Controlled/"Living" Radical Polymerization Applied to Water-Borne Systems

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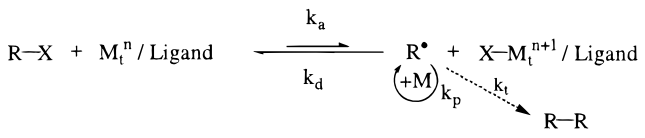
The preparation of well-defined polymers and copolymers by radical polymerization has recently been an area of high interest.[1] Although many systems have been proposed, the two most widely used are nitroxyl-mediated polymerizations, and atom transfer radical polymerization (ATRP). The nitroxyl-mediated polymerizations are generally confined to polymers and copolymers of styrene.[2−4] ATRP has been used for the successful polymerization of well-defined polymers and copolymers of styrenes, acrylates, methacrylates, and acrylonitrile.[5−9]

ATRP employs the reversible activation and deactivation of alkyl halides (R−X) by transition metal catalysts (M_t^n) to form radicals (R•) which can propagate by addition of monomer (M), Scheme 1. ATRP has been demonstrated with a wide variety of metal centers,[5,10−13] but the most successful to date have been those based on copper[5−7] or iron.[14−16]

Nearly all controlled/"living" radical polymerizations, however, have been confined to bulk or solution polymerization. Although some polymerizations have been conducted in water, either as homogeneous[17] or biphasic mixtures,[18] the preparation of well-defined polymers by emulsion or suspension systems has not been reported. A seeded emulsion polymerization of styrene has been conducted with TEMPO-mediated polymerization systems,[19] but a seeded emulsion is not desirable as the seeded polymer is generally not well-defined and cannot easily be separated from the desired homo- or copolymer; the resulting bulk polymer is not well-defined. Additionally, the use of ATRP in emulsions[20] or suspensions[11] has been reported, but the resulting polymers were not well defined as evidenced by broad molecular weight distributions, and the theoretical molecular weights did not correspond with predicted values ($DP_n = \Delta[M]/[I]_o$). Herein we report the extension of ATRP to aqueous emulsion systems to prepare well-defined polymers of butyl methacrylate, methyl methacrylate, styrene, and butyl acrylate.

Earlier attempts to use ATRP in emulsions by both our group and others used sodium dodecyl sulfate as an emulsifier. Unfortunately, the use of this surfactant generally led to the formation of high molecular weight polymer with broad polydispersities. We attribute this to the reaction of the copper(II) bromide (or chloride) with the sulfate anion to form copper(II) sulfate and sodium bromide. Thus, the growing radicals cannot be deactivated, as the sulfate group is not capable of being transferred to the growing radical, and the polymerization would behave as if it were a conventional, redox-initiated, radical polymerization. To overcome this problem, we looked to employ the use of nonionic surfactants.

Scheme 1



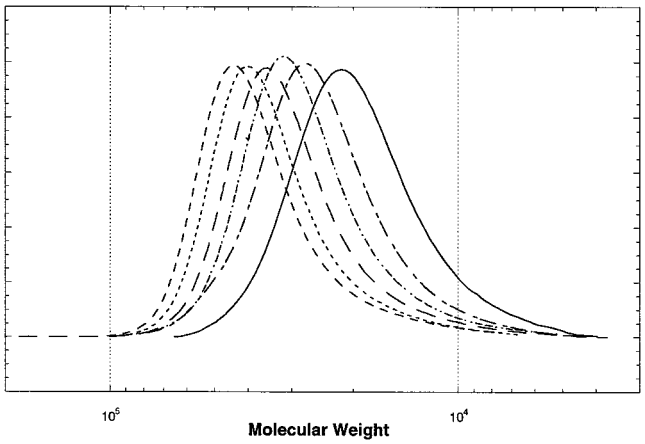


Figure 1. SEC chromatograms of the emulsion polymerization of *n*-butyl methacrylate by ATRP (second entry in Table 2).

