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ARTICLE

Surfactant-Free RAFT Emulsion Polymerization Using Poly(*N,N*-dimethylacrylamide) Trithiocarbonate Macromolecular Chain Transfer Agents

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ABSTRACT: Water-soluble poly(*N,N*-dimethylacrylamide)s (PDMAAm) with a reactive trithiocarbonate group exhibiting different structures were used as macromolecular RAFT (reversible addition−fragmentation chain transfer) agents in the surfactant-free emulsion polymerization of *n*-butyl acrylate and styrene, under *ab initio*, batch conditions. Independently of the structure of the RAFT group, the polymerizations were fast and controlled with molar masses that matched well the theoretical values and rather low polydispersity indexes. Monomer conversions close to 100% were reached and the polymerizations behaved as controlled systems, even when solids contents up to 40% were targeted. The system thus led to poly(*N,N*-dimethylacrylamide)-*b*-poly(*n*-butyl acrylate) and poly(*N,N*-dimethylacrylamide)-*b*-polystyrene amphiphilic diblock copolymers formed *in situ* and self-assembled upon chain extension. The stability of the aqueous dispersions, measured by the amount of coagulum formed, improved with increasing length of the stabilizing hydrophilic PDMAAm segments.

Introduction

The development of controlled/"living" radical polymerization (CRP) techniques since the mid-1990 has opened the door to the easy synthesis of complex macromolecular structures with size and compositional homogeneity along with high degree of functionality. CRP can be performed in simple experimental conditions and is tolerant to a wide variety of functional groups and solvents, for instance protic media such as water.[1] Among the different CRP techniques, the RAFT polymerization, relying on a reversible addition−fragmentation chain transfer[2,3] reaction, presents numerous advantages, such as versatility in terms of monomers and temperature.[4] The fundamental mechanism of RAFT is the same as that of radical polymerization, in which the radicals are created by a conventional (thermal) initiator. The presence of a reversible chain transfer agent (RAFT agent) is the key element allowing the simultaneous generation and growth of all chains, allowing polymers with controlled molar mass, narrow molar mass distribution, and high chain-end functionality to be targeted.

Hitherto, this technique has been successfully performed in homogeneous conditions (bulk or solution), but its application to heterogeneous media was less straightforward and is still an important challenge.[5−10] Nevertheless, the development of CRP relies largely on its application to emulsion polymerization (EP) process in water,[11,12] which allows the controlled synthesis of hydrophobic polymers, while preserving all technical advantages of EP (environmentally friendly solvent, efficient heat removal, low viscosity, fast polymerization and high conversions, accessibility to various particle morphologies allowing the polymer properties to be finely adjusted...). Surfactant-free EP is an ideal situation, since low molar mass surfactants often have deleterious effects on the polymer properties. However, they are highly needed to create the particles and stabilize them. A way of minimizing their impact is to use reactive species that participate in the polymerization reaction, while maintaining good colloidal stability.[13] Those species can be ionic or ionogenic comonomers, hydrophilic macromonomers, or surface-active monomers, initiators, or chain transfer agents. In classical radical polymerization, they sometimes exhibit low efficiency due to limitations in both their chemical incorporation into the polymer chains and their location at the particle surfaces. With CRP, additional possibilities in incorporating a reactive stabilizer have emerged. They are (i) water-soluble or amphiphilic (macro)-initiators such as alkoxyamines in nitroxide-mediated polymerization (NMP)[14−20] or alkyl halides in atom transfer radical polymerization (ATRP)[21−23] and (ii) water-soluble or amphiphilic (macromolecular) reversible chain transfer agents like in RAFT (see below).

The recourse to an amphiphilic, low molar mass RAFT agent was described quite recently by our group[24] and led to good results (i.e., good control over the polymerization along with formation of stable latexes) in the batch emulsion copolymerization of *n*-butyl methacrylate with a low percentage of either styrene or *n*-butyl acrylate. The corresponding homopolymerizations were less successful, mainly due to kinetic reasons, concerning essentially the water-phase propagation and transfer reactions.

Concerning macromolecular RAFT agents (also called macro-RAFT agents), amphiphilic poly(acrylic acid)-based trithiocarbonates (TTC) were first shown to be very successful for surfactant-free EP under slow monomer addition and starved-feed conditions.[25−29] For the batch process, most of the RAFT agents failed in achieving simultaneously a good control over the polymerization along with stable particles: generally they led to stable latexes via the *in situ* formation of amphiphilic block copolymer chains, but the polymer formed in the EP was not controlled.[30−32] Those species were actually polyelectrolytes with

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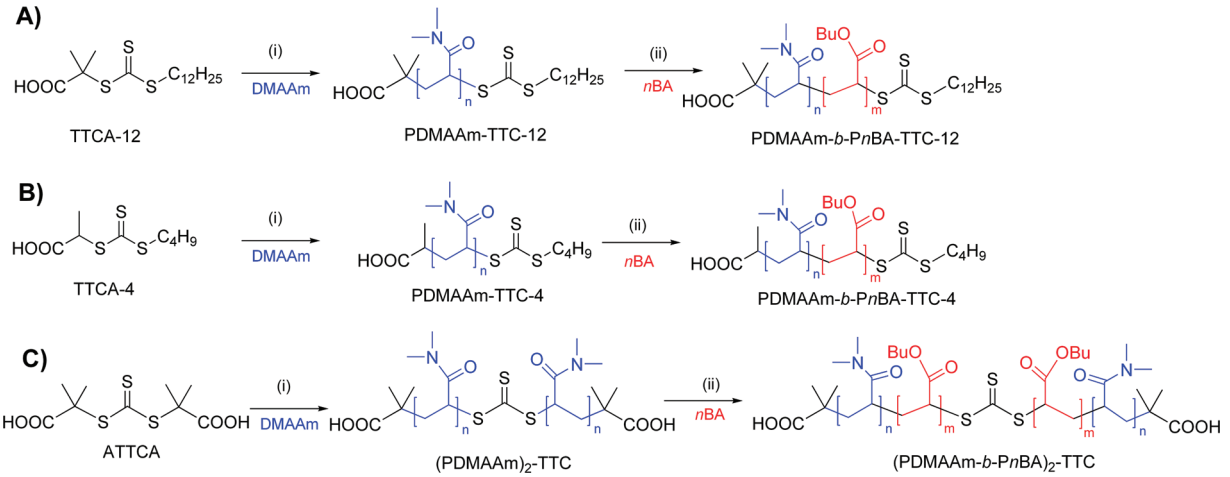

