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

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SUMMARY: Atom transfer radical polymerization (ATRP), a controlled/"living" radical polymerization, has been extended to water-borne polymerization systems. In order to obtain a controlled ATRP reaction in a water-borne system, various criteria must be met, which are not necessary when conducted in organic solvents. The effect of surfactant, monomer, catalyst and initiator employed will be discussed, as each had a profound effect on the success of the ATRP reaction.

Introduction

Control of polymer composition (homo-, statistical, block copolymers), architecture (linear, star, branched) and functionality (telechelics, site-specific) have been longstanding goals of polymer chemists. One of the most powerful methods to obtain such precision has been the use of living polymerizations. Such ideal polymerizations have only initiation and propagation as their elementary steps; chain breaking reactions such as transfer or termination do not occur. The classic living polymerization is the anionic polymerization of styrene first reported by Szwarc in 1956.1) Since then living polymerizations have been extended to a variety of polymerization systems including cationic and ring opening metathesis polymerizations.2) These systems however, face severe limitations in that they generally must be conducted in the absence of water and are limited to only a handful of monomers. To overcome these limitations, controlled/"living" radical polymerization systems have been developed as radical polymerizations are applicable to a wide range of monomers, can be performed at a wide range of easily accessible temperatures, and they can be performed as emulsions or suspensions.3)

One of the most successful controlled/"living" radical polymerizations has been atom transfer radical polymerization (ATRP).4-8) ATRP employs the activation of an alkyl halide by a transition metal catalyst to form a radical which can initiate polymerization. The growing polymeric radical is deactivated by reaction with the transition metal halide formed in the

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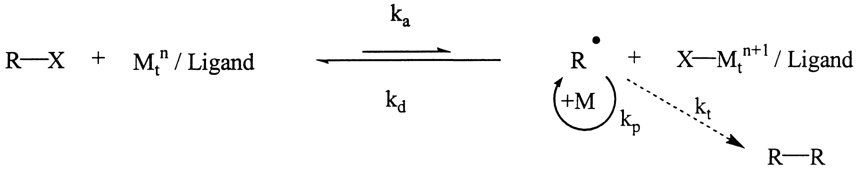
activation step, Scheme 1. Through this activation/deactivation cycle, each polymer chain grows at nearly the same rate, but there is very little termination, as a consequence of the persistent radical effect.[8,9] As termination can never be completely avoided, the term controlled or the use of "living" is used to denote this minor, but significant difference. ATRP has been successfully used in the preparation of a wide variety of polymeric materials, including well-defined polymers of styrenes, (meth)acrylates, and acrylonitrile. However, its extension to water-borne systems such as emulsions or suspensions has not been straightforward.

Scheme 1



The difficulties in obtaining a controlled/"living" radical polymerization in multi-phase systems, such as water-borne emulsions or suspensions, or even precipitation polymerizations in non-solvents such as alkanes or supercritical CO_2, is that for control of the polymerization, all of the components of the reaction (monomer, growing/dormant chain end, catalyst) must be in the same phase at some point. If these components are not in the same phase, then there will either be no reaction or an uncontrolled reaction.

To explore this, consider that if the catalyst were to be confined to the aqueous phase, but the monomer and initiator were solely in the organic phase of an emulsion. Since the catalyst can not interact with the initiator to generate a radical, then initiation does not occur and there is no polymerization. Similarly, if the initiator and catalyst are water soluble, upon formation of the polymer (and collapse into micelles or polymer particles), the growing radical and the deactivator can not come into contact with one another; the result is that there is no reversible deactivation of the growing polymer chain, and thus, the polymerization behaves as a conventional, redox initiated radical polymerization. The goal then is to have a system where at least some proportion of the components are available to perform the reaction; that the various components may change phase dynamically is acceptable, as long as the system still allows for rapid activation and deactivation of all chain ends. Another key feature of ATRP is the stability of the end group. Since ATRP utilizes an alkyl halide as an initiator/dormant chain end, this group must not be hydrolyzed in the aqueous reaction conditions.