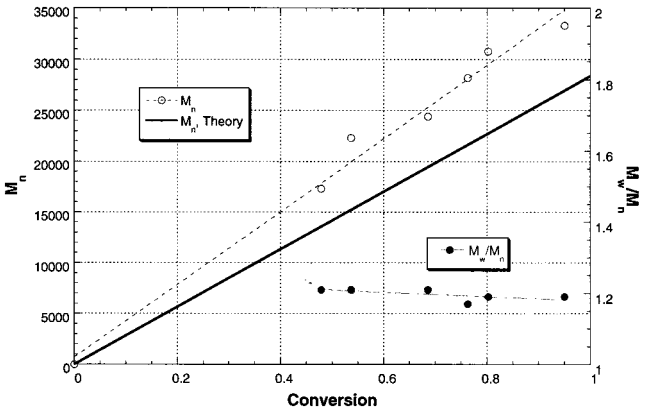


Figure 2. Dependence of molecular weight with conversion for the emulsion polymerization of *n*-butyl methacrylate by ATRP (second entry in Table 2).

Poly(ethylene glycol) (PEG) or poly(oxyethylene oleyl ethers) (Brij 97 or Brij 98) were used as emulsion stabilizers.[21] Initially, the polymerization of either *n*-butyl acrylate (BA) or *n*-butyl methacrylate (BMA) was conducted using low molecular weight PEG (M_n = 1000 or 4600). Although the polymerization yielded well-defined polymer, Table 1, the resulting colloids were not very stable and coagulation of the polymer was observed during the polymerization.

To obtain more stable reaction mixtures, the Brij surfactants were used. Of the two that were used, Brij 98 yielded stable emulsions of poly(BMA). The latexes of the resulting polymers were able to be passed through a 0.45 μm PTFE filter, but could not be passed through a 0.2 μm PTFE filter. Although the use of Brij 97 yielded well-defined poly(BMA) (Entry BMA-1, Table 2), the colloids were not stable and coagulated during the polymerization. The emulsion polymerization results using the Brij surfactants are summarized in Table 2.

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Table 1. ATRP Emulsion Polymerization Using Poly(Ethylene Glycol) as the Surfactant[a]