Figure 1. Synthesis routes for (i) the three different types **A** (TTCA-12), **B** (TTCA-4), and **C** (ATTCA) of poly(*N*,*N*-dimethylacrylamide), PDMAAm, macroRAFT agents in solution in 1,4-dioxane initiated by ACPA (4,4′-azobis(4-cyanopentanoic acid)) at 80 °C, and (ii) the PDMAAm-*b*-P*n*BA (P*n*BA = poly(*n*-butyl acrylate)) block copolymers in either 1,4-dioxane solution or aqueous emulsion initiated by ACPA.

dithiobenzoate functional group. A recent study based on poly(acrylic acid)-*b*-polystyrene trithiocarbonate macroRAFT agents demonstrated that the pH and hence the degree of neutralization of the acrylic acid units had a strong influence on the outcome of the reaction: only in acidic conditions (i.e., neutral polymer) was the polymerization well controlled.[33] In contrast, when neutral hydrophilic polymers were used, various situations were actually observed. Xanthate-functionalized dextran led to the synthesis of stable poly(vinyl acetate) latexes with poor control over the polymerization.[34] With polyacrylamide bearing a trithiocarbonate group, ultrasonication was required to yield stable formulations but little information on the controlled character of the polymers was given.[35] Finally, the best results so far were obtained with an amphiphilic poly(ethylene oxide) (PEO) trithiocarbonate macroRAFT agent possessing a hydrophobic $C_{12}H_{25}$ alkyl chain (PEO-TTC). The molecule was particularly efficient for the batch emulsion polymerization of *n*-butyl acrylate[36] and its copolymerization with methyl methacrylate.[37] In both cases, the system led to the formation of particles composed of well-defined amphiphilic diblock copolymers (i.e., quantitative transfer to the hydrophilic macroRAFT agent and controlled initiation and growth of the hydrophobic block). The particles were self-stabilized by the PEO hydrophilic fragment of the copolymer chains. The success of the PEO-based macromolecular RAFT agent is considered to be related to a judicious combination of solubility and reactivity. However, it is not so simple to tune the length of the PEO segment if one cannot have recourse to direct synthesis. Moreover, functionalization might only be performed at the chain-end. Consequently, it would be of high interest to use a hydrophilic segment that can be directly synthesized via RAFT-mediated radical polymerization or copolymerization. This technique would offer versatility in terms of chain length, chemical nature and composition, along with possible postmodification upon the choice of appropriate comonomers.

In this spirit, the aim of this study was 2-fold: (i) replace the PEO stabilizing chain by another nonionic hydrophilic polymer, whose molar mass can be easily tuned by controlled radical RAFT polymerization, and (ii) provide a better understanding of the parameters that determine the success of a RAFT emulsion polymerization.

N,*N*-Dimethylacrylamide (DMAAm) was chosen as a hydrophilic nonionic monomer for reasons of reactivity, solubility and acceptable (bio)compatibility/toxicity of the resulting polymer. For instance, poly(*N*,*N*-dimethylacrylamide) (PDMAAm) prepared via RAFT-mediated radical polymerization was previously shown to be an efficient macroRAFT agent for the synthesis of temperature-sensitive nanogels, via aqueous dispersion polymerization.[38,39] In this case, an important criterion for particle stability was the chain-length of the PDMAAm block.

In a first polymerization step, a variety of PDMAAm macroRAFT agents that differed in the molar mass and structure of the reactive group were easily prepared via RAFT-mediated radical polymerization. The objective of our study was first to elucidate whether macroRAFT agents made of PDMAAm were able to control the surfactant-free emulsion polymerization of *n*-butyl acrylate and styrene in *ab initio*, batch condition. Furthermore, the influence of the hydrophilic chain length and structure of the RAFT group on the EP kinetics, and on the control over molar mass, molar mass distribution (M_w/M_n), particle size, particle size distribution, and colloidal stability was investigated and discussed.

Experimental Section

Materials. *N*,*N*-Dimethylacrylamide (DMAAm, > 98%, Fluka), *n*-butyl acrylate (*n*BA, > 99%, Aldrich) and styrene (S, > 99%, Fluka) were distilled under reduced pressure before use. 1,3,5-Trioxane (99%, Aldrich), 4,4′-azobis(4-cyanopentanoic acid) (ACPA, > 98%, Fluka), sodium hydrogen carbonate ($NaHCO_3$, > 99.7%, Aldrich) and 1,4-dioxane (VWR Rectapur), were used as received. Deionized water was used for all emulsion polymerizations. *S*-1-Dodecyl-*S*′-(α,α′-dimethyl-α′′-acetic acid) trithiocarbonate (TTCA-12),[40] *S*-1-butyl-*S*′-(α-methyl-α′-acetic acid) trithiocarbonate (TTCA-4)[26] and *S*,*S*′-bis(α,α′-dimethyl- α′′-acetic acid)-trithiocarbonate (ATTCA)[40] were synthesized as reported before (see the NMR spectra in the Supporting Information, Figures SI-1, SI-2, and SI-3).

Synthesis of the Poly(*N*,*N*-dimethylacrylamide) MacroRAFT Agents, PDMAAm-TTC-12, PDMAAm-TTC-4, and $(PDMAAm)_2$-TTC. Polymerizations of DMAAm in 1,4-dioxane were initiated by ACPA at 80 °C, in the presence of the three RAFT agents, TTCA-12, TTCA-4, and ATTCA (see Figure 1). In a typical experiment (Table 1, entry **C2**), the polymerization of 4.0 g of DMAAm (2.0 mol L^{-1}) was carried out in 16 mL of 1,4-dioxane with 5.7 mg of ACPA (1.0×10^{-3} mol L^{-1}) and 57 mg of ATTCA (1.0×10^{-2} mol L^{-1}). A small amount (242 mg, 0.13 mol L^{-1}) of 1,3,5-trioxane was added as an internal reference for determination of the monomer consumption by ^{1}H NMR. The solution was poured in a septum-sealed flask, purged for 30 min with nitrogen in an ice bath and heated to 80 °C in a thermostated oil bath under stirring. For kinetic studies, sampling was performed at regular time intervals, and the polymerization was finally quenched after 180 min by immersion of the flask in iced water. The monomer conversion was determined by ^{1}H NMR spectroscopy in D_2O