The Problems

Previously, our group(10) and others(11) have attempted to obtain ATRP as an emulsion system. Our initial attempts were based on the polymerization of styrene using 1-phenylethyl bromide (PEBr) as the initiator and Cu(I)Br/2bpy (bpy = 2, 2'-bipyridine) as the catalyst. Using sodium lauryl sulfate (SLS) as the surfactant and hexadecane as a cosurfactant, no polymer was obtained, even after prolonged heating. It was then discovered that during ultrasonication (used to pre-form the emulsion) the PEBr was hydrolyzed into the corresponding alcohol and subsequent ether. In model studies, ethyl 2-bromoisobutyrate (EBiB) was found to be stable under reaction conditions similar to those employed in the polymerizations.

After discovery of the requirement that the end group be stable, the polymerization of butyl acrylate (BA) using ethyl 2-bromoisobutyrate as the initiator was explored. In this system, there was initiation, but the product polymer had very high molecular weight ($M_n > 200{,}000$) and broad polydispersities ($M_w/M_n > 2$). The reaction was very fast, with the polymerization being exothermic and turning green upon addition of initiator to the emulsified mixture of monomer, surfactant, and catalyst (which was originally red, indicative of the Cu(I) complex with bpy). The formation of the green color suggested that after initiation, the Cu(II)-Br complex accumulated rapidly but did not deactivate the growing radicals; it was in effect, "removed" from the reaction by some mechanism. To understand this, we investigated the relative solubility of the copper species in water and in organic solutions. Cu(II)Br_2/2bpy complexes were prepared in butyl acrylate; these were not completely soluble, but the solutions were colored green. Addition of water and mixing immediately resulted in the butyl acrylate layer turning colorless and the water layer becoming colored. These results indicated that the catalyst was partitioning into the aqueous phase and preventing deactivation of the growing radical. The use of 4, 4'-di(5-nonyl)-2, 2'-bipyridine(7) (dNbpy) was able to confine the catalyst to the organic phase and thus was used as the ligand for the catalyst.

However, even with this new ligand, dNbpy, the polymerization was still uncontrolled. Various orders of addition of the catalyst and initiator did not yield successful polymerizations. Attention then turned to the surfactant. Polymerization of butyl acrylate in the presence of water was successful in the absence of surfactant. The use of poly(ethylene oxide) was then tried for the polymerization of butyl methacrylate; although severe coagulation of the polymer was observed, a well-defined poly(butyl methacrylate) was obtained (M_n = 20, 300; M_w/M_n = 1.19). Based on these results, it is speculated that there is some type of interaction of SLS with the Cu(II)-Br complex which renders the catalyst unable to deactivate the growing polymer chain. One possibility is that the SLS reacts with the Cu(II)-Br to form copper(II) sulfate and NaBr. As the copper(II) sulfate can no longer transfer a halogen to the growing radical (transfer of sulfate radicals has not been observed), there is no deactivation. The final analysis suggested that the use of non-ionic surfactants would not interfere with the ATRP process.

The Monomers

To enhance the particle stability of the dispersed system, a surfactant with both hydrophilic and hydrophobic segments was investigated in the polymerization of *n*-butyl methacrylate; the Brij surfactants are linear polymers containing poly(ethylene oxide) (PEO) and a C_{18} hydrophobic chain. The use of Brij 97 (PEO, DP_n~10) resulted in a controlled polymerization, but small, visually observable particles were obtained. With Brij 98, the longer PEO segment (DP_n~20) was apparently able to stabilize the particles to a greater degree; stable latexes were obtained (the "emulsions" were obtained by simple stirring using a magnetic stir bar). The kinetics of the polymerization in water showed some curvature in the first order plot, Figure 1, but the molecular weights increased with conversion and had narrow molecular weight distributions, Figure 2. Remarkably, the kinetics of the polymerization were similar for those observed in bulk BMA; the initiator efficiency (*f* = 0.76) was lower for the water based system, although polydispersities were lower.

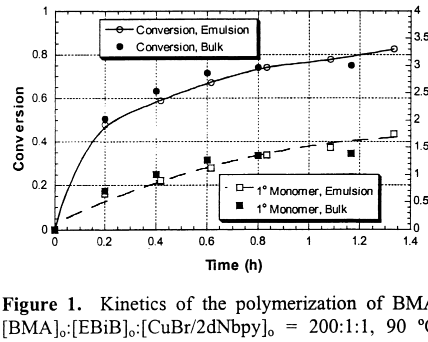


Figure 1. Kinetics of the polymerization of BMA. $[BMA]_o$:$[EBiB]_o$:$[CuBr/2dNbpy]_o$ = 200:1:1, 90 °C, Emulsion = 15% BMA, 3% Brij 98 (rel. to water).

