Water-Borne Block and Statistical Copolymers Synthesized Using Atom Transfer Radical Polymerization

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Introduction. The synthesis of polymers that have well-defined structure (e.g., predictable molecular weight and low polydispersity) and functionality using radical intermediates has been an area of intense interest in recent years.[1] In particular, atom transfer radical polymerization (ATRP) has been used to produce a variety of novel polymer architectures under nonstrenuous reaction conditions.[1,2] It has also been applied to water-borne[3,4] and emulsion[5] systems, where polymers with predefined molecular weights and low polydispersities were obtained in stable latexes.

Emulsion polymerizations, and water-borne polymerizations in general, have been widely used in industry for nearly 70 years. There are several advantages of these methods, including the use of water as a solvent, efficient heat transfer, fast reaction rates, formation of polymer of high molecular weight, and relatively easy handling because of the low viscosity. However, such polymerizations involve free radicals, and therefore control of molecular weight and functionality during the polymerization is difficult to achieve. With controlled/"living" radical polymerizations now able to be conducted in water-borne systems the same diversity of polymer architectures that have been explored in bulk or solution can be attempted within such media. We report in this communication the synthesis of water-borne statistical and block copolymers by ATRP.

Results and Discussion. The preparations of statistical copolymers of *n*-butyl acrylate (BA) and methyl methacrylate (MMA) and then *n*-butyl methacrylate (BMA) and MMA were attempted. Table 1 contains the monomer conversion and molecular weight data from these reactions. For the BA/MMA monomer pair, BA is consumed more slowly than MMA, the number-averaged molecular weight (M_n) is generally in good agreement with the theoretical molecular weight (M_n^{theo}), and polydispersities (M_w/M_n) remain below 1.25 for the whole polymerization. These facts indicate that good control was obtained during the polymerization. The polymerization of BMA/MMA also proceeded with good control, albeit faster than the BA/MMA pair. Almost full conversion of both monomers was observed after 5 h, M_n increased in a linear fashion with conversion (although slightly higher than M_n^{theo}, indicating that initiator efficiency was slightly lower than unity), and M_w/M_n was again 1.25 or less during the polymerization.

Table 1. Results from the Water-Borne Simultaneous ATRP of MMA/BA and MMA/BMA Monomer Pairs

time (h)	% conversion M$_1$	M$_2$	M_n	M_n^{theo}	M_w/M_n
MMA/BA pair[a]					
1	46	20	11 100	7 000	1.22
1.5	55	24	12 300	10 850	1.22
3	65	25	15 350	12 200	1.21
5.5	78	39	18 300	16 150	1.20
10	90	54	21 550	20 100	1.19
24	100	67	24 150	23 600	1.21
48	100	80	26 850	25 750	1.22
MMA/BMA pair[b]					
0.5	41	43	17 300	10 250	1.22
1	56	67	22 250	15 100	1.23
1.5	66	76	25 950	17 400	1.24
2.5	86	92	29 700	21 650	1.25
5	93	100	33 550	23 500	1.25

[a] M_1 = MMA, M_2 = BA. MMA:BA:Et-2BriB:CuBr:dAbpy = 125:129:1:1:2; 0.3 g of Brij98, 10 mL of H_2O, 0.1 mL of hexadecane, 90 °C. [b] M_1 = MMA, M_2 = BMA. MMA:BMA:Et-2BriB:CuBr:dAbpy = 100: 100: 1:1: 2; 0.3 g of Brij98, 10 mL of H_2O, 0.1 mL of hexadecane, 90 °C.

Block copolymers were also synthesized. The initial method utilized polymeric initiators (macroinitiators) that were produced during ATRP of bulk monomer (in this case BA) and then mixing the poly(BA) (PBA) with surfactant, water, and the second monomer, styrene. A second method, where a water-borne macroinitiator is produced in situ by ATRP and then the second monomer is added as an emulsion (i.e., sequential monomer addition), will be reported in a later publication.