Table 1. Polymerization Conditions and Characteristics of the Macromolecular Poly(*N*,*N*-dimethylacrylamide), PDMAAm, RAFT Agents Prepared by Solution Polymerization of DMAAm in 1,4-Dioxane at 80 °C[a]

Entry	RAFT agent	time (min)	convn (%)[b]	$DP_{n,th}$[c]	$M_{n,th}$[c] (g mol^{-1})	$M_{n,LS}$[d] (g mol^{-1})	$M_{n,\ PMMA}$[e] (g mol^{-1})	M_w/M_n[e]
A1	**A** = TTCA-12	24	49	28	3100	3200	2400	1.10
A2		15	53	62	6500	7300	5600	1.07
A3		13	47	85	8700	10700	7400	1.09
B1	**B** = TTCA-4	16	42	34	3600	4200	2450	1.18
B2		21	65	78	8000	8700	6200	1.09
B3		15	62	123	12400	12400	9100	1.09
C1	**C** = ATTCA	25	55	53	5600	6600	3700	1.13
C2		15	46	92	9500	9800	6900	1.12

[a] $[DMAAm]_0 = 2$ M, $[RAFT\ agent]_0/[ACPA]_0 = 10$. [b] Monomer conversion determined by ^{1}H NMR. [c] Theoretical number-average molar mass, $M_{n,th}$, and number-average degree of polymerization, DP_n, calculated using the experimental conversion. [d] M_n determined by SEC in DMF with the light scattering (LS) detector ($dn/dc = 0.081$ mL·g^{-1}). [e] M_n and M_w/M_n determined by SEC in DMF with a PMMA calibration.

by the relative integration of the protons of 1,3,5-trioxane at 5.1 ppm and the vinylic protons of DMAAm at 5.6, 6.1, and 6.6 ppm, respectively. For the synthesis of the living PDMAAm-based macroRAFT agents (see Table 1), polymerizations were stopped at monomer conversion ≤70%. The polymers were recovered by two precipitations in petroleum ether and dried under reduced pressure. For all experiments with PDMAAm macroRAFT agents, the copolymer molar concentrations were calculated using the number-average molar mass values derived from size exclusion chromatography in DMF using a combined refractive index and light scattering detection (see the Characterization Technique section).

Surfactant-Free Emulsion Polymerization of *n*-Butyl Acrylate in the Presence of Poly(*N*,*N*-dimethylacrylamide) MacroRAFT Agents. Generally, the aqueous emulsion polymerizations of *n*BA were performed at 70 °C at a stirring speed of 375 rpm, using an initial monomer concentration of 1.8 mol L_{latex}^{-1}, i.e., 23−24 wt % with respect to the latex, and a macroRAFT/initiator molar ratio of 5. The monomer/macroRAFT molar ratio was always between 270 and 630 (experimental details are reported in Table 2). In a typical experiment (Table 2, entry **A2-E1**), 179 mg of PDMAAm-TTC-12, **A2** ($M_n = 7300$ g mol^{-1}; 4.3×10^{-3} mol L_{aq}^{-1}), were dissolved in 5.2 mL of deionized water. Then, 0.5 mL of a stock solution of ACPA in water (concentration of 3.2 g·L^{-1} neutralized by 3.5 molar equiv of $NaHCO_3$) and 1.8 g (1.4×10^{-2} mol) of *n*BA were added. After deoxygenation by bubbling with nitrogen for 30 min, the septum-sealed flask containing the reaction mixture was immersed in an oil bath thermostated at 70 °C. Samples were periodically withdrawn to monitor the conversion by gravimetry, the evolution of the average particle diameter and the number-average molar mass, M_n, of the polymer with conversion. The polymerizations were quenched by immersion of the sample vials in iced water.

For comparison, the polymerization of *n*BA in the presence of the PDMAAm macroRAFT agents were also performed in solution, in 1,4-dioxane at 70 °C (see the Supporting Information, Table SI-1, Figure SI-5, and Figure SI-6).

Surfactant-Free Emulsion Polymerization of Styrene in the Presence of Poly(*N*,*N*-dimethylacrylamide) MacroRAFT Agents. Generally, the aqueous emulsion polymerizations of styrene (S) were performed at 80 °C at a stirring speed of 375 rpm, using an initial monomer concentration of 1.1 mol L_{latex}^{-1} (i.e., 11 wt % with respect to the total latex) and a macroRAFT/initiator molar ratio of 5. In a typical experiment (Table 3, entry **A3-ES1**), 323 mg of PDMAAm-TTC-12, **A3** ($M_n = 10700$ g mol^{-1}; 3.8×10^{-3} mol L^{-1}), were dissolved in 7.39 mL of deionized water. Then, 0.5 mL of a stock solution of ACPA in water (concentration of 4.4 g·L^{-1} neutralized by 3.5 molar equiv of $NaHCO_3$) and 1.01 g (9.7×10^{-3} mol) of styrene were added. After deoxygenation by bubbling with nitrogen for 30 min, the septum-sealed flask containing the reaction mixture was immersed in an oil bath thermostated at 80 °C. The polymerizations were quenched by immersion of the sample vials in iced water and conversion was determined by gravimetry.

For comparison, the polymerization of styrene in the presence of the PDMAAm macro RAFT agents were also performed in solution, in 1,4-dioxane at 80 °C (see the Supporting Information, Table SI-2 and Figure SI-7).