							results		
reference	monomer	initiator[b]	catalyst	ligand	surfactant	water	time	$M_{n,SEC}$	M_w/M_n
BA-8	BA, 2.5 mL (17 mmol)	EBiB, 12.8 μL (0.087 mmol)	CuBr, 12.5 mg (0.087 mmol)	dNbpy, 71.3 mg (0.174 mmol)	PEG(1000), 1 g	10 mL	1 h	9 821	1.12
							4.3 h	13 430	1.11
							22 h	19 270	1.18
BA-9	BA, 2.5 mL (17 mmol)	EBP, 11.3 μL (0.087 mmol)	CuBr, 12.5 mg (0.087 mmol)	dNbpy, 71.3 mg (0.174 mmol)	PEG(1000), 1 g	10 mL	1 h	11 480	1.21
							4.3 h	14 530	1.16
							22 h	20 260	1.19
BA-10	BA, 2.5 mL (17 mmol)	EBP, 11.3 μL (0.087 mmol)	CuBr, 12.5 mg (0.087 mmol)	dNbpy, 71.3 mg (0.174 mmol)	PEG(1000), 0.5 g	10 mL	1 h	12 160	1.18
							4.3 h	16 600	1.16
							22 h	22 800	1.17
BA-11	BA, 2.5 mL (17 mmol)	EBP, 11.3 μL (0.087 mmol)	CuBr, 12.5 mg (0.087 mmol)	dNbpy, 71.3 mg (0.174 mmol)	PEG(4600), 1 g	10 mL	70 min	15 000	1.27
							4.2 h	16 540	1.21
							11 h	21 200	1.15
							22 h	21 750	1.18
BMA-1	BMA, 2.5 mL (15.7 mmol)	EBiB, 11.5 μL (0.079 mmol)	CuBr, 11.3 mg (0.079 mmol)	dNbpy, 64.2 mg (0.157 mmol)	PEG(4600), 1 g	10 mL	1 h	23 010	1.20
BMA-2	BMA, 2.5 mL (15.7 mmol)	EBiB, 11.5 μL (0.079 mmol)	CuBr, 11.3 mg (0.079 mmol)	dNbpy, 64.2 mg (0.157 mmol)	PEG(1000), 1 g	10 mL	30 min	23 250	1.21
BMA-3	BMA, 1.5 mL (9.4 mmol)	EBiB, 6.9 μL (0.047 mmol)	CuBr, 6.8 mg (0.047 mmol)	dNbpy, 38.4 mg (0.094 mmol)	PEG(4600), 134 mg	10 mL	16 min	17 790	1.21
							20 min	25 460	1.61
							45 min	26 030	1.22
BMA-4	BMA, 1.5 mL (9.4 mmol)	EBiB, 6.9 μL (0.047 mmol)	CuBr, 6.8 mg (0.047 mmol)	dNbpy, 38.4 mg (0.094 mmol)	PEG(4600), 1 g	10 mL	20 min	25 200	1.40
							40 min	27 760	1.51
							70 min	28 280	1.19
BMA-5	BMA, 3 × 0.5 mL (9.4 mmol)	EBiB, 3.5 μL (0.024 mmol)	CuBr, 6.8 mg (0.047 mmol)	dNbpy, 38.4 mg (0.094 mmol)	PEG(4600), 1 g	10 mL	45 min	40 140	2.09
							2 h	41 340	2.56
							3.5 h	55 120	1.81
BMA-6	BMA, 1.5 mL (9.4 mmol)	EBiB, 6.9 μL (0.047 mmol)	CuBr, 6.8 mg (0.047 mmol)	dNbpy, 38.4 mg (0.094 mmol)	PEG(1000), 16.8 mg	10 mL	16 min	21 980	1.25
							20 min	22 940	1.26
							50 min	29 910	1.27

[a] All polymerizations conducted at 90 °C. [b] EBiB = ethyl 2-bromoisobutyrate.

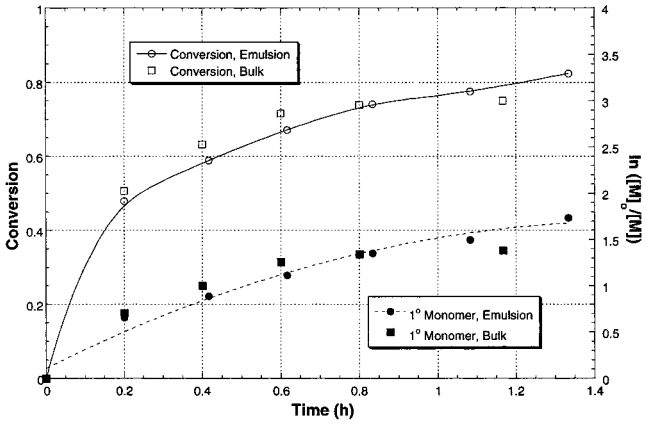

Figure 3. Comparison of kinetics for bulk and emulsion polymerizations of *n*-butyl methacrylate (90 °C).

