Amphiphilic Poly(ethylene oxide) Macromolecular RAFT Agent as a Stabilizer and Control Agent in ab Initio Batch Emulsion Polymerization

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Among the available controlled free-radical polymerization techniques (CRP), the RAFT (reversible addition–fragmentation chain transfer)[1] polymerization allows the controlled polymerization of a wide variety of monomers at convenient temperatures. While RAFT is well developed for use in homogeneous conditions,[2] its application to dispersed systems is far from being perfectly accomplished. Hitherto, most of the RAFT polymerizations in conventional emulsion polymerization systems showed slow polymerization rates, low colloidal stability, poor control of the molar mass, or a broad molar mass distribution.[3–5] Because of reversible transfer reactions that are inherent to the RAFT mechanism, transport of the RAFT agent across the aqueous phase must be considered, which diminishes the chance for all propagating chains to be under RAFT control. To circumvent this problem, Prescott at al.[6] localized the RAFT agent in seed particles before polymerization. Further developments sought the realization of unseeded (ab initio) emulsion polymerization under RAFT control in the absence of free surfactant: Hawkett et al.[7–10] and later Klumperman et al.[11] succeeded in controlling the molar mass of the created chains (at low polydispersity indices) by working in starved feed conditions with hydrophilic macro-RAFT agents. Their strategy relies on the in situ formation of an amphiphilic reactive diblock copolymer self-assembling into micelles. The controlled feed of monomer allows the polymerization to be conducted in the absence of monomer droplets, which might cause loss of control. The polymerization could thus be controlled by the RAFT moiety present at the chain end of the hydrophobic block and localized in the inner part of the micelles. On the basis of a similar strategy but in batch conditions, hydrophilic macro-RAFT agents were successfully employed in the surfactant-free ab initio batch emulsion polymerization of styrene. Stable latex particles were thus obtained thanks to the in situ created amphiphilic diblock copolymer, but either the polymerizations did not display controlled features or the controlled character was not studied.[12–14] In a different approach the batch emulsion polymerization of styrene was controlled by using a phase inversion process with an amphiphilic random copolymer prepared under RAFT control.[15]

In this communication, we report a straightforward method to achieve stable, hydrophilic–hydrophobic, core–shell latex particles composed of polymer chains with controlled molar mass and narrow molar mass distribution. The novelty of our approach is the use of a simple poly(ethylene oxide) (PEO) macro-RAFT agent as both the stabilizer and the control agent in ab initio batch emulsion polymerization of styrene (S) and *n*-butyl acrylate (*n*BA). PEO-based macromolecules have demonstrated their unique potential as steric stabilizers for latex synthesis and may enhance their stability against freeze–thaw or shear force.[16] With the ultimate goal to afford amphiphilic diblock copolymers with controlled molar mass and narrow molar mass distribution in autostabilized latex particles, PEO-based amphiphilic RAFT agent (PEO-TTC) was synthesized from 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid) (TTCA)[17] (Scheme 1). The latter is known for its ability to control the polymerization of styrene and *n*-butyl acrylate in bulk.[17,18] Using a 2-fold excess of TTCA, the esterification with an α-methoxy-ω-hydroxypoly(ethylene oxide) was close to quantitative, as confirmed by ^{1}H NMR spectroscopy (Supporting Information, Figure SI-1). The number-average molar mass, M_n, determined by ^{1}H NMR spectroscopy was 2420 g mol^{-1}. The PEO-TTC demonstrated amphiphilic properties, and the critical micelle concentration (cmc) determined by dynamic light scattering (DLS) (Supporting Information, Figure SI-2) was 0.5 mM, which is in the expected range for a similar Brij surfactant.[19] At the concentrations used for the aqueous emulsion polymerizations of styrene and *n*-butyl acrylate (i.e., above 10^{-3} M; see Table 1), most of the PEO-TTC macromolecules exist as micelles.

In a typical emulsion polymerization, the PEO-TTC macro-RAFT agent and the initiatior were solubilized in deionized water containing $NaHCO_3$. The monomer, styrene or *n*-butyl acrylate, was then added under stirring. After deoxygenation by nitrogen bubbling for 30 min, the flask was immersed in an oil bath thermostated at 70 °C (*n*BA) or 80 °C (S). Samples were periodically withdrawn to monitor the particle size and the monomer conversion by gravimetry. After drying, the number-average molar masses, M_n, and polydispersity indices, M_w/M_n, of the polymer were determined by size exclusion chromatography (SEC) in tetrahydrofuran. Detailed information on the experimental conditions of polymerization and the characterization techniques can be found in Table 1 and in the Supporting Information.