Characterization Techniques. DMAAm conversion and purity of the macroRAFT agents were determined by ^{1}H NMR spectroscopy in D_2O at room temperature (250 MHz Bruker). Size exclusion chromatography (SEC) was performed in tetrahydrofuran (THF) or in *N*,*N*-dimethylformamide (DMF). In THF, samples were analyzed at a concentration of 5 mg·mL^{-1} after filtration through a 0.45 μm pore-size membrane. The flow rate was 1 mL·min^{-1} and the separation 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 g mol^{-1}). A differential refractive index detector (Viscotek VE 3580 RI Detector) was used, and molar masses (M_n, the number-average molar mass, M_w, the weight-average molar mass) and polydispersity indexes (M_w/M_n = PDI) were derived from a calibration curve based on polystyrene (PS) standards from Polymer Standards Service. The macroRAFT agents were also analyzed by SEC in DMF (+LiBr, 1 g·L^{-1}). The analyses were performed at 60 °C at a flow rate of 0.8 mL·min^{-1}, with a polymer concentration of 5 mg·mL^{-1} after filtration through a 0.2 μm pore-size membrane. The steric exclusion was carried out on two PSS GRAM 1000 Å columns (8 × 300 mm; separation limits 1 to 1000 kg mol^{-1}) and one PSS GRAM 30 Å (8 × 300 mm; separation limits 0.1 to 10 kg mol^{-1}) coupled with a differential refractive index (RI) detector (Viscotek, Dual 250) and a light scattering (LS) detector (MiniDawn from Wyatt Technology, laser $\lambda = 690$ nm at 90°, 45°, and 135°). Polydispersity indexes were derived from the RI signal by a calibration curve based on PMMA standards (Polymer Standards Service). The number-average molar masses, M_n, of the PDMAAm macroRAFT agents were calculated from combined LS and RI signals with the OmniSEC 4.2 software, using a refractive index increment (dn/dc) of 0.081 mL·g^{-1}. In all plots showing the evolution of M_n with monomer conversion, the straight line corresponds to the expected evolution of the theoretical number-average molar mass, $M_{n,th}$, calculated by the introduced mass of monomer multiplied by conversion divided by the initial mole number of macroRAFT agent plus the molar mass of the latter. The *z*-average particle diameter (D_z) and the particle dispersity factor (σ) of the diluted aqueous dispersions were determined by dynamic light scattering (DLS) at 25 °C at 90°, with a Zetasizer Nano S90 from Malvern using a 5 mW He−Ne laser at 633 nm. For transmission electron microscopy (TEM) samples were dropped on a carbon-coated copper grid and dried under air. The TEM images were recorded without staining using a JEOL JEM 100CX II electron microscope at an accelerating voltage of 100 kV equipped with a 1376 × 1032 pixels CCD camera (Olympus, KeenView).

Results and Discussion

1. Synthesis of the Poly(*N*,*N*-dimethylacrylamide) MacroRAFT Agents. Three types of RAFT agents (**A** = TTCA-12, **B** = TTCA-4, **C** = ATTCA, see Figure 1) with a reactive

Table 2. Experimental Conditions and Results for the *ab Initio* Batch Emulsion Polymerizations of *n*-Butyl Acrylate (*n*BA) in the Presence of Different PDMAAm MacroRAFT Agents at 70 °C[a]

	macroRAFT					RAFT									
entry	no.	M_n (kg mol^{-1})[b]	DP_n[c] (*n*BA)	$[RAFT]_{0,\,aq}$ (mM)	$[ACPA]_{0,\,aq}$(mM)	RAFT + *n*BA (wt %)	solids content (100% convn) (wt %)	t (min)	convn[d](%)	$M_{n,th}$[c] (kg mol^{-1})	$M_{n,exp}$[e] (kg mol^{-1})	M_w/M_n[e]	D_z[f] (nm)	σ[f]	P[g]
A1-E1	**A1**	3.2	270	9.7	2.0	8.4	27	38	64	25.4	28.2	1.38	91	0.14	
								45	86	33.0	37.3	1.48	100	0.05	
								244	96	36.5	59.6	1.52	131	0.10	++
A1-E2[h]	**A1**	3.2	270	17.9	1.9	8.6	40	39	44	18.2	17.6	1.27	76	0.29	
								45	71	27.5	30.2	1.30	101	0.11	
								215	100	37.4	48.0	1.53	152	0.06	++
A2-E1	**A2**	7.3	580	4.3	1.0	9.0	26	50	61	52.5	67.3	1.53	82	0.12	
								58	87	71.8	96.5	1.60	94	0.13	
								68	98	79.9	114	1.68	95	0.11	−
A2-E2	**A2**	7.3	290	8.5	1.9	16.3	28	40	85	39.1	39.4	1.93	88	0.29	
								50	96	43.2	48.0	1.82	87	0.17	
								165	100	44.7	65.7	1.78	92	0.14	o
A3-E1	**A3**	10.7	630	4.0	1.0	11.8	27	40	55	54.9	49.2	1.70	88	0.16	
								46	81	75.8	81.6	1.66	99	0.12	
								58	96	87.8	104	1.86	104	0.06	o
B1-E1	**B1**	4.2	390	6.3	1.4	7.7	26	41	70	39.3	41.7	1.39	77	0.18	
								46	89	52.8	48.9	1.60	90	0.16	
								60	97	54.3	59.3	1.63	108	0.19	+(+)
B2-E1	**B2**	8.7	570	4.4	1.0	10.6	26	41	69	59.1	70.0	1.50	94	0.18	
								50	80	67.1	86.5	1.57	97	0.13	
								65	93	76.6	99.2	1.78	102	0.09	o
C1-E1	**C1**	6.6	270	9.0	2.2	15.8	27	81	93	39.1	26.6	1.61	130	0.32	
								90	100	41.6	30.7	1.53	126	0.30	++
C1-E2	**C1**	6.6	610	4.6	1.1	7.8	28	55	66	57.9	58.2	1.40	68	0.25	
								60	79	68.0	71.7	1.37	68	0.25	
								77	95	80.4	85.5	1.32	79	0.23	+
C2-E1	**C2**	9.8	540	4.6	0.9	12.4	27	48	55	47.9	42.3	1.76	87	0.28	
								53	76	62.5	63.1	1.67	89	0.14	
								75	96	76.4	85.4	1.60	94	0.17	+

[a] $[nBA]_{0,latex}$ = 1.83 M (24 wt % based on the total latex). [b] M_n determined by SEC in DMF with the light scattering (LS) detector (dn/dc = 0.081 mL·g^{-1}). [c] Theoretical number-average molar mass, $M_{n,th}$, and number-average degree of polymerization, DP_n, calculated using the experimental conversion. [d] Monomer conversion determined by gravimetry. [e] M_n and M_w/M_n determined by SEC in THF with a PS calibration. [f] D_z is the *Z*-average particle diameter and σ the dispersity factor derived from dynamic light scattering. [g] ++, +, −, and o quantify the amount of coagulum in the final reaction medium (high to low from ++ to o). [h] Experiment **A1-E2** was performed at a monomer concentration of $[nBA]_{0,latex}$ = 2.84 M, overall solids content = 40 wt %.