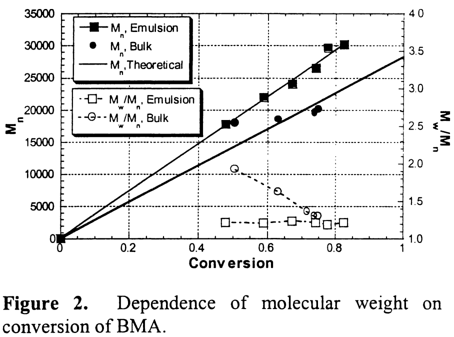


Figure 2. Dependence of molecular weight on conversion of BMA.

It was also observed that cationic surfactants could be employed. The cationic surfactant dodecyltrimethylammonium bromide (DTMAB) allowed for the synthesis of a well-defined polyBMA ($M_n = 21,200$; $M_w/M_n = 1.24$; $M_{n,\,th.} = 18,300$), but coagulation and sedimentation was observed when stirring was stopped.

Other monomers were polymerized as well. *n*-Butyl acrylate showed an initially rapid polymerization rate, but then became much slower, Figure 3. Molecular weight control, however, was very good, with observed molecular weights agreeing well with theoretical and the polymer having narrow molecular weight distributions ($M_w/M_n < 1.2$), Figure 4. In Figure 5, the SEC traces of the polymer samples taken from the polymerization can be seen to move steadily to higher molecular weights as well.

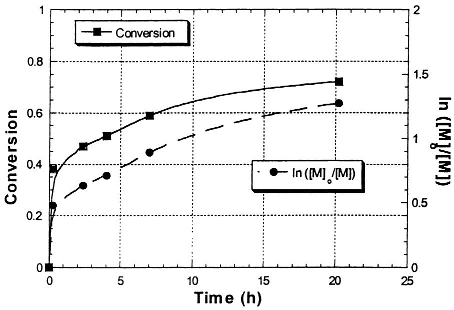


Figure 3. Kinetics of the polymerization of BA. $[BA]_0$:$[EBiB]_0$:$[CuBr/2dNbpy]_0$ = 200:1:1, 90 °C, 15% BA, 3% Tween 80 (rel. to water).

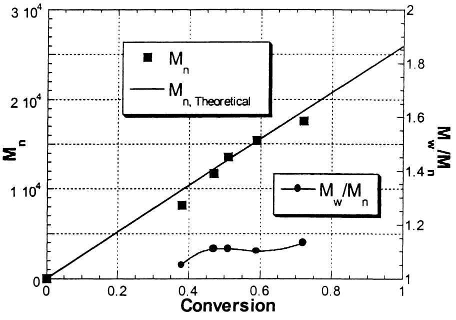


Figure 4. Dependence of molecular weight on conversion of BA.

Using the surfactant Tween 20, a branched polyoxyethylene oleyl ether, as the surfactant the polymerization of styrene was found to be much slower than in bulk, requiring 20 hours to reach sixty percent conversion, Polymers with very narrow molecular weight distributions were obtained ($M_w/M_n < 1.1$), however. Initially, some of the styrene monomer phase separated forming small pools in the reaction mixture, but these dissipated as the polymerization progressed and there was no coagulation of polymer at higher conversions.

Apparently, the halogen end group on polymer chain was not hydrolyzed during the polymerization (*vida supra*). This may be the result of the hydrophobic polymer chain acting as a protective shield, preventing water from hydrolyzing the halogen end group to the corresponding alcohol.

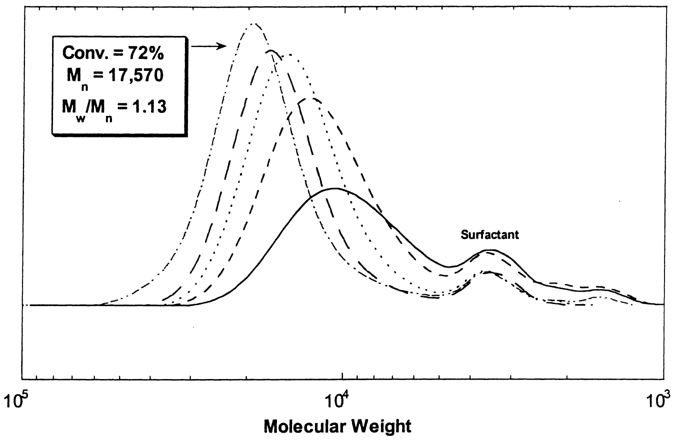


Figure 5. SEC traces of poly(BA) prepared in a water-borne ATRP reaction.