Dos Santos et al. previously commented on the batch emulsion polymerization of styrene in the presence of a PEO-based dithiobenzoate macro-RAFT agent (PEO-DTB).[13] Polymerization was very slow and reached less than 5% conversion after 7 h of polymerization. We performed a similar experiment, and again reaction was slow (26% after 23.3 h or 18% after 6 h), and the latex particles lacked stability (Supporting Information, Table SI-1).

Our approach was thus the use of an amphiphilic transfer agent of the trithiocarbonate type. Employing similar polymerization conditions (Table 1, entry S1), 67% styrene conversion was reached within 22.7 h and stable latexes were obtained. As depicted in Figure 1b, the recovered polymers exhibited the macromolecular characteristics expected in controlled radical polymerization, such as the linear increase of M_n with monomer conversion and low polydispersity indices. Indeed, the size exclusion chromatogram of the final polymer was symmetric, the experimental M_n matched well the theoretical one, and M_w/

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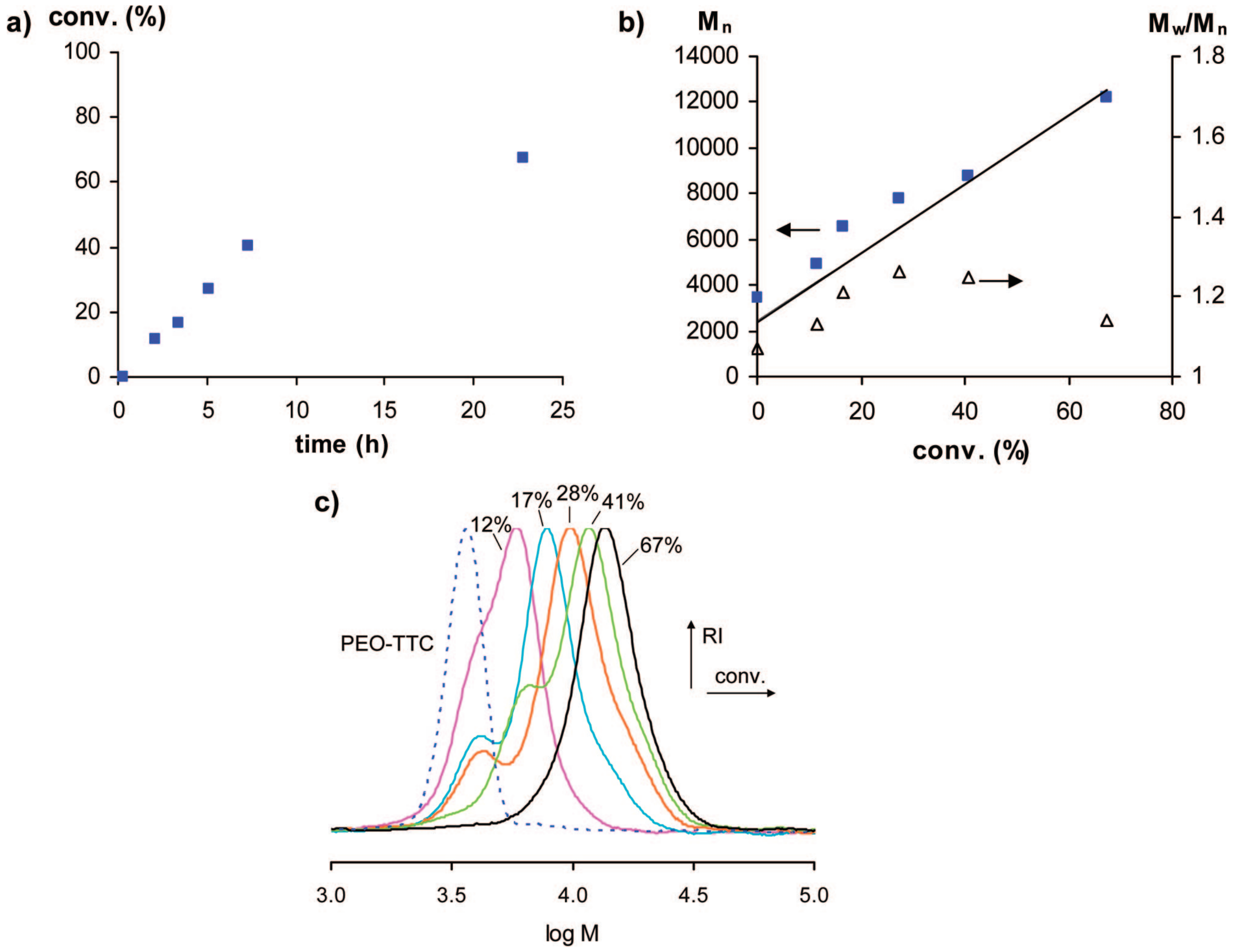