Table 3. Experimental Conditions and Results for the *ab Initio* Batch Emulsion Polymerizations of Styrene (S) at 80 °C in the Presence of PDMAAm-TTC-12, A1 and A3[a]

	macroRAFT												
entry	no.	M_n (kg mol^{-1})[b]	DP_n[c](S)	$[RAFT]_{0,aq}$ (mmol L^{-1})	solids content (100% convn) (wt %)	t (h)	convn[d](%)	$M_{n,th}$[c] (kg mol^{-1})	$M_{n,exp}$[e] (kg mol^{-1})	M_w/M_n[e]	D_z[f] (nm)	σ[f]
A1-ES1	**A1**	3.2	270	4.5	12.5	4	84	26.9	24.3	2.24	68	0.39
						20	88	28.0	27.2	1.92	69	0.40
A3-ES1	**A3**	10.7	320	3.8	14.5	4	83	38.4	30.2	1.73	65	0.72
						19	86	39.6	31.6	1.73	78	0.59

[a] $[S]_0$ = 1.1 mol·L_{latex}^{-1}; $[ACPA]_{0,aq}$ = 1.0 mM. [b] M_n determined by SEC in DMF with the light scattering (LS) detector (dn/dc = 0.081 mL·g^{-1}). [c] Theoretical number-average molar mass, $M_{n,th}$, and number-average degree of polymerization, DP_n, calculated using the experimental conversion. [d] Monomer conversion determined by gravimetry. [e] M_n and M_w/M_n determined by SEC in THF with a PS calibration. [f] D_z is the average particle diameter and σ the dispersity factor derived from dynamic light scattering.

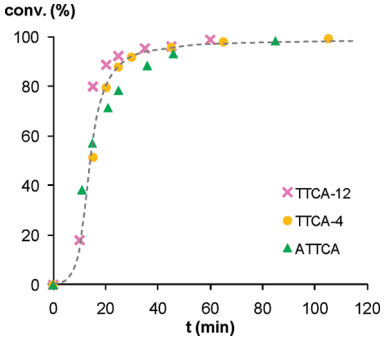

Figure 2. Evolution of DMAAm conversion versus time in the presence of the different RAFT agents (TTCA-12, TTCA-4, and ATTCA, see Figure 1). $[DMAAm]_0$ = 2 M, $[DMAAm]_0/[RAFT]_0$ = 200 (ATTCA and TTCA-4) or 180 (TTCA-12), $[ACPA]_0 = 1 \times 10^{-3}$ M, 80 °C in 1,4-dioxane (the experimental conditions for the determination of the polymerization kinetics correspond to entry **A3**, **B3** and **C2** in Table 1). ACPA = 4,4′-azobis(4-cyanopentanoic acid); DMAAm = *N*,*N*-dimethylacrylamide.

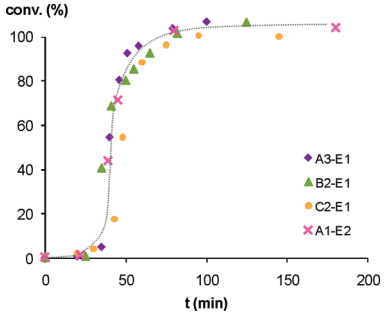

Figure 3. Surfactant-free *ab initio* emulsion polymerization of *n*-butyl acrylate (*n*BA, 1.83 mol·L_{latex}^{-1}) in the presence of the PDMAAm macroRAFT agents **A3**, **B2**, and **C2** (4−5 mmol L_{aq}^{-1}) initiated by ACPA (1 mmol L_{aq}^{-1}) at 70 °C, or in the presence of **A1** (17.9 mmol L_{aq}^{-1}) initiated by ACPA (1.9 mmol L_{aq}^{-1}): Evolution of *n*BA conversion vs time.

trithiocarbonate group were used for the synthesis of different poly(*N*,*N*-dimethylacrylamide) macromolecular RAFT agents (PDMAAm macroRAFT agents). They were either asymmetric - varying in the length of the alkyl chain of the stabilizing group (dodecyl for **A** vs. butyl for **B**) - and possessing a tertiary (**A**) or secondary (**B**) leaving group or symmetric and possessing a tertiary leaving group (type **C**) (Figure 1). They have all been reported to control efficiently the polymerization of styrenic and acrylate monomers as well as acrylamides.[36,38,40]

According to earlier results, the polymerizations of DMAAm were conducted in 1,4-dioxane at 80 °C.[38] Independently of the RAFT agent used, the polymerizations, showing no inhibition or a very short induction period, were fast and monomer conversions close to 100% were reached within 1 h (Figure 2). The different samples were first analyzed by SEC in THF. As demonstrated in Figure SI-4, all chromatograms showed tailing toward the lower molar mass side, most probably due to interaction of PDMAAm with the column material. SEC analyses were thus performed in DMF, using more polar SEC columns. Actually, in DMF the SEC traces were symmetric and narrow (Figure SI-4 and Table 1) with lower M_w/M_n and higher M_n compared to THF. The experimental M_n derived from the light scattering detector signal were closer to the theoretical ones than those determined with conventional calibration based on PMMA standards, which may not be appropriate for PDMAAm.

Independently of the RAFT agent used, all polymerizations exhibited the characteristics of a controlled system with the linear increase of M_n with monomer conversion, low polydispersity indexes in the range of 1.1 to 1.2 and molar masses that matched very well the theoretical values (Table 1). MacroRAFT agents of different molar masses were thus prepared (Table 1) and then used in heterogeneous conditions, in the surfactant-free, aqueous emulsion polymerization of *n*BA and styrene under batch conditions.

