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High Molecular Weight Poly(butyl methacrylate) via ATRP Miniemulsions

*Ryan W. Simms, Michael F. Cunningham**

Summary: The reverse atom transfer radical polymerization of butyl methacrylate in miniemulsion, initiated with the redox pair hydrogen peroxide/ascorbic acid and mediated with copper(II) bromide tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine is capable of producing well-controlled high-molecular weight poly(butyl methacrylate).

Keywords: atom transfer radical polymerization (ATRP); high molecular weight; miniemulsion

Introduction

Atom transfer radical polymerization (ATRP) provides exceptional control of radical polymerizations allowing for the facile syntheses of polymers with predetermined microstructure and narrow molecular weight distributions. Control of the polymerization is achieved by the reversible termination mechanism shown in Figure 1, where the position of the equilibrium influences both the degree of control and rate of the polymerization.[1] The active radicals can propagate, be reversibly deactivated by the high oxidation state metal complex, terminate by combination/disproportionation, or transfer to monomer, polymer, or solvent. The termination and transfer reactions form irreversibly terminated (dead) polymer chains which decreases the livingness of the polymerization. The rate of these side reactions limits the lifetime of the propagating radicals and, consequently, the molecular weight of the polymer. For linear polymers produced by ATRP, good control of the polymerization can be maintained for number-average molecular weights (M_n) up to ~200 000 g/mol, after which the accumulation of dead polymer chains decreases the livingness of the system.

The adaptation of ATRP to aqueous based systems has been facilitated by the miniemulsion technique, which produce colloidally robust latexes and alleviate the issues of transporting the metal complex to the site of the polymerization (a concern in emulsion based systems).[2] Reverse ATRP[3] is a common technique used in miniemulsion ATRP because it employs the metal complex in its higher oxidation state (which does not degrade during the formation of the miniemulsion) and uses a conventional free radical initiator (employing a water-soluble initiator allows for the uniform distribution the initiator throughout the latex). Initiators that thermally decompose generate radicals over a period of time leading to long induction periods (where no polymerization occurs), and polymers with a broad polydispersity index (PDI) because the chains are not created at the same time. We investigated the use of the redox pair hydrogen peroxide (HPO)/ascorbic acid (AA) as an initiator that would create all the polymer chains almost instantaneously. This technique was expected to eliminate the induction period, as well as reduce the polydispersity of the final polymer. Unexpectedly, initiation with HPO/AA produced well-controlled high-molecular weight polymers; the preliminary results are presented here.

Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada, K7L 3N6
E-mail: michael.cunningham@chee.queensu.ca

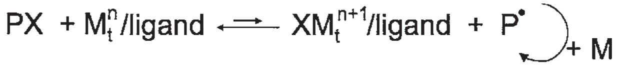

Figure 1.
Mechanism of Control for ATRP.

Experimental Part

The organic phase was prepared by adding copper(II) bromide ($CuBr_2$, 0.153 g, 6.85×10^{-4} mol), tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine (EHA_6TREN, 0.901 g, 7.20×10^{-4} mol), hexadecane (HD, 1.48 g, 3.8 wt% vs. monomer) and butyl methacrylate (BMA, 39 g, 0.274 mol, 15 wt% vs. deionized water) to a beaker and stirring overnight at room temperature to form a homogeneous solution. The aqueous phase that consisted of the surfactant Brij 98 (3.9 g, 10 wt% vs. monomer) and deionized water (DIW, 221 g) was stirred overnight at room temperature. The organic phase was added to the surfactant solution and stirred for approximately 30 min prior to passing through a Microfluidizer 110S (Microfluidics International Corporation) operating at an inlet pressure of 275 kPa. The miniemulsion (200 g) was transferred to a 500 mL round-bottom flask fitted with a condenser and was purged with ultra-high-purity nitrogen for 30 min before being immersed in a 60 °C oil bath with the magnetic stirring speed set to 250 rpm. Fifteen minutes elapsed before the addition of the initiator. The AA (0.0227 g, 1.29×10^{-4} mol) and HPO (0.02916 g, 2.57×10^{-4} mol) were added to separate schlenk tubes, mixed with 2 mL of deionized water, and purged with ultra-high-purity nitrogen for 20 min prior to injection. Using a deoxygenated syringe, the HPO was added prior to the AA, which was added dropwise over 5 minutes. Samples were withdrawn with a deoxygenated syringe and placed in an ice bath.

Results and Discussion

The reverse ATRP of BMA was carried out in miniemulsion with the redox pair HPO/AA as the initiator and the mediating complex $CuBr_2EHA_6TREN$. With a ratio $[BMA]_0$:$[CuBr_2EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0$ of 400:1:1:1 the polymerization was uncontrolled ($M_n = 424\,000$ g/mol, PDI = 2.3), attaining complete conversion in less than 30 minutes. A lack of control would be expected if the number of radicals generated by the redox pair HPO/AA exceeded the amount that could be effectively controlled by the $CuBr_2EHA_6TREN$ in the system. To test this, the amount of initiator was reduced, $[BMA]_0$:$[CuBr_2EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0 = 400$:1:0.5:0.5, which still led to an uncontrolled polymerization, but a further reduction in the amount of HPO/AA ($[BMA]_0$:$[CuBr_2EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0 = 400$:1:0.25:0.25) produced a system with high molecular weight polymer that was well-controlled (Figure 2, exp 1).