Now that polymers of controlled molecular weight and polydispersity could be prepared, the next goal was to examine the effect of monomer and surfactant concentrations. In Table 1, it can be seen that water-borne systems with relatively high monomer concentrations were successfully conducted, yielding well-defined polymer. With the higher monomer concentrations, somewhat higher concentrations of surfactant were required to obtain stable latexes, but with lower amounts of monomer, less surfactant was needed, Table 2.

Table 1. Effect of monomer concentration in the water-borne ATRP of butyl methacrylate.

M/Water	*Brij 98*	*T (C)*	*Time (m)*	*Conv. (%)*	$M_{n,\,th.}$	$M_{n,\,SEC}$	M_w/M_n
0.15/1	2 %	70	105	88	25 000	34 000	1.25
0.5/1	1.5 %	90	130	66	62 800	65 000	1.29
1/1	5 %	70	125	83	23 600	29 800	1.16

Table 2. Effect of varying Brij 98 concentration in the polymerization of butyl methacrylate in water; $[M]_0$/Water = 0.15:1.

% Brij 98	*Temp (C)*	*Time (m)*	*Conv. (%)*	$M_{n,\,th.}$	$M_{n,\,SEC}$	M_w/M_n
5	90	75	89	25 200	34 000	1.29
3	90	80	82	23 400	30 200	1.22
2	90	75	85	24 200	32 300	1.26
1	90	70	81	22 900	28 200	1.26
0.2	70	123	85	24 200	33 900	1.30

Temperature

The original polymerizations of BMA were conducted at 90 °C, but lowering the temperature to 70 °C did not seem to have a dramatic effect on the rate of polymerization, Figure 6. Interestingly, it was observed that the polymerization proceeded even at room temperature but was much slower, requiring seven hours to reach 95% conversion. Molecular weight behavior at all temperatures was similar although at room temperature there appears to be some slow initiation, Figures 7 and 8.

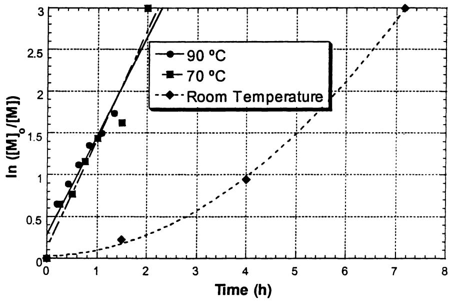


Figure 6. Kinetics of the polymerization of BMA at various temperatures. $[BMA]_o$:$[EBiB]_o$:$[CuBr/2dNbpy]_o$ = 200:1:1, 15% BMA, 2% Brij 98 (rel. to water).

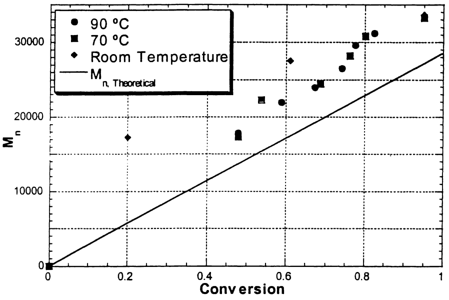


Figure 7. Behavior of molecular weight as a function of conversion for various temperatures.

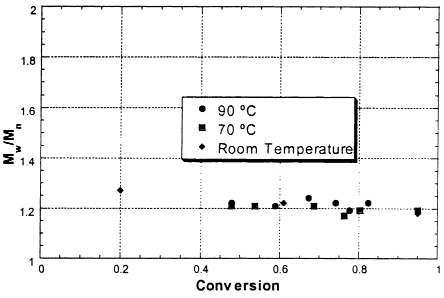


Figure 8. Behavior of polydispersity as a function of conversion for various temperatures.