Figure 1 shows the molecular weight distributions (MWDs) of the samples taken during the polymerization, along with the conversion, M_n, and M_w/M_n data. Styrene conversion reached nearly 80% within 24 h and exhibited close to first-order kinetics. The reaction mixture was not quite homogeneous—there appeared to be a separate styrene phase during the early part of the polymerization; however, this disappeared during the course of the reaction. The final mixture appeared homogeneous and was stable indefinitely. The molecular weight increased with conversion, following closely the theoretical molecular weight, and polydispersity remained low (<1.19). The peak at a molecular weight of approximately 1500 is due to the Brij98 surfactant and is present in each sample, although the amount of surfactant relative to the (co)polymer decreases throughout the polymerization. The peak due to the macroinitiator (peak molecular weight ~ 6500) apparently moves to higher molecular weight and becomes narrower as conversion increases. The signal at higher molecular weights in the 0% conversion MWD is most likely due to polymer that is formed at the very beginning of the polymerization. (This sample was taken after the addition of macroinitiator, catalyst, and monomer.) At the very early stages of ATRP there is not enough oxidized species (XCu^{II} in this case) to provide effective deactivation; thus chains grow to high molecular weight before terminating. However, each of these termination events provides the excess deactivator necessary for controlled growth so that the majority of chains grow in a uniform manner. In other words, the persistent radical effect is in operation.

A portion of the final mixture was taken; the polymer was isolated and dried, and a ^{1}H NMR spectrum was recorded. Integration of each components' peaks yield a mole ratio of BA:styrene of 1:3.8, which is very close to that calculated from conversion (1:3.9) and similar

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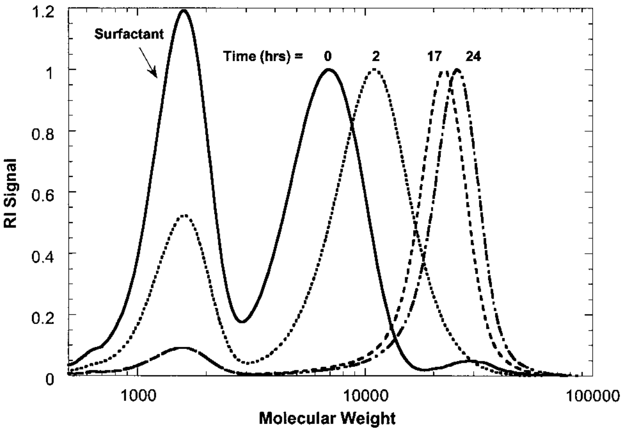

Figure 1. Molecular weight distribution development as a function of time and monomer conversion for the water-borne chain extension of PBA by styrene with Brij98, CuBr/dAbpy, and hexadecane. Time (h)/% conversion/M_n/M_w/M_n data: 0/0/6200/1.18, 2/25/9500/1.19, 17/70/19100/1.14, 24/78/21400/1.15 (M_n and M_w/M_n data calculated not including surfactant peak).

Table 2. Results of Water-Borne Styrene Chain Extensions of PBA by ATRP. Experiment 1: Tween20, BPMODA and Hexadecane; Experiment 2: Brij98 and BPMODA, without Hexadecane

time (h)	% conversion	M_n	M_n^{theo}	M_w/M_n
expt 1				
0	0	10 200	9 600	1.22
0.5	14	13 300	12 500	1.12
1	20	14 800	13 800	1.21
2	30	17 450	15 900	1.17
4	46	22 500	19 200	1.14
9	71	32 200	24 350	1.13
18[a]	97	42 700	29 900	1.15
expt 2				
0	0	10 050[b]	9 600	1.25
0.5	34	12 350[b]	16 650	1.25
1	36	13 900[b]	17 100	1.23
2	45	16 800[b]	18 950	1.19
8	73	24 150[b]	24 800	1.17
16	87	25 500[b]	27 800	1.16

[a] Reaction mixture had coagulated. [b] MWDs showed the presence of some high molecular weight material (~500 000). This peak was stationary and was not included in the calculation of M_n or M_w/M_n.

to the value obtained from GPC analysis (1:3.3). From the evidence presented above, it appears that the water-borne block copolymerization has been successful. While the question of particle size and stability has not been addressed directly, the latex did not coagulate over several months.

