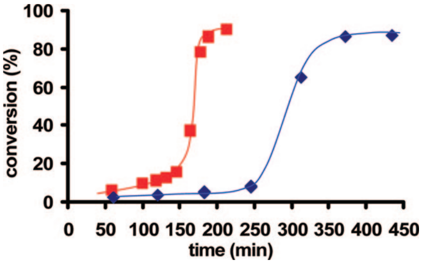

Figure 8. Conversion versus time for the surfactant-free, *ab initio*, batch emulsion copolymerizations of *n*-butyl methacrylate with 10.7 wt % (14.2 mol %) of styrene (◆, experiment **E8** in Table 2) and with 12.8 wt % (14.0 mol %) of *n*-butyl acrylate (■, experiment **E13** in Table 2) at 70 °C in the presence of the 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid, sodium salt, RAFT agent.

comparison with that found in the homopolymerization of BMA. It was actually bimodal when lower and larger amounts of styrene were used (see the experiments **E7** and **E9** in Table 2). We have then tested the effect of the addition of a conventional surfactant (sodium dodecyl sulfate, SDS) on the polymerization kinetics and on the control over the molar masses (experiment **E10** in Table 2). In comparison with the experiment **E8**, the presence of the surfactant led to much faster polymerization (with also an induction period), significantly lower particle diameter (41 nm instead of 104 nm) and broader molar mass distribution while keeping a good agreement between the experimental and the theoretical molar masses. The heterogeneity in molar mass distribution may possibly be due to a heterogeneous distribution of the TTCA reactive molecules within the particles.

Copolymerization of n-Butyl Methacrylate with 10 wt % of Styrene: Effect of the Amount of TTCA (Experiments ***E8****,* ***E11****, and* ***E12****).* In a series of experiments conducted with 10 wt % of styrene as a comonomer in the absence of added surfactant, the initial amount of RAFT agent was varied from $4.5\ \text{mmol}\cdot\text{L}_{\text{aq}}^{-1}$ (experiment **E11**), to $8.7\ \text{mmol}\cdot\text{L}_{\text{aq}}^{-1}$ (experiment **E8**) and finally to $17.3\ \text{mmol}\cdot\text{L}_{\text{aq}}^{-1}$ (experiment **E12**). In all cases the polymerizations exhibited an induction period (Figure 6), which slightly increased when the amount of RAFT agent was increased. Stable latexes with monomodal particle size distributions were recovered, but no direct correlation between the average particle diameter and the initial amount of surface-active RAFT agent could be found: with $4.5\ \text{mmol}\cdot\text{L}_{\text{aq}}^{-1}$, D_z was 113 nm, with $8.7\ \text{mmol}\cdot\text{L}_{\text{aq}}^{-1}$, D_z was 104 nm and with $17.3\ \text{mmol}\cdot\text{L}_{\text{aq}}^{-1}$, D_z was 145 nm. It is even surprising to note that the highest amount of TTCA actually resulted in the largest particle size, indicating a rather complex nucleation step, which would require deeper investigation. The number-average molar masses were in good agreement with the predicted values (Figure 7), the best results being obtained when the initial TTCA concentration was 8.7 mM_{aq} and 17.3 mM_{aq}. In contrast, the polydispersity indexes were not significantly affected.

Copolymerization of n-Butyl Methacrylate with 12.8 wt % n-Butyl Acrylate (Experiment ***E13****).* Finally, styrene was replaced by a small percentage of *n*-butyl acrylate, to synthesize an all-acrylic latex. Actually the results were even better than with styrene, with much shorter induction period and faster polymerization (Figure 8), good control over molar mass (M_ns were close to the predicted values, and final polydispersity index was 1.36 at 90% conversion) together with good colloidal stability, very small particle size (average diameter was 49 nm) and monomodal particle size distribution. Those results open the door to new surfactant-free acrylic latexes of high interest for industrial applications.

Conclusion

The RAFT-mediated controlled free-radical polymerizations of styrene and *n*-butyl methacrylate and their copolymerizations were studied in bulk and in emulsifier-free, *ab initio*, batch emulsion processes, using a surface-active trithiocarbonate RAFT agent, the 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid, sodium salt. In bulk the homopolymerization of styrene was well controlled but not the homopolymerization of *n*-butyl methacrylate, due to inappropriate leaving/initiating group. For the latter, only the copolymerizations with styrene exhibited good control over molar mass and narrow molar mass distribution, even when a low proportion of styrene was used (as low as 5%). In emulsion polymerization, the reaction was inhibited for styrene, whereas it was fast with *n*-butyl methacrylate but again the control over molar mass was not very effective. In the presence of a small percentage of styrene, the polymers were however well-controlled, with number-average molar masses in agreement with the predicted values based on the initial concentration of the RAFT agent, indicating complete conversion of the latter. Moreover, in all cases, using the RAFT agent as the sole surfactant being eventually attached at the chain-end, autostabilized latexes were recovered with small particle diameter, below 150 nm. Similar results were obtained when styrene was replaced by a small percentage of *n*-butyl acrylate, leading to well-defined all acrylic polymer latexes. This work is the first example of the direct and efficient use of a low molar mass, surface-active RAFT agent in emulsifier-free, *ab initio*, batch, emulsion polymerization, leading simultaneously to a good control over molar mass and narrow molar mass distribution, together with good colloidal properties. Although low molar mass, surface-active RAFT agents are of great interest for emulsion polymerization, they exhibit inherent difficulties (inhibition or poor control depending on the monomer) that have been partially overcome in this work, for a particular class of monomers. Further investigations are in progress to develop new molecules with better efficiency over a broader range of monomers.

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