Ligands

Recently, our group has developed a variety of ligands which result in faster polymerizations or are simpler/cheaper to obtain than bpy and its derivatives (Figure 9).[12,13] Among these, the linear, aliphatic triamine, pentamethyldiethylenetriamine, shows much promise as it is commercially available and relatively inexpensive. Additionally, the branched aliphatic amine (Me_6-TREN) is interesting in that it can be employed in amounts much lower than bpy, while still maintaining good rates of polymerization. Both of these ligands, however, did not afford a controlled radical polymerization, Table 3. Similar to the use of bpy, it was apparent that these ligands did not sufficiently partition the catalyst into the organic phases. The two bis(2-pyridylmethyl) alkyl amines were synthesized to impart a greater organic preference for the catalyst, while maintaining the "triamine" nature of the faster, aliphatic catalyst. While use of BPMOA yielded polymers with molecular weights closer to theory than the other ligands, the polydispersity was much broader; only limited enhancement was observed with BPMODA with the C_{18} alkyl chain.

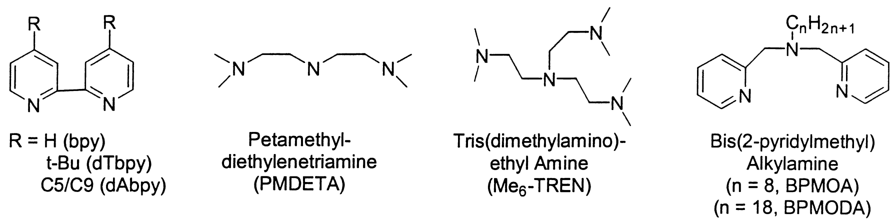


Figure 9. Catalysts used in water-borne ATRP

Table 3. Effect of varying the ligand in the ATRP of BMA in water-borne systems.[a]

Ligand	*Temp (C)*	$M_{n,\,th}$	$M_{n,\,SEC}$	M_w/M_n
dAbpy	70	28 400	33 300	1.2
dTbpy[b]	70	28 400	33 800	1.4
BPMOA	70	28 400	48 300	2.0
BPMODA	70	27 300	43 100	1.8
bpy	70	28 400	272 000	3.3
PMDETA	70	28 400	3 800 000	6.7
Me_6-TREN	70	28 400	9 800 000	3.8
Me_6-TREN	20	28 400	930 000	2.2

[a] $[BMA]_o$:$[EBiB]_o$:$[CuBr/2dNbpy]_o$ = 200:1:1, 15% BMA, 2% Brij 98 (rel. to water)
[b] 8% Cu(II)Br2 added (rel. to Cu(I))

Although the use of BPMOA and BPMODA were not successful for the polymerization of BMA; a controlled radical polymerization was observed when BPMODA was used for BA. An enhancement of the rate, when compared to using the CuBr/2dNbpy catalyst, was also observed, Figure 10. With the faster rate of polymerization, the molecular weight control was still relatively good, albeit with slightly higher polydispersities, Figure 11. Similar results were observed in the polymerization of styrene, Figures 12 and 13.

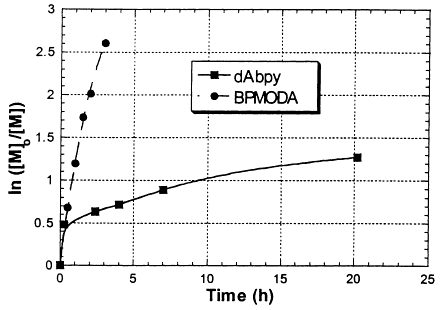


Figure 10. Comparison of the kinetics of the polymerization of BA using BPMODA or dAbpy as the ligand. $[BA]_0:[EBiB]_0:[CuBr/L]_0 = 200:1:1$; 15% BMA; 90 °C; 2% Brij 98 (BPMODA), 2% Tween 20 (dAbpy).

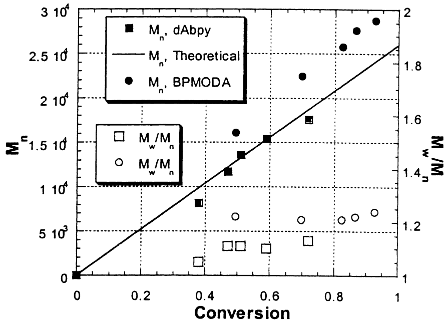


Figure 11. Molecular weight comparison for the polymerization of BA using BPMODA or dAbpy as the ligand.

