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Communications to the Editor

Use of an Amphiphilic Block Copolymer as a Stabilizer and a Macroinitiator in Miniemulsion Polymerization under AGET ATRP Conditions

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Controlled free-radical polymerization[1] has become an intensively investigated area of research due to its high tolerance of polar functionalities and its ability to develop well-defined macromolecular architectures (e.g., stable free-radical polymerization,[2] atom transfer radical polymerization (ATRP),[3−5] reversible addition−fragmentation chain transfer,[6] and degenerative chain transfer polymerization[7]). Recently, attempts to conduct the synthesis of well-defined polymers by ATRP in more environmentally friendly media, such as aqueous dispersed systems, have been explored.[8] In particular, the miniemulsion polymerization approach[9] is well-suited to enhance the colloidal stability and facilitate a controlled radical polymerization by eliminating the requirement for mass transfer of the radical activator/deactivator through the aqueous phase, normally occurring during an emulsion polymerization.[10,11] Under miniemulsion conditions, block copolymers can be successfully synthesized using the simultaneous reverse and normal initiation (SR&NI)[12] or activator generated by electron transfer (AGET),[13] both requiring the use of surfactants as particle stabilizers (mainly commercially available low-molecular-weight surfactants). Amphiphilic copolymers can also be used as stabilizers for their advantages over commercially available surfactants in classical free-radical emulsion and miniemulsion polymerizations.[14−18] For instance, Limer et al.[19] reported the use of nonionic poly(ethylene oxide)-*b*-poly(methyl methacrylate) and ionic poly(methyl methacrylate)-*b*-poly(dimethylaminoethyl methacrylate) amphiphilic block copolymers made by ATRP, to stabilize the suspension polymerization of *n*-butyl methacrylate from different polymeric macroinitiators.

In this communication, we report a new approach to carry out miniemulsion polymerization, wherein a living, amphiphilic diblock copolymer is used to emulsify the monomer phase in water, stabilize the particles, and initiate the polymerization of a third monomer for the preparation of ABC triblock copolymers using AGET ATRP. Polymer latexes prepared by this approach do not contain free surfactant and by covalently linking the stabilizer to the polymer particle, the deleterious effects of common surfactants, such as desorption and migration, may be prevented, and the stability of the latex should be improved. In addition, aqueous polymerization systems in the presence of a limited number of reactants are of great interest for the development of environmentally friendly processes. This promising approach, in which a single molecule plays the role of both the initiator and the stabilizer in miniemulsion and emulsion polymerizations[20,21] has been made much more accessible by the development of living free-radical polymerization methods, in particular NMP.[22] The novelty of this paper is to describe a similar strategy under AGET ATRP miniemulsion polymerization conditions. In this respect, a well-defined poly(ethylene oxide)-*b*-polystyrene diblock copolymer (PEO-*b*-PS) was synthesized using ATRP from a halogen-functionalized poly(ethylene oxide) macroinitiator. PEO-*b*-PS block copolymer is a typical example of polymeric stabilizer used for emulsion polymerization.[14] Our copolymer (PEO_{111}-*b*-PS_{33}−Br, with M_n (number-average molar mass obtained by NMR) = 8 400 g mol^{-1}, M_n (obtained by size exclusion chromatography, SEC) = 10 640 g mol^{-1} and polydispersity index (PDI obtained by SEC) = 1.05) bears a reactive end group, able to initiate an aqueous dispersed ATRP. This block copolymer was utilized

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Scheme 1. Synthetic Route for the Formation of Triblock Copolymers via Miniemulsion Polymerization (ATRP, Atom Transfer Radical Polymerization; AGET, Activator Generated by Electron Transfer; Bipy, 2,2′-Bipyridyl; BPMODA: Bis(2-pyridylmethyl)octadecylamine; AA, Ascorbic Acid)

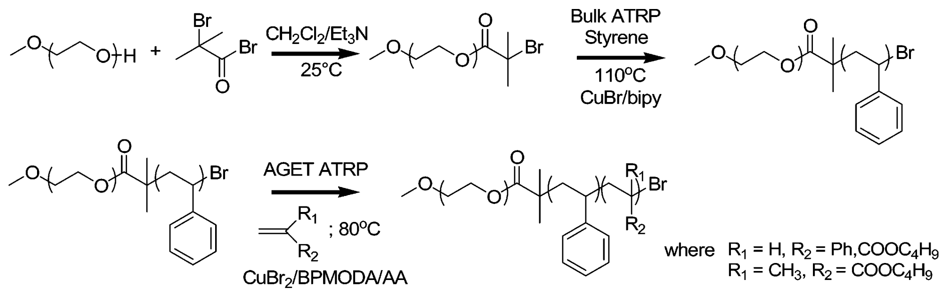

Table 1. Atom Transfer Radical Polymerization in Miniemulsion with Activator Generated by Electron Transfer Using PEO$_{111}$-*b*-PS$_{33}$−Br Block Copolymer as a Macroinitiator and a Stabilizer[a]