2. Surfactant-Free Emulsion Polymerization of *n*-Butyl Acrylate in the Presence of Poly(*N*,*N*-dimethylacrylamide) MacroRAFT Agents. *Kinetics of the Emulsion Polymerization of nBA.* The different macroRAFT agents were first used in the surfactant-free, aqueous emulsion polymerization of *n*BA. All polymerizations were performed at quite high monomer weight percentages (i.e., 24 wt % of *n*BA with respect to the total latex) in batch conditions. Figure 3 shows the evolution of the monomer conversion with time. Independently of the type (**A**, **B**, or **C**) of macroRAFT agent used, the kinetics of the polymerizations were essentially the same. After an induction period of about 35 min corresponding to the initial stage of formation of the amphiphilic block copolymer chains in the aqueous phase,[24,30,34,36,37] the monomer conversion increased rapidly and conversions close to 100% were reached within only 100 min. In the molar mass range investigated (M_n = 3200 to 12400 g·mol^{-1}) for the PDMAAm macroRAFT agents, no influence of the chain length on the kinetics could be observed. It should be noted that for the PEO-TTC macroRAFT agents previously studied in comparable reaction conditions, a very similar conversion vs time plot was observed, however with a longer induction period of about 60 min.[36,37]

Particle Size and Stability. As reported in Table 2, independently of the type (**A**, **B**, or **C**) and chain length of the macroRAFT agent, the particle diameter of the final aqueous dispersions was always in the 80−130 nm range and the particle dispersity factor, σ, ranged from 0.1 to 0.2 with the macroRAFT agents **A** and **B**, and from 0.2 to 0.3 with the macroRAFT **C** ($\sigma < 0.1$ denoting a monodisperse sample with narrow particle size distribution). Furthermore, the initial monomer/RAFT agent molar ratio, which determines the

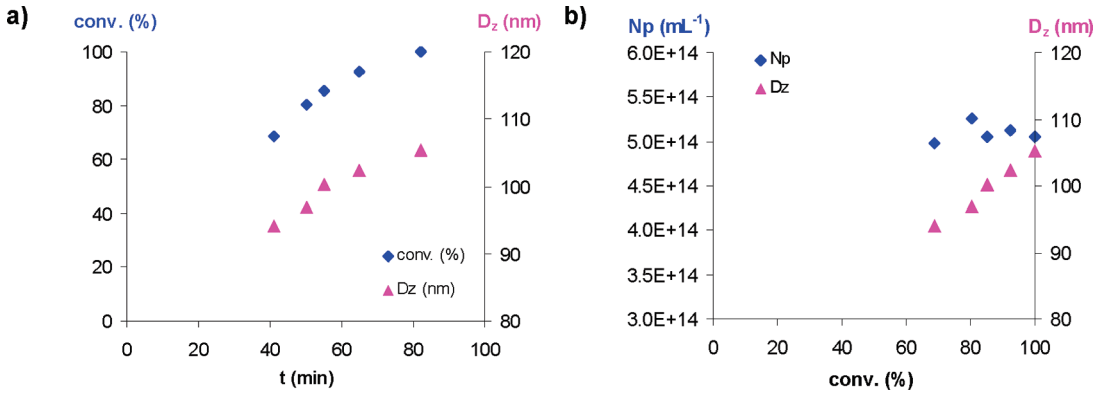

Figure 4. Emulsion polymerization of *n*BA in the presence of PDMAAm **B2** (entry **B2-E1**): (a) Evolution of *n*BA conversion and particle diameter and (b) evolution of number of particles (N_p) with conversion.

length of the hydrophobic second block in a controlled radical RAFT polymerization did not have a significant impact on the particle size (compare **A2-E1** and **A2-E2**), which stands in contrast to results obtained with the PEO-TTC macroRAFT agents previously used in the emulsion polymerization of *n*BA.[36] Only when the monomer concentration was enhanced to 37 wt % with respect to the total latex (Table 2, entry **A1-E2**), did the *z*-average diameter, D_z, increase significantly to 152 nm. The very similar particle size, denoting similar particle number, explains the superimposing polymerization kinetics. In some experiments, depending on the length and the structure of the macroRAFT agents, coagulum was observed. With the asymmetric macroRAFT agents **A** and **B** exhibiting a PDMAAm chain with M_n = 3200 and 4200 g·mol^{-1} respectively, coagulum was present in the final dispersions at the bottom of the polymerization flask. However, when longer stabilizing macroRAFT agents ($M_n \geq$ 7300 g·mol^{-1}) were used, no coagulum was observed. These results confirm the observations previously made with the PEO-TTC macroRAFT agents, for which a longer PEO chain was found to lead to more stable aqueous dispersions of PEO-*b*-P*n*BA.[37] It should also be noted that with increasing length of the hydrophilic PDMAAm chain, enhanced viscosity of the final latex was observed. With the symmetric macroRAFT agents **C**, $(PDMAAm)_2$-TTC, coagulum was present in all experiments whatever the PDMAAm chain length. In addition, the final dispersions were always more viscous than the initial reaction medium. Here, the structure of the final polymer was that of a triblock copolymer, PDMAAm-*b*-P*n*BA-*b*-PDMAAm, whereas it was a PDMAAm-*b*-P*n*BA diblock copolymer with the RAFT agent **A** and **B**. Consequently, the stabilizing PDMAAm segments have M_n of 3300 and 4900 g·mol^{-1} for **C1** and **C2**, respectively, which may be insufficient for correct stabilization (also reflected by the relatively higher dispersity factors σ as compared to the polymers derived from the RAFT agents **A** and **B**). These results confirm the very strong influence of the length of the hydrophilic segment on the nucleation step and particle stabilization. Such an observation can be corroborated by the comparison of experiment **C1-E1** with experiment **A1-E1** and experiment **A2-E2**. It appears that the same proportion of PDMAAm polymer with respect to P*n*BA but shorter hydrophilic chain (**C1-E1** vs. **A2-E2**) led to poorer latex stability. When **C1-E1** is compared with **A1-E1**, i.e., the same length of the hydrophilic segments but higher overall proportion for **C1-E1**, the stability was the same with the presence of coagulum in both cases.

Figure 4 shows an example of the evolution of the particle diameter, D_z, and the number of particles, N_p, per mL of water for experiment **B2-E1** (eq 1, with D_z, the average particle diameter, τ, the mass of polymer per mL of water [g·mL$^{-1}{}_{water}$] and d_p, the P*n*BA density: d_p = 1.08 g.cm^{-3} at 25 °C).

$$N_p = \frac{6\tau}{\pi D_z{}^3 d_p} \quad (1)$$

The particle diameters increased with increasing conversion whereas the number of particles remained essentially unchanged during the last polymerization period. These results suggest
that the emulsion polymerization mechanism with PDMAAm-
TTC-4 was that of a typical radical emulsion polymerization with good stability throughout the polymerization course.