Figure 1. Reversible addition−fragmentation chain transfer (RAFT) polymerization of styrene in emulsion using the poly(ethylene oxide)-based trithiocarbonate (PEO-TTC) RAFT agent at 80 °C (entry S1, Table 1): (a) monomer conversion determined by gravimetry vs time; (b) number-average molar mass, M_n, and polydispersity index, M_w/M_n, determined by size exclusion chromatography (polystyrene calibration) vs conversion; the straight line corresponds to the theoretical M_n vs conversion; (c) evolution of size exclusion chromatograms with conversion.

Table 1. Macromolecular and Colloidal Characteristics of the Polymer Latexes Prepared via ab Initio Batch Emulsion Polymerizations of Styrene (S) and *n*-Butyl Acrylate (*n*BA) in the Presence of PEO-TTC as a Macromolecular RAFT Agent

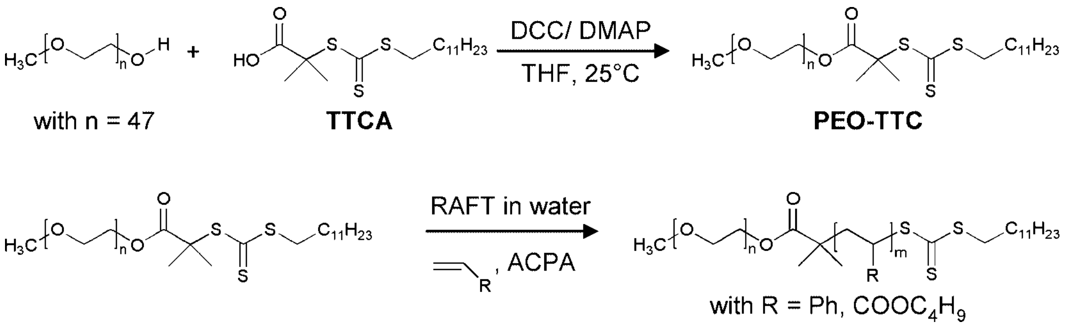
expt[a]	monomer (wt %)	T (°C)	[PEO-TTC]$_0$ (mmol L_{latex}^{-1})	[ACPA]$_0$[b] (mmol L_{latex}^{-1})	[monomer]$_0$/[PEO-TTC]$_0$	time (h)	conv[c] (%)	$M_{n,\text{th}}$[d] (kg mol^{-1})	$M_{n,\text{exp}}$ (kg mol^{-1})	M_w/M_n	D_z (nm); (dispersity)[e]	N_p[f] (g_{latex}^{-1})
S1	S (11)	80	7.5	1.6	145	22.7	67	12.5	12.2	1.16	260 (0.16)	9.7×10^{12}
A1	*n*BA (9)	70	8.1	1.6	90	20.0	66	10.0	9.9	1.41	89 (0.05)	2.1×10^{14}
A2	*n*BA (13)	70	7.1	1.8	145	7.0	96	20.3	22.2	1.26	200 (0.04)	3.3×10^{13}
A3	*n*BA (24)	70	7.0	1.4	262	3.7	96	34.6	33.8	1.24	510 (0.09)[g]	3.4×10^{12}
A4	*n*BA (23)	70	14.2	3.0	130	5.1	99	18.8	18.9	1.21	220 (0.02)	4.5×10^{13}

[a] Typical recipe (A2): 0.1670 g of PEO-TTC (0.069 mmol), 7.63 g of deionized water, 1.28 g of *n*-butyl acrylate (10.0 mmol), and 0.48 mL of a stock solution of neutralized ACPA (10 mg/mL, 0.017 mmol) were mixed in a 25 mL septum-sealed flask. [b] ACPA (4,4′-azobis-4-cyanopentanoic acid) was neutralized by 3.5 mol equiv of $NaHCO_3$. [c] Monomer conversion was determined by gravimetry. [d] Theoretical number-average molar mass at the experimentally determined conversion. [e] D_z is the average particle diameter from dynamic light scattering analysis (the lower the dispersity factor, the narrower the particle size distribution). [f] Number of particles per g of latex calculated from gravimetry: $N_p = 6\tau/\pi D_z^3 d_p$, with τ the mass of polymer per gram of latex [g g_{latex}^{-1}] and d_p the polymer density: PS = 1.05 g cm^{-3}, P*n*BuA = 1.055 g cm^{-3} at 25 °C. [g] 5.5 wt % precipitate, based on the total polymer mass.