entry	[macroinitiator] (mM)	[monomer]/[macroinitiator]/ [CuBr$_2$]/ [BPMODA]/[AA]	monomer[b]	time (min)	% conv.	$M_{n,th}$	$M_{n,SEC}$	PDI	D (nm)[c]	Poly[c]
1	2.5	420/1/1.2/1.2/0.22	BMA	5	15.3	17 510	27 700	1.45	204	0.17
				11	28.3	25 280	33 800	1.44	191	0.20
				21	42.8	33 900	44 350	1.38	196	0.18
				42	55.9	41 730	52 150	1.34	195	0.20
				77	65.9	47 700	51 100	1.46	195	0.23
				120	72.2	51 420	52 000	1.47	198	0.20
2	2.5	440/1/1.2/1.3/0.22	90% BMA + 10% S	10	9.5	14 170	20 500	1.22	187	0.17
				21	18.7	19 720	26 300	1.24	182	0.16
				40	31.3	27 300	32 000	1.30	180	0.17
				81	41.9	33 730	40 450	1.32	177	0.19
				120	46.4	36 470	42 900	1.31	176	0.16
3[d]	2.3	470/1/1.2/1.2/0.48	S	240	15.8	16 790	15 700	1.07	-	-
4	2.4	440/1/1.2/1.3/0.50	BA	61	11.1	14 620	16 950	1.12	-	-
				121	17.6	18 260	19 100	1.11	-	-
				210	22.7	21 120	20 250	1.12	-	-
5	4.8	215/1/1.2/1.2/0.23	BMA	5	30.5	17 720	25 550	1.46	137	0.17
				10	46.0	22 450	32 000	1.42	135	0.19
				16	56.6	25 680	32 650	1.45	135	0.20
				60	87.3	35 060	39 000	1.45	131	0.21
6	1.2	860/1/1.2/1.2/0.23	BMA	10	15.0	26 720	37 300	1.49	247	0.20
				20	26.7	41 010	49 650	1.52	233	0.20
				80	44.4	62 700	64 150	1.49	233	0.21

[a] All miniemulsions contained 15 wt % monomer, and the amount of hexadecane used in each polymerization was 4 wt % based on the amount of monomer. [b] BMA: *n*-butyl methacrylate. S: styrene. BA: *n*-butyl acrylate [c] The average diameter, *D*, and the polydispersity factor (the lower values indicating the narrower particle size distribution), Poly, were determined by dynamic light scattering analysis. [d] All polymerizations were conducted at 80 °C except for the extension with styrene (entry **3**) which was performed at 90 °C.

as a stabilizer and a macroinitiator in the miniemulsion AGET ATRP of *n*-butyl methacrylate (BMA), styrene (S), and butyl acrylate (BA) (see Scheme 1 and Table 1).

In a typical recipe, the PEO-*b*-PS−Br macroinitiator was dispersed in deionized water while CuBr$_2$, bis(2-pyridylmethyl)-octadecylamine (BPMODA)[23] ligand and hexadecane were dissolved in monomer. After the formation of the Cu(II) complex, the organic and water phases were mixed, cooled by ice bath and subjected to ultrasonication (Branson 450 sonifier; power 7; 10 min). This led to a stabilized monomer-in-water emulsion, which was deoxygenated by argon bubbling for 30 min at room temperature and transferred to a Schlenk flask, immersed in an oil bath thermostated at 80 °C. An aqueous solution of ascorbic acid (AA) was injected into the flask to reduce the copper(II) complex and initiate the reaction. Samples were periodically withdrawn to monitor the average particle diameter and to measure the conversion by gravimetry. After complete drying, the raw polymer from each sample was dissolved in tetrahydrofuran and the polymer solution was passed through a neutral aluminum oxide column to remove the copper catalyst before SEC analysis. Detailed information on the experimental conditions can be found in Table 1 and in the Supporting Information.