Table 2 contains data from other water-borne block copolymerizations. The first experiment in Table 2 shows that the polymerization using a different surfactant (Tween20), ligand (BPMODA[6]), and Br end groups was also successful in producing a PBA-*b*-PSTY block copolymer. The stability of the latex was poor beyond 70% monomer conversion. However, throughout the reaction the molecular weight increased and polydispersity remained low. A third block copolymerization is also described in Table 2 (experiment 2). For this reaction, no hexadecane was added to the mixture. Again, M_n increased and M_w/M_n decreased with conversion. This reaction had a small amount of polymer phase deposited on the walls of the reactor at the highest conversion.

Other block copolymerization experiments were also performed under similar conditions, but it became apparent that the stability of the mixture was difficult to reproduce. Typically, any one or more of the following would occur: (i) the macroinitiator would precipitate before the addition of the catalyst, (ii) the reaction would proceed with a separate monomer phase present, and (iii) the mixture would be homogeneous until approximately 60−80% conversion where polymer would precipitate. On most occasions where the polymerization at least started without coagulation, the M_n increased with conversion and M_w/M_n remained low (<1.3). This indicates that while the polymerization can be controlled and the formation of the required block copolymer is attainable, it is a matter of particle size and stability that remains the greatest problem. A host of factors will affect the stability of the latex formed, such as the surfactant used, the presence of macroinitiator, metal catalyst and ligand, the order of reactant addition, and the degree and efficiency of mixing (which is in turn dependent on several other parameters). These are currently being examined in order to understand their effects better.

Conclusions. While there are literature accounts of utilizing controlled/"living" radical polymerizations for the synthesis of water-borne polymers, none of these report the synthesis of block or statistical copolymers. Other than our previous work,[3−5] water-borne polymers were limited to homopolymers of styrene (for nitroxide-mediated polymerizations),[7−12] butyl methacrylate (RAFT),[13] and MMA (ATRP).[14] In conclusion, we have successfully synthesized water-borne statistical (gradient) copolymers and PBA-*b*-PSTY block copolymers using ATRP. This work has shown that, in principle, the synthesis of water-borne polymers of varying compositions and architectures can be achieved through the application of controlled/"living" ATRP. There is, however, much more research to be done to answer fundamental mechanistic questions.

Experimental Section. a. Materials. Styrene, MMA, BA, and BMA were obtained from Fisher, purified by passing through an alumina column, distilling under vacuum, and stored under N_2 at −4 °C. CuBr was purified by washing with glacial acetic acid, rinsing with ethanol, and drying under vacuum. Ethyl 2-bromoisobutyrate (Et-2-BriB), hexadecane, Brij98, and Tween20 were obtained from Aldrich and used without purification. 4,4′-Di(alkyl)-4,4′-bipyridine (dAbpy) (where alkyl groups are a mixture of C_5 and C_9) and *N*,*N*-bis(2-pyridylmethyl)dooctylamine (BPMODA) were synthesized using previously reported methods. Monomer conversions were measured by GC on either a Shimadzu GC14 or 17A, relative to an internal standard. Molecular weights were measured on a GPC system consisting of a Waters 515 pump, Waters 717 plus Autoinjector, PSS 10^5, 10^3, and 10^2 Å columns, and a Waters 410 RI detector and were calibrated with either polystyrene or poly(methyl methacrylate) standards. ^1H NMR spectra were collected on a Bruker AM 300 MHz spectrometer in $CDCl_3$.

b. Statistical Copolymerizations. *MMA/BA.* CuBr (6.7 mg, 0.047 mmol), dAbpy (40 mg, 0.105 mmol), and Brij98 (0.3 g) were weighed into a Schlenk flask containing a magnetic stirring bar and deoxygenated (three vacuum/N_2 cycles). Deoxygenated MMA (0.63 mL, 5.89 mmol), BA (0.87 mL, 6.07 mmol), water (10 mL), and hexadecane (0.1 mL) were added and the solids dissolved, and the solution was stirred vigorously at 90

°C. Et-2BriB (6.9 μL, 0.047 mmol) was added, and samples were taken periodically.