M_n was particularly low (1.2). However, the chromatograms at lower monomer conversion (Figure 1c) were slightly asymmetric, indicating heterogeneity of chains. With increasing monomer conversion the totality of chains was shifted toward higher molar masses, demonstrating the “livingness” of all polymer chains and the complete consumption of the macro-RAFT agent. This phenomenon was repeatedly observed. A possible explanation for the chain heterogeneity might be found in the complexity of the emulsion polymerization process itself with an effect of the rather broad particle size distribution on the molar mass distribution.

Then, a second type of monomer, *n*-butyl acrylate, was tested, and a series of batch emulsion polymerizations were performed. When conducted in the presence of PEO-DTB, the polymerization was inhibited (Supporting Information, Table SI-1). In contrast, with PEO-TTC (Table 1, entries A1 to A4), the polymerizations proceeded rapidly (with however a marked induction period of about 1 h) and reached very high monomer conversions (>95%) (Figure 2a). The SEC traces of the polymers were narrow and symmetric and completely shifted toward higher molar masses with increasing monomer conversion (Figure 2c). M_n increased linearly with

Scheme 1. Synthetic Route for the Controlled RAFT (Reversible Addition−Fragmentation Chain Transfer) Polymerization of Styrene and *n*-Butyl Acrylate in Aqueous Emulsion[a]



[a] ACPA = 4,4′-azobis-4-cyanopentanoic acid; DCC = *N,N*′-dicyclohexylcarbodiimide; DMPA = 4-(dimethylamino)pyridine; THF = tetrahydrofuran.