Because of the solubility properties of the PEO hydrophilic block, the PEO$_{111}$-*b*-PS$_{33}$−Br macroinitiator can be located either at the surface or buried inside the monomer droplets and the latex particles. All initial miniemulsions and resulting latexes had good stability with submicrometer-sized particles (<300 nm) indicating that the amphiphilic copolymer was mainly located at the particle surface. In all cases, however, latexes exhibited a rather broad particle size distribution.

As shown in Table 1, the recovered polymers exhibited the characteristics expected in controlled free-radical polymerizations, such as the linear increase of M_n with monomer conversion and the polydispersity indexes below 1.5. However, the M_n's measured by SEC for the triblock copolymers were significantly higher than the theoretical M_n values. The reason for this is 2-fold; the difference can be ascribed to the hydrodynamic properties of the copolymer vs poly(methyl methacrylate) standards used for calibration and also to the loss of low molecular weight polymers when the SEC samples were passed through a neutral aluminum oxide column. The later hypothesis has been verified by NMR studies with several triblock copolymers before and after one elution through the column. For example, with the copolymer of entry **1** in Table 1, the absolute molecular weights calculated by NMR before and after purification were equal to 22 040 and 32 300 g mol^{-1}, respectively. These values correspond well with the theoretical value, 25 280 g mol^{-1}, and the SEC value, 33 800 g mol^{-1},

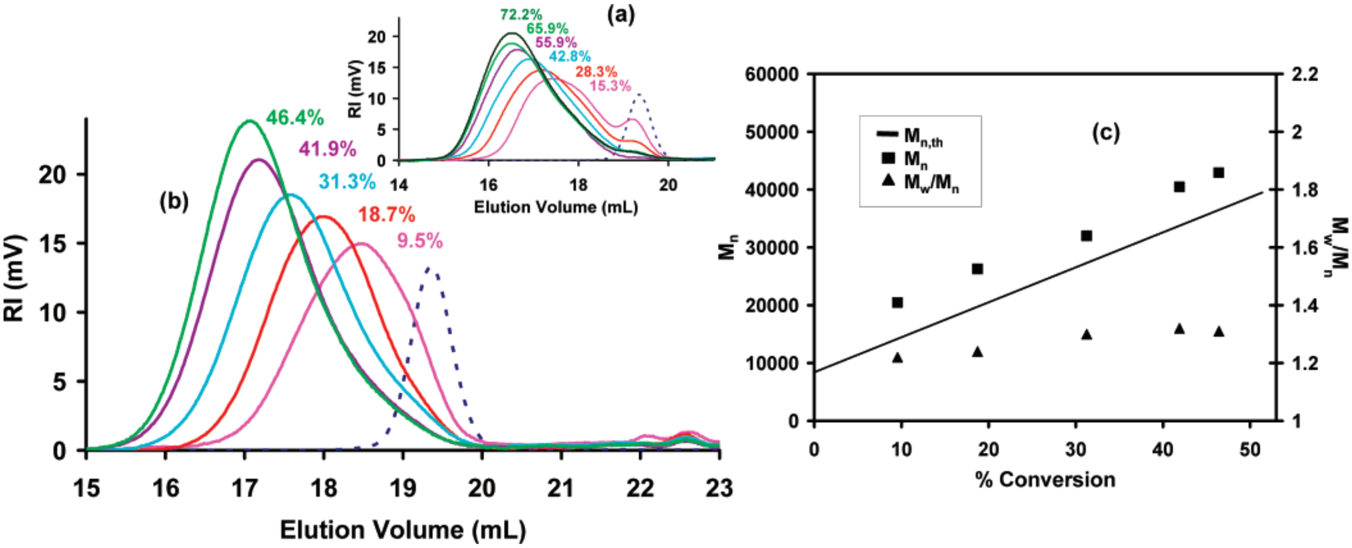

Figure 1. Atom transfer radical polymerization of *n*-butyl methacrylate in miniemulsion at 80 °C using the PEO_{111}-*b*-PS_{33}−Br macroinitiator with activator generated by electron transfer. Left: Evolution of the size exclusion chromatography traces with monomer conversion during the preparation of PEO-*b*-PS-*b*-PBMA (a, entry **1** in Table 1) and PEO-*b*-PS-*b*-P(BMA-*co*-S) (b, entry **2** in Table 1) block copolymers initiated by PEO-*b*-PS−Br macroinitiator (- - -). Right: Number-average molar mass (M_n) and polydispersity index (PDI = M_w/M_n) dependence on conversion (c, entry **2** in Table 1).

confirming the loss of low molecular weight polymers to the aluminum oxide column.