Control of Molar Mass and Molar Mass Distribution. The control over the polymer characteristics was investigated by SEC in THF. As reported in Table 2 and in Figure 5, the number-average molar masses, M_n, increased with the progress of monomer conversion, demonstrating the livingness of the polymerizations. Generally, the consumption of the macroRAFT agent, i.e., the transfer reaction, was rather slow as residual macroRAFT agent was always detected at low conversions (~20%). Independently of the macroRAFT agent used, at higher conversion (i.e., 40−60%; it should be mentioned that with such fast polymerizations it is difficult to be very precise on the values) all experiments showed a complete shift of the initial PDMAAm macroRAFT agent peak toward higher molar masses (Figure 5b), indicating high crossover efficiency and the formation of block copolymers.

At monomer conversion ≤80% the experimental values, $M_{n,exp}$, matched quite well the theoretical values, $M_{n,th}$, and polydispersity indexes, M_w/M_n, ranged from 1.3 to 1.6 (Table 2). With higher conversion (> 80%), the molar masses exceeded the theoretical values and M_w/M_n increased. In some cases, a shoulder on the higher molar mass side became clearly visible in the SEC chromatograms. This is very often observed in the RAFT-mediated polymerization of acrylates and can be attributed either to self-termination by recombination of the propagating radicals or to chain transfer to polymer.

For a given type of macroRAFT agent, the control seemed to be slightly influenced by the chain length of the hydrophilic segment. Whereas the match of the theoretical and experimental molar masses was essentially the same whatever the hydrophilic block (Figure 5a, entry **A1-E2** and **A2-E2** and Figure 5d, **C1-E1** and **C2-E1**), the polydispersity indexes increased with increasing the PDMAAm block length (Table 2 and Figure 5). In addition, for the asymmetric macroRAFT agents **A** the correlation between $M_{n,th}$

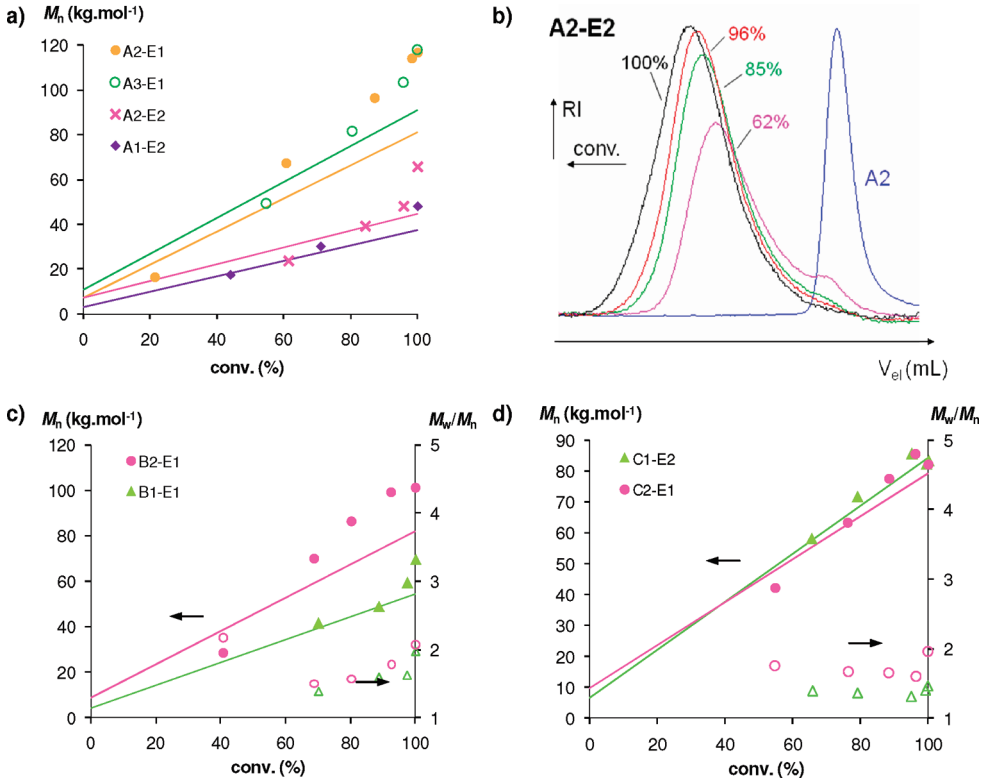

Figure 5. Surfactant-free, batch emulsion polymerization of *n*BA in the presence of different PDMAAm macroRAFT agents. (a) M_n versus monomer conversion for experiments **A1-E2**, **A2-E2**, **A2-E2**, and **A3-E1** (derived from TTCA-12). (b) Evolution of the SEC chromatograms with monomer conversion for experiment **A2-E1**. (c) M_n and M_w/M_n versus monomer conversion for experiments **B1-E1** and **B2-E1** (derived from TTCA-4). (d) M_n and M_w/M_n versus monomer conversion for experiments **C1-E2** and **C2-E1** (derived from ATTCA).

and $M_{n,exp}$ was better when shorter hydrophobic blocks were targeted, i.e. when the initial macroRAFT agent concentration was higher (Figure 5a **A2-E2** vs. **A2-E1**).

It can then be concluded that macroRAFT agents based on PDMAAm and possessing a reactive trithiocarbonate group are able to control the emulsion polymerization of *n*BA in a simple *ab initio*, batch process and to lead to stable latexes at high solids contents. From all the presented results, no significant influence of the structure of the macroRAFT agent on the polymerization control could be emphasized. It was demonstrated that the most important structural parameter is the hydrophilic block length rather than the structure of the reactive (hydrophobic) moiety. It appeared that a compromise has to be found between a long PDMAAm block, which favors the particle stability, and a shorter one, which leads to a better control over the P*n*BA block formed in the EP process.