MMA/BMA. The same procedure as given for MMA/BA (above) except the following quantities were used: CuBr (6.8 mg, 0.047 mmol), dAbpy (40 mg, 0.105 mmol), Brij98 (0.3 g), MMA (0.5 mL, 4.7 mmol), BMA (0.75 mL, 4.7 mmol), water (10 mL), hexadecane (0.1 mL), Et-2BriB (6.8 μL, 0.047 mmol).

c. Block Copolymerizations. *Figure 1*. PBA (0.22 g, $M_n = 5750$, 0.039 mmol) and Brij98 (0.10 g) were weighed into a round-bottom flask that was then deoxygenated by three vacuum/N_2 cycles. Styrene (0.5 mL, 4.36 mmol, deoxygenated by bubbling N_2 for 30 min) was added and the PBA and Brij98 dissolved. Water (5 mL, deoxygenated by bubbling N_2 for 30 min) was then added and the mixture stirred vigorously. For the second solution CuBr (5.6 mg, 0.039 mmol), dAbpy (30 mg, 0.078 mmol), and Brij98 (0.2 g) were weighed into a Schlenk flask containing a magnetic stirring bar and deoxygenated (three vacuum/N_2 cycles). Styrene (0.5 mL, 4.26 mmol) was added and the solids dissolved. Deoxygenated water (5 mL) and hexadecane (0.1 mL) were added, and the solution was stirred vigorously. The contents of the round-bottom flask were then transferred to the Schlenk flask, which was then immersed in a 90 °C oil bath.

Experiment 1, Table 2. Tween20 (0.5 g) was weighed into a round-bottom flask, deoxygenated by three vacuum/N_2 cycles, and then dissolved in deoxygenated water (10 mL). PBA (0.79 g, $M_n = 9600$, 0.082 mmol) was weighed into a Schlenk flask containing a magnetic stirring bar and deoxygentated, and then hexadecane (0.1 mL) was added. CuBr (11.8 mg, 0.082 mmol) and BPMODA (37.1 mg, 0.082 mmol) were weighed into a round-bottom flask and deoxygenated (three vacuum/N_2 cycles). Styrene (1.9 mL, 16.5 mmol) was added to the CuBr/BPMODA and the solids dissolved. The CuBr/BPMODA/styrene solution was then transferred to the Schlenk flask with vigorous stirring, and the Schlenk flask was immersed in a 90 °C oil bath.

Experiment 2, Table 2. Brij98 (0.3 g) was weighed into a Schlenk flask containing a magnetic stirring bar, deoxygenated by three vacuum/N_2 cycles, and then dissolved in deoxygenated water (10 mL, bubbled with N_2 for 30 min). PBA (1.05 g, $M_n = 9600$, 0.110 mmol) was weighed into a round-bottom flask, deoxygenated, and then dissolved in deoxygenated styrene (1.25 mL, 11.0 mmol). CuBr (15.8 mg, 0.110 mmol) and BPMODA (49.7 mg, 0.110 mmol) were weighed into a second round-bottom flask and deoxygenated (three vacuum/N_2 cycles). Styrene (1.25 mL, 11.0 mmol) was added to the CuBr/BPMODA and the solids dissolved. The PBA/styrene solution was transferred into the Schlenk with vigorous stirring for 20 min. Likewise, the CuBr/BPMODA/styrene solution was then transferred to the Schlenk flask with vigorous stirring, and the Schlenk flask was immersed in a 90 °C oil bath. Samples (0.2 mL) were taken at intervals and added to 0.05 mL hexadecane (as a standard for GC analysis).

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