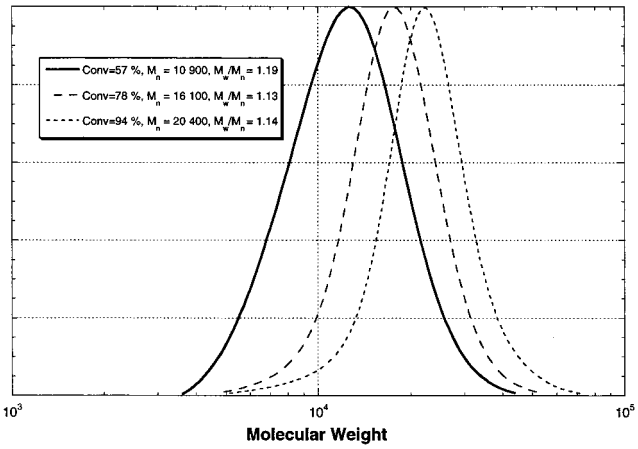

Figure 4. SEC chromatograms of the emulsion polymerization of *n*-butyl acrylate by ATRP.

As can be seen in Figures 1 and 2, the molecular weight of the poly(BMA) increased with conversion. Although some tailing of the chromatograms was observed, it was possible to diminish this by lowering the temperature; the polymerization at 70 °C displayed less tailing than those polymers obtained at 90 °C.

The increase of molecular weight with conversion was close to that predicted by theory, Figure 2. The reason for the slightly higher molecular weights than predicted may be the result of the difference in the hydrodynamic volumes of BMA vs the poly(MMA) standards used for calibration, or could arise due to inefficient initiation. Since the parts of the catalyst (both activator, Cu(I), and deactivator, Cu(II)) are predominately confined to the organic phase by the use of the alkyl substituted bipyridines, inefficient initiation is possible if a portion of the radicals diffuses out of the micelles and/or monomer droplets into the aqueous phase and terminate. This would most likely occur with low molecular weight oligomers (low monomer conversion) or with the initiator itself.

The kinetics of the emulsion polymerization at 90 °C were compared to those obtained for the bulk polymerization of BMA, Figure 3. As can be seen, the kinetics of the two polymerizations were nearly identical. The slowing of the polymerization rate at longer reaction times was attributed to a too high polymerization temperature. Too high reaction temperatures can lead to a higher radical concentration, and thus added termination, a gradual buildup of deactivator, and a slower polymerization rate. If the reaction temperature was lowered to 70 °C, the semilogarithmic plots of monomer conversion vs time were linear for the emulsion polymerization, indicating that the polymerization was first order in monomer and that termination of the growing chains could be reduced, compared to the polymerization at 90 °C.

Table 2. ATRP Emulsion Polymerization Using Brij as the Surfactant[a]