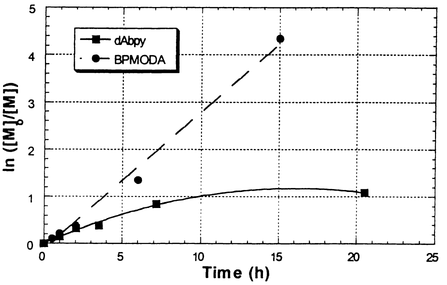


Figure 12. Comparison of the kinetics of the polymerization of Sty using BPMODA or dAbpy as the ligand. $[Sty]_0:[EBiB]_0:[CuBr/L]_0 = 100:1:1$; 90 °C; 15% BMA;, 3% (dAbpy), 4% (BPMODA) Tween 20.

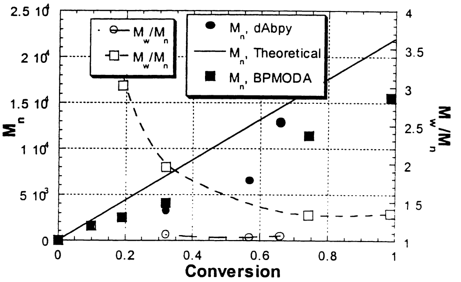


Figure 13. Molecular weight comparison for the polymerization of Sty using BPMODA or dAbpy as the ligand.

Partitioning of the Catalyst

One key question to be resolved is: How much deactivator is in the organic phases? As copper (II) salts are generally more soluble in water, and less soluble in organic solvents, one would expect that there may be partitioning, i.e., loss of some of the deactivator from the growing polymer particles. To investigate this, mixtures of water (30 ml), monomer (4.5 ml), $Cu(II)Br_2/2dAbpy$ (25 mM in monomer) were prepared at room temperature, stirred, separated and the organic layer examined by UV spectroscopy. What was found was that in the case of styrene, 92% of the original Cu(II) salt remained in the organic layer, while for BMA, only 56% remained. Although it was found that the amount of partioning changes with the initial amount of Cu(II) addd and temperature, these results would support the observation that the polymerization of BMA was fast, while the polymerization of Sty was very slow. Since the rate of polymerization by ATRP has been shown to have a negative order in deactivator (Cu(II)X),14) reduction of the effective concentration of the deactivator will result in faster rates of polymerization. Such increases in rate by removal of the deactivator has been demonstrated both for ATRP15) and nitroxide16) based controlled radical polymerizations.

The enhanced rate with the use of BPMODA may be the result of a higher partitioning of the deactivator, Cu(II)Br/L, into water for the BPMODA catalyst relative to the alkylated bipyridine. Such behavior would also explain the higher than theoretical molecular weights and higher polydispersities that are observed with the BPMODA ligands. This partitioning may be too much for BMA and control is lost. For BA the loss of Cu(II) may not be too detrimental, while for styrene it is significant as the polydispersities are relatively high, M_w/M_n ~1.4.

These results show that it is possible to adjust the rate and control of the polymerization not just by conventional methods (changing redox potential of the catalyst, addition of more/less catalyst, increase in monomer concentration, etc.) but also by making fine adjustments in the catalyst solubility. This may prove beneficial, but may also require that for each monomer the catalyst be fine tuned to obtain optimum results.

The Initiator

Conventional ATRP Initiators

As discussed above, the stability of the halogen group in the initiator played a key role in obtaining a controlled polymerization. With the use of ethyl 2-bromoisobutyrate, the polymerizations were successful, but the question of where does initiation take place still remains? In the aqueous or monomer phases? The answers to such questions will have profound influence on the kinetics, stability and formation of polymer particles in the water-borne ATRP. Simply put, the question is whether the ATRP reaction is a “true” emulsion or more like a mini-emulsion.

Although the EBiB is poorly soluble in water, with the small amounts used in the ATRP polymerization (~10 μL in 10 – 20 mL of water), some, or all, may be soluble in the aqueous phase. To elucidate the effect of the solubility of the initiator, a water soluble initiator, 2-hydroxyethyl 2-bromoisobutyrate was used for the polymerization. Although a controlled polymerization was obtained, the latex became severely coagulated during the polymerization. The reason for the instability of the latex is not clear and is being investigated.

The order of addition of the initiator also played a role in obtaining stable latexes as well. When the initiator was added last, or when mixed first with water/surfactant then monomer and catalyst added, stable latexes and controlled polymerizations were obtained. However, coagulation of the polymer was observed when the initiator was mixed with the monomer then added to water/surfactant. The reason for this instability is the subject of further study.