Figure 1 shows the SEC traces of PEO-*b*-PS-*b*-PBMA and PEO-*b*-PS-*b*-P(BMA-*co*-S) block copolymers obtained under AGET ATRP conditions (entries **1** and **2**, Table 1). The clear shift of the SEC traces toward higher molecular weights with monomer conversion indicates that the macroinitiator chains were extended in a well-controlled way to form triblock copolymers. The slow initiation in the AGET ATRP of *n*-butyl methacrylate monomer from the polystyrene-based macroinitiator is due to the difference in activation/deactivation equilibrium constants between the macroinitiator and the formed polymer. A recent technique was used to provide efficient initiation by using a small percentage of styrene as a comonomer in an extension polymerization.[24−26] Under these conditions (entry **2** in Table 1), the polymerization was slower and a block copolymer with monomodal molecular weight distribution was formed (Figure 1b), indicating fast reinitiation, as expected. The plot of M_n and PDI dependence on conversion in this polymerization is shown in Figure 1c. The features of controlled radical polymerization were observed with a linear increase of M_n with respect to monomer conversion and low polydispersity indexes (~1.2−1.3), indicating that the number of chains was constant throughout the polymerization.

In miniemulsion polymerizations under AGET ATRP, a "plateau" in the conversion vs time plot was often observed (see Figure 2 and Table 1). This phenomenon seems to occur after 1−2 h of reaction time, and the final conversion is dependent on the nature of the monomer used for the extension (with *n*-butyl methacrylate the polymerization was fast, whereas it was very slow for styrene and *n*-butyl acrylate) and also on the concentrations of the macroinitiator and copper used. The curvature of the kinetic plot could be explained by a possible loss of the bromine end groups through hydrolysis or a progressive migration of the catalyst to the aqueous phase.[13] Plateaus in AGET ATRP have also been observed in the literature.[13,27] Investigations are now underway for an explanation of this phenomenon. Figure 2 shows the conversion vs time for the polymerization of *n*-butyl methacrylate under AGET ATRP conditions obtained with three different concentrations of macroinitiator. Keeping the same [macroinitiator]/[$CuBr_2$]/[AA] ratio, the rate of polymerization increased when the concentration of macroinitiator increased, and the M_n values decreased accordingly at a given conversion; in parallel, the average particle diameter also decreased with increasing macroinitiator concentration (Table 1).

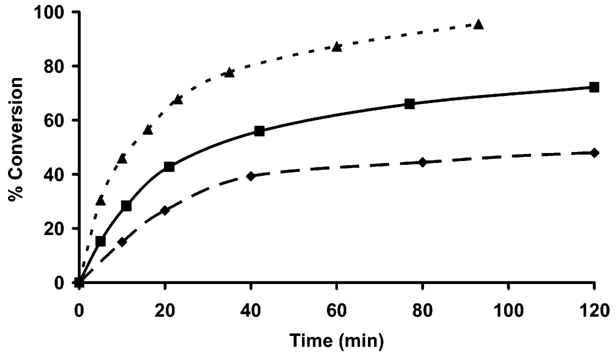

Figure 2. Comparison of kinetics for miniemulsion polymerization of *n*-butyl methacrylate (80 °C) with three different poly(ethylene oxide)-*b*-polystyrene macroinitiator concentrations. Key: (▲) [PEO-*b*-PS−Br] = 4.8 mM (entry **5**); (■) [PEO-*b*-PS−Br] = 2.5 mM (entry **1**); (◆) [PEO-*b*-PS−Br] = 1.2 mM (entry **6**).

In summary, the use of a living amphiphilic diblock copolymer, PEO-*b*-PS−Br, as both a stabilizer and a macroinitiator in miniemulsion ATRP under AGET conditions was successfully demonstrated. This novel method eliminates the requirement for free surfactant, optimizes the covalent linking of the stabilizer to the polymer particle, and provides well-defined block copolymer particles in situ. A change in the copolymer macroinitiator concentration modified the rate of polymerization, the average particle size and the molecular weight of the last block. Initial experiments using the PEO-*b*-PS−Br copolymer in true emulsion polymerization without sonication were successful and will be studied more extensively. These studies along with the use of ionic (cationic and anionic) amphiphilic block copolymers as stabilizer/macroinitiator will be further investigated.

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Supporting Information Available: Text giving the experimental part including description of all materials and their purification, preparation of PEO-*b*-PS−Br diblock copolymer, and measurement techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

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