3. Surfactant-Free Emulsion Polymerization of Styrene in the Presence of Poly(*N*,*N*-dimethylacrylamide) MacroRAFT Agents. In view of the promising results for the emulsion polymerization of *n*BA with the PDMAAm-TTC-12 macroRAFT agents, they were further employed in the surfactant-free emulsion polymerization of styrene. Two different PDMAAm chain lengths (**A1** and **A3** with M_n = 3200 g·mol^{-1} and 10700 g·mol^{-1} respectively) were tested at a monomer concentration of 1.1 mol·L_{latex}^{-1} (e.g. 11 wt %) with respect to the total latex (which corresponds to the concentration used in former experiments with the PEO-TTC macroRAFT agent, M_n = 2000 g·mol^{-1}).[36] With both macroRAFT agents, stable and fluid latexes presenting no coagulum were obtained. As reported in Table 3, no significant influence of the PDMAAm block length on the particle size could be observed. The *z*-average diameters determined by DLS were in the 70−80 nm range, and the dispersity factors were above 0.1. The TEM micrograph in Figure 6a confirms this result

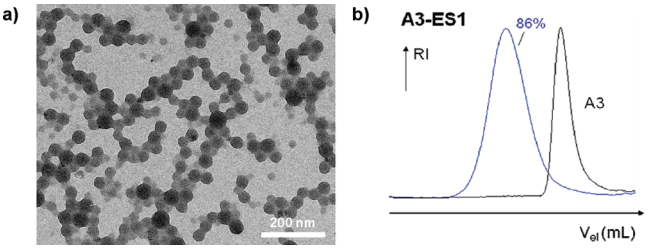

Figure 6. (a) TEM image for the sample **A3-ES1** prepared by the emulsion polymerization of styrene with the macroRAFT agent **A3**; (b) SEC chromatograms in THF of the polymer from the same experiment.

and shows particles of about 50 nm in diameter, which were rather heterogeneous in size. The SEC analysis of the final polymers revealed the formation of block copolymers (Figure 6b). The molar masses matched quite well the theoretical values and the polydispersity indexes were between 1.7 and 2.0, higher than those obtained in solution (Table SI-2 and Figure SI-7). These encouraging results suggest that the macroRAFT agent PDMAAm-TTC-12 is capable of playing simultaneously the role of a stabilizer and that of a reversible transfer agent in the surfactant-free emulsion polymerization of styrene, as was the case for *n*-butyl acrylate.

4. Discussion. We have shown here that the *ab initio*, batch emulsion polymerization of *n*-butyl acrylate or styrene could be performed in the presence of nonionic PDMAAm macromolecular RAFT agents with a trithiocarbonate reactive group. An efficient chain transfer reaction took place (although slower than in the case of PEO-TTC, explaining the slightly broader molar mass and particle size distributions), hence

leading to a complete consumption of the water-soluble macroRAFT agent and the formation of amphiphilic block copolymers. Those results are in good agreement with previous works using PEO-based macroRAFT agents.[36,37] They confirm that nonionic macromolecular RAFT agents may be more favorable to a controlled batch EP than charged ones. As a possible explanation, the bimolecular chain transfer reaction between a polyelectrolyte macroRAFT agent and a polyelectrolyte macroradical of same charge, in dilute conditions and low salt concentration, might be significantly slowed down due to electrostatic repulsion. Such a situation would favor propagation over transfer in the aqueous phase and consequently lead to slow and incomplete crossover reaction, even more visible in heterogeneous conditions than in homogeneous ones.

The presence and the length of the hydrophobic aliphatic group do not seem to be parameters of major consequence on both the particle stability and the control over the molar mass and molar mass distribution. The most important factor is rather the length of the hydrophilic PDMAAm block: longer chains led to more stable latexes but to broader molar mass distribution. All those results show that besides the reactivity of the RAFT group (trithiocarbonate here), the water-solubility of the macroRAFT agent and its behavior in aqueous solution have to be considered. A possible option for nucleation of particles and creation of diblock copolymers is indeed the transfer reaction in the aqueous phase. This event depends strongly on two parameters: the local concentration of macroRAFT agent and its transfer constant. The chain transfer reaction to the PDMAAm macroRAFT agent leads to the formation of a water-soluble PDMAAm initiating macroradical, which then chain extends, essentially in water in a first step, with the addition of hydrophobic monomer units. It is only when the degree of polymerization of the hydrophobic block is large enough that the so-formed amphiphilic block copolymer chains can self-assemble into micelles or adsorb at the surface of existing particles. It seems that too long a residence time in the aqueous phase, induced by a long hydrophilic segment, is not favorable to a good control over the polymerization and may have the same effect on the molar mass distribution as a slow initiation. Another option presented by Ganeva et al.[28] would be homogeneous nucleation, i.e. the formation of particles from precipitation of initiator-generated oligoradicals, followed by adsorption of the macroRAFT agents at the particle surface, where they will eventually react. It is actually difficult to discriminate between both mechanisms in the state of our knowledge. However, the strong hydrophilicity of our macroRAFT agents, in particular the **C** ones, the high reactivity of the trithiocarbonate group along with the high concentration in the aqueous phase lead us to suppose that chain extension in the aqueous phase may be the most favorable initial step.

Conclusions

Water-soluble poly(*N,N*-dimethylacrylamide) (PDMAAm) macroRAFT agents with a reactive trithiocarbonate group were shown to be efficient in controlling the formation of PDMAAm-*b*-P*n*BA and PDMAAm-*b*-PS diblock copolymers in the surfactant-free emulsion polymerization of *n*BA and S respectively, in *ab initio,* batch conditions. Independently of the structure of the RAFT group (symmetric or not), the polymerizations were fast and controlled with molar masses that matched well the theoretical values and rather low polydispersity indexes. Monomer conversions close to 100% were reached and the polymerizations behaved as controlled systems, even when solids contents up to 40% were targeted. The stability of the aqueous dispersions, measured by the amount of coagulum formed, improved with increasing length of the stabilizing hydrophilic PDMAAm segments. In comparison with the poly(ethylene oxide) macroRAFT agents similarly able to play the role of both the stabilizer and the reversible chain transfer agent in emulsion polymerization, the nonionic PDMAAm macroRAFT agents present an interesting alternative, especially in terms of chain length and composition versatility and ease of synthesis.

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Supporting Information Available: (A) Figures showing NMR characterization of the RAFT agents TTCA-12, TTCA-4 and ATTCA and (B) SEC characterization of the PDMAAm macroRAFT agents and (C) text discussing solution polymerization of *n*-butyl acrylate and styrene in the presence of the PDMAAm macroRAFT agents and characterization of the formed diblock copolymers with tables of experimental conditions and results and figures showing conversion and SEC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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