Reverse ATRP Initiators

Reverse ATRP describes the use of conventional radical initiators in the presence of the deactivator transition metal catalyst. For example, AIBN has been used in conjunction with $Cu(II)Br_2$/dNbpy for the controlled polymerization of vinyl monomers.17) Decomposition of the initiator forms radicals which can add monomer, but are rapidly deactivated to form an alkyl halide and the lower oxidation state transition metal halide; once the initiator and deactivator are sufficiently consumed, the ATRP process becomes dominant.

AMPA (V-50)

Potassium Persulfate (KPS)

Figure 14. Conventional radical initiators used in water-borne, reverse ATRP.

The first initiator employed was the azo compound, AMPA, Figure 14. The ratio of AMPA:$Cu(II)Br_2$ was varied to account for the imperfect initiator efficiency expected from conventional radical initiators. As can be seen, the rate decreased with increasing [Cu(II)] (Figure 15), although molecular weight was not greatly affected (Figure 16); final polydispersities were lowest with a AMPA:Cu(II) of 1:1.5.

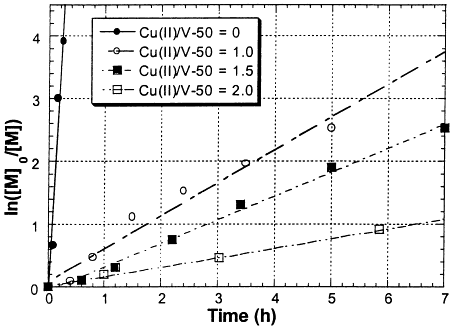


Figure 15. Comparison of the kinetics of the polymerization of BMA by reverse ATRP using AMPA. $[BMA]_o$:$[AMPA]_o$:$[Cu(II)Br_2]_o$ = 400:1:X, 15% BMA, 2% Brij 98, 70 °C.

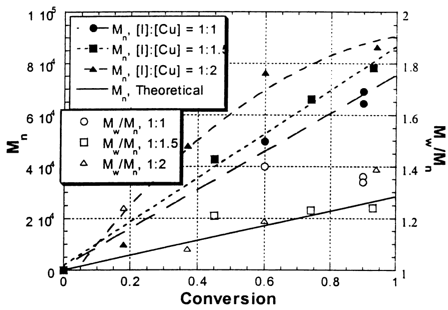


Figure 16. Molecular weight comparison for the reverse ATRP of BMA using AMPA.

When the conventional initiator, potassium persulfate, Figure 14, was used, no polymerization was observed even after 20 hours. This was overcome with the use of a phosphate buffer solution (KH_2PO_4/NaOH, pH=7); the addition of $NaHCO_3$ (6.8 mM) afforded polymer, but with high molecular weight (M_n > 100,000). Similar to the AMPA initiator, the ratio of KPS to $Cu(II)Br_2$ was varied, with the best molecular weight control obtained with a 1:2 ratio of Cu(II) to KPS but the reaction was slow, Figures 17 and 18.

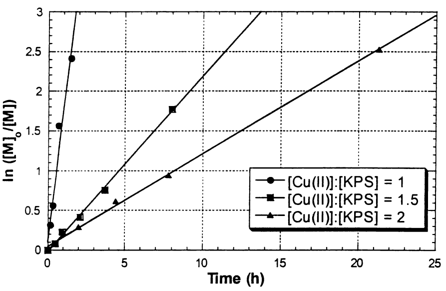


Figure 17. Comparison of the kinetics of the polymerization of BMA by reverse ATRP using KPS. $[BMA]_o$:$[KPS]_o$:$[Cu(II)Br_2]_o$ = 400:1:X, 15% BMA, 2% Brij 98, 70 °C.

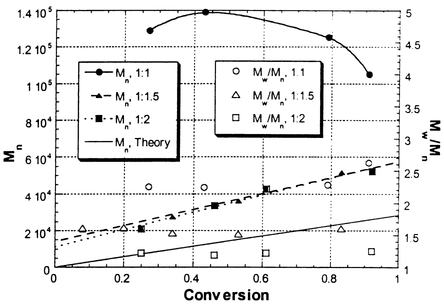


Figure 18. Molecular weight comparison for the reverse ATRP of BMA using AMPA.