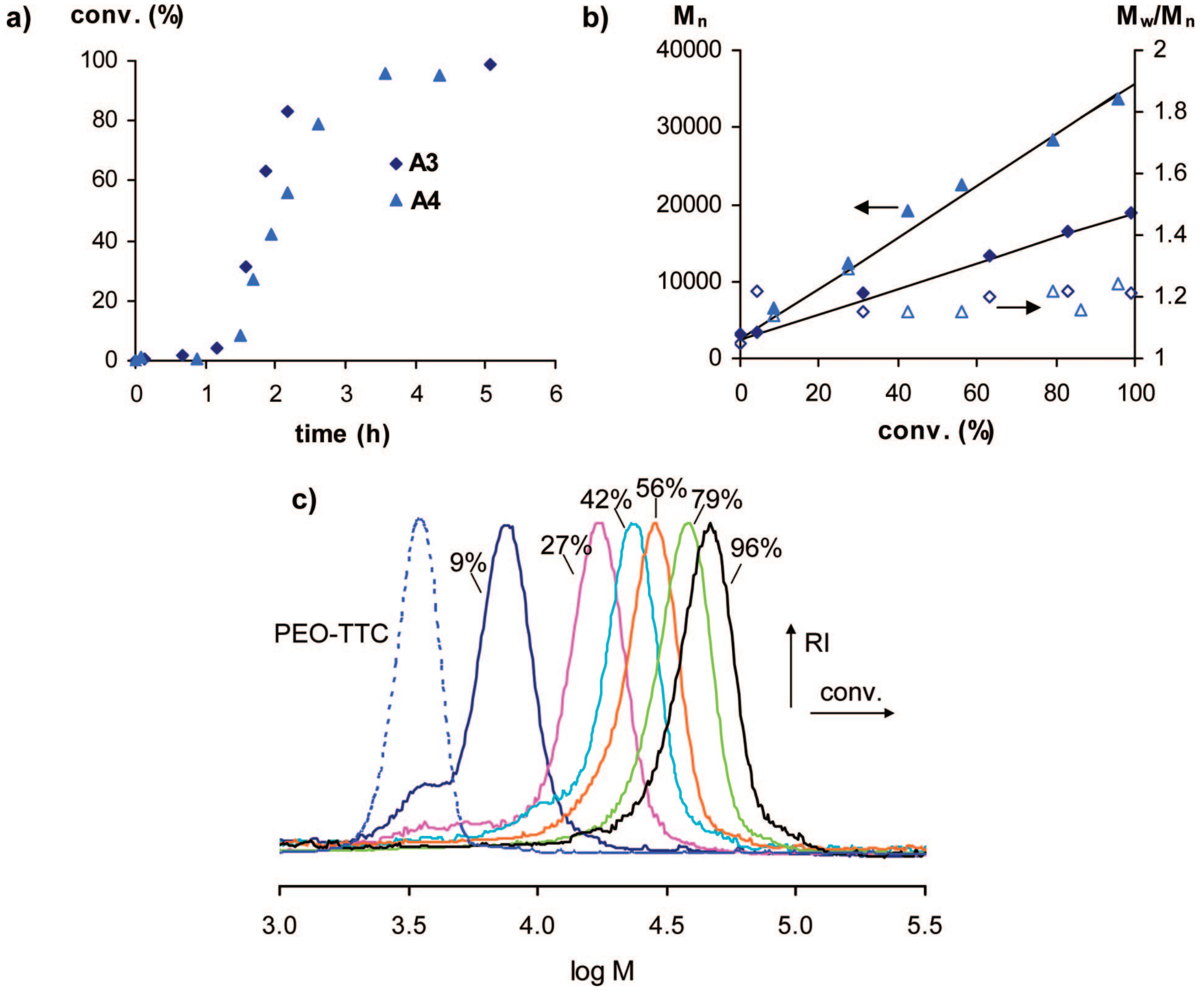


Figure 2. Reversible addition−fragmentation chain transfer (RAFT) polymerization of *n*-butyl acrylate in emulsion at 70 °C with two different amounts of poly(ethylene oxide)-based trithiocarbonate (PEO-TTC) RAFT agent (7.0 mmol L_{latex}^{-1} for experiment A3 and 14.2 mmol L_{latex}^{-1} for experiment A4, Table 1): (a) monomer conversion determined by gravimetry vs time, (b) number-average molar mass, M_n, and polydispersity index, M_w/M_n, determined by size exclusion chromatography (polystyrene calibration) vs conversion; the straight line corresponds to the theoretical M_n vs conversion; (c) evolution of size exclusion chromatograms with conversion for experiment A3.

monomer conversion (Figure 2b), exhibiting very good agreement with the theoretical values and low M_w/M_n. Such a difference in behavior between a dithiobenzoate and a trithiocarbonate RAFT agent in dispersed state polymerization was already observed in the past[20] and is currently under investigation.

In a series of experiments (A1, A2, and A3, Table 1), the concentration of the macro-RAFT agent was kept approximately constant (constant concentration of surface-active material) and the monomer concentration was varied. With increasing monomer/RAFT ratio, the length of the hydrophobic block increased as expected, the particle diameters also increased (from 89 to 510 nm), and the particle number decreased substantially. At the highest monomer/RAFT ratio (262, experiment A3, in Table 1), quite big latex particles ($D_z = 510$ nm) were formed, and some precipitate occurred (5.5 wt % of the total polymer). In order to elucidate the impact of the solids content, a further experiment was performed, at the same high monomer content (23−24 wt %) but at lower monomer/RAFT ratio (130, entry A4, Table 1). This time no precipitate was observed, which was attributed to the increase in stabilizing RAFT agent concentration. The average particle diameter was decreased to 220 nm, which was similar to that of latex particles formed at a comparable monomer/RAFT ratio (145, entry A2, $D_z = 200$ nm) but at lower solids content (13 wt %). The final particle number was actually governed by the monomer/RAFT ratio rather than by the surface-active RAFT agent concentration. Stable latexes together with narrow particle distributions are a good indication of negligible impact of droplet nucleation in our system, contrary to usual observations made in most batch emulsion polymerizations under RAFT control.[3–5]

In summary, for the first time an amphiphilic PEO macro-RAFT agent with a trithiocarbonate reactive group was successfully used as both a stabilizer and a reversible chain transfer agent in the ab initio batch emulsion polymerization of styrene and *n*-butyl acrylate. This novel approach, with a minimum of components and in the absence of free surfactant, allows easy formation of autostabilized latexes composed of diblock copolymers, with solids content as high as 24 wt %. By changing the macro-RAFT/monomer ratio, the molar mass of the hydrophobic block and the size of the particles can be tuned.

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Supporting Information Available: Detailed information on “materials and methods” used for the synthesis and purification of the macro-RAFT agents, the polymerization conditions, and the characterization techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

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