While the polymerization was well controlled, it was also slow, requiring 6 hours to achieve 30% conversion. We found that by varying the $[HPO]_0$:$[AA]_0$ ratio the number of propagating polymer chains could be increased, while maintaining good control of the polymerization. In exp 2 a $[HPO]_0$:$[AA]_0$ ratio of 0.5:0.25 resulted in an approximately 4 fold increase in the number of polymer chains in the system, illustrated here by the molecular weight versus conversion profile in Figure 2. The linear increase in M_n with conversion and a PDI that remained below 1.4 confirms that the polymerization was controlled. In exp 3 the $[HPO]_0$:$[AA]_0$ ratio was further increased to 1:0.25, which approximately doubled the number of propagating polymer chains in the system, and control over the polymerization was still maintianed.

The molecular weight versus conversion data illustrates the unusual behavior of this system. The number of polymer chains in the system can be varied over a wide range

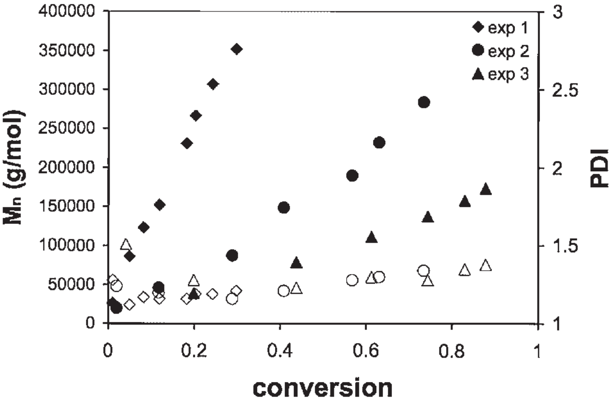

Figure 2.
Evolution of M_n (filled symbols) and PDI (open symbols) with conversion for the HPO/AA initiated miniemulsion ATRP of BMA; exp 1 $[BMA]_0$:$[CuBr_2EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0 = 400$:1:0.25:0.25; exp 2 $[BMA]_0$:$[CuBr_2EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0 = 400$:1:0.5:0.25; exp 3 $[BMA]_0$:$[CuBr_2EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0 = 400$:1:1:0.25.

while maintianing a constant $CuBr_2EHA_6TREN$ loading (Figure 2). Typically this is not possible in reverse ATRP systems because the amount of $CuBr_2EHA_6TREN$ present during the course of the polymerization is determined by the number of polymer chains (primary radicals). With the conditions in exp 1 leading to a controlled polymerization it would be expected that in exp 3 (with 4 times the number of polymer chains) there would be insufficient $CuBr_2EHA_6TREN$ to control the polymerization. A comparison of the conversion versus time profiles in Figure 3 further illustrates the complexity of the system.

The conversion versus time plots shown in Figure 3 show only a brief induction period of approximately 20 minutes (compared to a 100 minute induction period when using initiators that thermally decompose), attributed to the time required for the radicals to be generated by the reaction of HPO with AA. Figure 3 illustrates the increase in the rate of the polymerization in

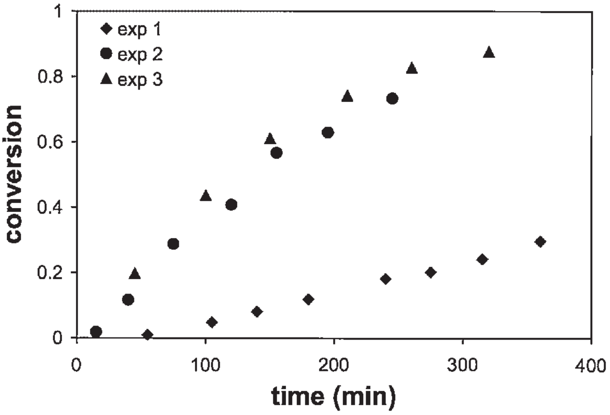

Figure 3.
Conversion versus time profile for the HPO/AA initiated miniemulsion ATRP of BMA. exp 1 $[BMA]_0$:$[CuBr_2EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0 = 400$:1:0.25:0.25; exp 2 $[BMA]_0$:$[CuBr_2EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0 = 400$:1:0.5:0.25; exp 3 $[BMA]_0$: $[CuBr_2EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0 = 400$:1:1:0.25.

experiment 2 ($[HPO]_0$:$[AA]_0 = 0.5:0.25$) relative to experiment 1 ($[HPO]_0$:$[AA]_0 = 0.25:0.25$). This is the expected result for a reverse ATRP system when the number of propagating chains are increased and the amount of $CuBr_2EHA_6TREN$ is held constant. It is attributed not only to the increase in the number of polymer chains, but also the subsequent increase in the amount of copper(I) complex relative to the copper(II) complex.[4] The expected trend is not present when comparing experiments 2 and 3 that have very similar conversion versus time profiles in spite of the difference in the number of polymer chains in the system.

The use of the HPO/AA redox pair to initiate an ATRP system, which controls the polymerization through a reversible redox process leads to a complicated system. It is hypothesized that the HPO/AA redox pair not only generate primary radicals that form polymer chains but also react with the copper species in the system. Reactions between copper(II) complexes and reducing agents, such as AA, have been used to initiate ATRP polymerizations,[5] as well, the decomposition of peroxides by copper(I) has been used to initiate ATRP.[6] The exact redox reactions occurring in this system are currently not known, but the HPO/AA pair appears to yield an advantageous ratio of copper(I) species to copper(II) species that allows for the controlled polymerization of high molecular weight polymers.

Conclusion

The miniemulsion reverse ATRP using $CuBr_2EHA_6TREN$ as the mediating complex and HPO/AA as the initiator has been carried out for BMA. The use of the HPO/AA redox pair as an initiator enables the formation of well-controlled high molecular weight polymers. A definitive explanation for this ability is unknown, but the preliminary data suggests that the copper complexes are reacting with HPO and/or AA to provide an advantageous ratio of the copper(I) complex to the copper(II) complex.

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