Particle Size

The particle size of the resulting latexes prepared by either conventional ATRP or reverse ATRP were examined, Figure 19. As can be seen, in the normal ATRP polymerization of BMA, the particle size is generally very large, greater than 1 micron. In contrast, the particle sizes obtained by reverse ATRP are submicron (~ 250 nm above 30% conversion). Based on these results, one could conclude that for reverse ATRP, a more emulsion-like system was formed, while in conventional ATRP water-borne polymerizations, the system is more suspension-like.

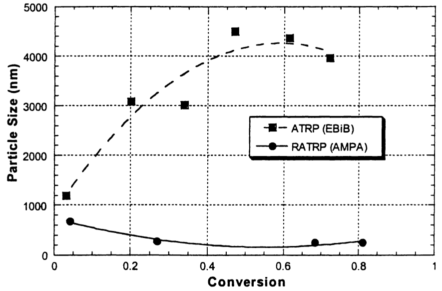


Figure 19. Particle sizes as a function of conversion for conventional and reverse ATRPs of BMA.

Materials

Statistical Copolymers

The simple mixing of two monomers and using this monomer mixture in the conventional ATRP water-borne system was successful for a variety of monomer pairs including BMA/MMA, MMA/BA, Sty/BA, etc. Figure 20 shows the molecular weight behavior for the copolymerization of MMA and BA.

Block Copolymers

The synthesis of block copolymers in heterogeneous systems is more complicated than for bulk or solution systems. This is due to the requirements that there be good cross-over of growing radicals between chain segments and the differences in deactivator concentration when using different monomers. For systems in solution or bulk, the use of a "halogen-switch,"[18] the use of a bromine containing inititator and Cu(I)Cl as the catalyst, is used to insure efficent initiation; the preparation of block copolymers in a completely water-borne system make the use of the halogen switch much more difficult when trying to form the second block.

In the equilibrium established between active and dormant species, some monomers (styrene, methacrylates) generate more deactivator ($Cu(II)Br_2$) than other monomers (acrylates). The presence of higher amounts of deactivation when going from polystyrene/polyMMA to polyacrylates, would result in very slow polymerization of acrylic monomers. Additionally, any termination that may have resulted during the water-borne polymerization would result in incomplete block copolymer formation.

To overcome these limitations, we used a poly(butyl acrylate) macroinitiator prepared in bulk, then isolated and used it in the suspension polymerization of styrene. This proved to be successful resulting in the formation of a butyl acrylate-styrene block copolymer. The SEC traces in Figure 21, show the macroinitiator (M_n = 6,200, M_w/M_n = 1.18) and the resulting block copolymer.

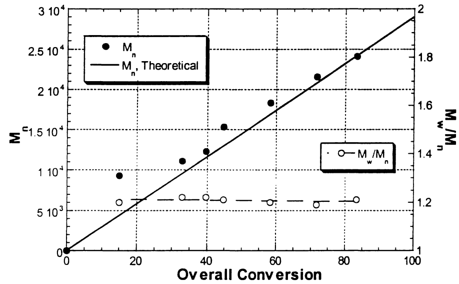


Figure 20. Molecular weight as a function of conversion for the statistical copolymerization of MMA/BA by water-borne ATRP.

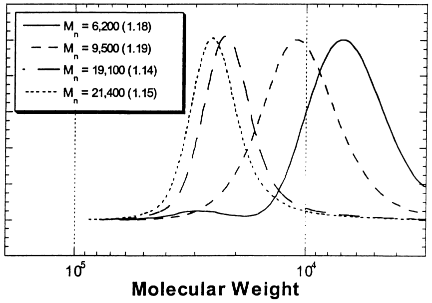


Figure 21. SEC traces for the formation of poly(butyl acrylate-*b*-styrene) by water-borne ATRP.

Conclusion

ATRP has been extended to water-borne systems for a variety of monomers including, styrenes, acrylates, and methacrylates. The systems were able to be conducted with high monomer loadings and to prepare polymers with well-defined properties. Many variables in understanding and obtaining a controlled ATRP polymerization in heterophase systems were described and the steps that were taken to overcome these problems were disscussed. Current work is focusing on understanding the role each component plays in the systems and how the polymer particles are formed during the polymerization, in order to develop better systems for water-borne ATRP. Copolymers (block, statistical) have been prepared and work is currently under way to optimize these systems.

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