							results				
reference	monomer	initiator	catalyst	ligand	surfactant	water	time	conv (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
BMA-7	BMA, 1.5 mL (9.4 mmol)	EBiB, 6.9 μL (0.047 mmol)	CuBr, 6.8 mg (0.047 mmol)	dNbpy, 38.4 mg (0.094 mmol)	Brij 97, 0.5 g	10 mL	25 min	90	25 450	22 860	1.24
							40 min	85	24 220	26 750	1.25
							60 min			28 380	1.23
BMA-Kinetics	[b]BMA, 3.0 mL (18.8 mmol)	EBiB, 19 μL (0.094 mmol)	CuBr, 13.6 mg (0.094 mmol)	dAbpy, 66 mg (0.188 mmol)	Brij 98, 0.2 g	20 mL	15 min	48	13 600	17 300	1.21
							30 min	54	15 300	22 300	1.21
							45 min	69	19 600	24 400	1.21
							60 min	76	21 600	28 200	1.17
							90 min	80	22 700	30 800	1.19
							120 min	95	27 000	33 300	1.19
BMA-8	BMA, 1.5 mL (9.4 mmol)	EBiB, 6.9 μL (0.047 mmol)	CuBr, 6.8 mg (0.047 mmol)	dNbpy, 38.4 mg (0.094 mmol)	Brij 98, 0.5 g	10 mL	26 min	70	19 820	26 240	1.23
							45 min	83	23 550	29 190	1.30
							75 min	89	25 200	33 950	1.29
BMA-9	BMA, 1.5 mL (9.4 mmol)	EBiB, 6.9 μL (0.047 mmol)	CuBr, 6.8 mg (0.047 mmol)	dNbpy, 38.4 mg (0.094 mmol)	Brij 98, 0.1 g	10 mL	70 min	81	22 890	28 170	1.26
BMA-10	BMA, 1.5 mL (9.4 mmol)	EBiB, 6.9 μL (0.047 mmol)	CuBr, 6.8 mg (0.047 mmol)	dNbpy, 38.4 mg (0.094 mmol)	Brij 98, 0.2 g	10 mL	75 min	81	24 170	32 290	1.28
BMA-11	BMA, 1.5 mL (9.4 mmol)	EBiB, 6.9 μL (0.047 mmol)	CuBr, 6.8 mg (0.047 mmol)	dNbpy, 38.4 mg (0.094 mmol)	Brij 98, 0.3 g	10 mL	12 min	48	13 600	17 800	1.22
							25 min	59	16 800	21 900	1.21
							37 min	67	19 100	24 000	1.24
							50 min	74	21 100	26 500	1.22
							65 min	78	22 100	29 600	1.19
							80 min	82	23 400	30 200	1.22
BMA-13	BMA, 5.0 mL (31.3 mmol)	EBiB, 6.9 μL (0.047 mmol)	CuBr, 6.8 mg (0.047 mmol)	dNbpy, 38.4 mg (0.094 mmol)	Brij 98, 0.15 g	10 mL	130 min	67	62 760	64 950	1.29
BMA-14	BMA, 2.4 mL (15.1 mmol)	EBiB, 2.8 μL (0.019 mmol)	CuBr, 2.7 mg (0.019 mmol)	dNbpy, 15.4 mg (0.038 mmol)	Brij 98, 0.8 g	16 mL	135 min	76	85 890	98 340	1.73
BMA-15	BMA, 3mL (18.8 mmol)	EBiB, 13.8 μL (0.094 mmol)	CuBr, 2.7 mg (0.019 mmol)	dAbpy, 71.6 mg	none	none	12 min	51	14 400	18 000	1.92
							24 min	63	18 000	18 600	1.62
							37 min	72	20 400	19 000	1.36
							48 min	74	21 000	19 700	1.30
							70 min	75	21 300	20 100	1.30
BMA-16	BMA, 1.5 mL (9.4 mmol)	KPS, 6.2 mg (0.023 mmol)	$CuBr_2$, 8.6 mg (0.039 mmol)	dAbpy, 27.1 mg	Brij 98, 0.3 g	10 mL	20 h	no polymer			
BMA-18	[b]BMA, 20 mL	EBiB, 93 μL	CuBr, 13.6 mL	dAbpy, 66 mg	Brij 98, 0.5 g	20 mL	3 h			15 800	1.32
BMA-19	[b]BMA, 3 mL	EBiB, 14 μL	CuBr, 13.6 mL	bpy, 29.4 mg (0.188 mmol)	Brij 98, 1.0 g	20 mL	3 h	100	28 400	272 000	3.27
BMA-20	[b]BMA, 3 mL	EBiB, 14 μL	CuBr, 13.6 mL	3N, 20 μL (0.094 mmol)	Brij 98, 1.0 g	20 mL	3 h	100	28 400	3 800 00	6.7
BMA-21	[b]BMA, 3 mL	EBiB, 14 μL	CuBr, 13.6 mL	Me6-TREN, 26 μL (0.094 mmol)	Brij 98, 1.0 g	20 mL	3 h	100	28 400	9 800 000	3.8
MMA	MMA, 1.5 mL (14.0 mmol)	EBiB, 9.2 μL (0.07 mmol)	CuBr, 5 mg (0.035 mmol) $CuBr_2$, 8 mg (0.004 mmol)	dAbpy,[c] 26.6 mg (0.07 mmol)	Brij 98, 0.5 g	10 mL	3.5	90	17 300	23 400	1.36
Sty	Sty, 1.5 mL (13.1 mmol)	EBiB, 9.6 μL (0.066 mmol)	CuBr, 9.4 mg (0.066 mmol)	dAbpy,[c] 49.8 mg (0.131 mmol)	Brij 98, 0.2 g	10 mL	7.6 h			4 800	1.06
							20.5 h			10 600	1.07
BA	BA, 1.5 mL (10.5 mmol)	EBiB, 7.7 μL (0.053 mmol)	CuBr, 7.5 mg (0.053 mmol)	dAbpy,[c] 40.0 mg (0.105 mmol)	Brij 98, 0.2 g	10 mL	1.2 h	57	14 500	10 900	1.19
							4.0 h	78	20 000	16 100	1.13
							20.3 h	94	24 200	20 400	1.14

[a] All polymerizations conducted at 90 °C, unless noted. [b] Polymerization conducted at 70 °C. [c] dAbpy = 4,4′-di(alkyl)-4,4′-bipyridine; the alkyl group is a mixture of C_5 and C_9 alkyl chains.

Various surfactant-to-water ratios were used, with successful polymerizations being obtained with surfactant concentrations ranging from 1% to 5% (wt/v) (cf. BMA-8 to BMA-11, Table 2). Additionally, the use of monomer concentrations ranging from 15% to 50% were successful as well (BMA-17, -18).

The application of ATRP in emulsion systems was applied to other monomers as well. Styrene, butyl acrylate and methyl methacrylate were all successfully polymerized. However, the reaction times for the polymerization of styrene and butyl acrylate were much longer than that observed for the methacrylates and the polymerization of either styrene or butyl acrylate in bulk. The reason for the increased reaction times is not clear and is the subject of further study.

The role of the ligand was explored (cf. BMA-Kinetics, BMA -18 to -21). When ligands were used that formed copper complexes which were preferentially soluble in the aqueous phase, vs the monomer droplets/micelles, the emulsions were uncontrolled. For example, only when 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) or 4,4′-di-(alkyl)-2,2′-bipyridine (dAbpy) were used were well-defined polymers obtained; in contrast, the water-soluble copper complexes with bpy, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (3N), and tris((2-dimethylamino)ethyl)amine (Me_6-TREN) yielded polymer with very high molecular weights and broad molecular weight distributions. The loss of control was attributed to the preferential partitioning of the copper(II) halide (the deactivator) to the aqueous phase; the addition of the long alkyl chains on the ligands enhanced the solubility of the catalyst in the organic monomer/polymer phase where it must be present to obtain a controlled radical polymerization.

Additional improvements to the system will come with the application/optimization of better emulsifiers. Also,

because this is an ATRP process, it is expected that other metal centers, e.g., iron, nickel, ruthenium, etc., that are successful for polymerizations conducted in bulk or in organic solvents will also be applicable to these types of water-borne polymerization systems. We are currently investigating the synthesis of polymers with novel compositions, functionalities, and architectures in these water-borne systems.

Conclusion. We have successfully demonstrated that an emulsion polymerization using ATRP can be conducted to yield well-defined polymers. The monomers that were successfully polymerized include methyl methacrylate, butyl methacrylate, butyl acrylate, and styrene. The polymers had molecular weights that were close to those predicted by the ratio of consumed monomer to added initiator, and they also displayed narrow molecular weight distributions ($M_w/M_n < 1.3$).

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(21) General procedure for polymerization: To a round-bottom flask with stir bar, were added copper(I) bromide, ligand, and surfactant. The contents of the flask were degassed by applying vacuum and backfilling with nitrogen. Degassed monomer and water were added to the flask via syringe. The mixture was stirred until the surfactant dissolved and an emulsified mixture was obtained. The reaction was heated to the desired reaction temperature and the initiator added. Upon completion of the polymerization, the copper complex was removed by addition of an ion-exchange resin (Dowex MSC-1), stirring and filtration of the resin.

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