High Molecular Weight Poly(methacrylic acid) with Narrow Polydispersity by RAFT Polymerization

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ABSTRACT: Poly(methacrylic acid) is an adaptable macromolecule that offers many benefits in the development of new materials for a host of applications. Herein we report the reversible addition−fragmentation chain transfer (RAFT) polymerization of methacrylic acid (MAA) under a range of synthesis conditions by adjusting the ratio of reactants and the type of solvent employed. The RAFT system was composed of 4,4-azobis(cyanopentanoic acid) and 4-cyanopentanoic acid dithiobenzoate as the radical initiator (I) and chain transfer agent (CTA), respectively. This system was previously applied to synthesize MAA oligomers, but high molecular weight MAA homopolymers, to our knowledge, have yet to be reported. Three distinct $[MAA]_0$:$[I]_0$:$[CTA]_0$ ratios (150:0.25:1, 250:0.25:1, and 150:0.1:1), in addition to two solvents (methanol and water/1,4-dioxane), initial monomer concentration and pH were evaluated and contrasted. It was determined that the polymerization evolved in a controlled fashion particularly in methanol. In addition, by adjusting the reactant ratios, we were able to obtain MAA homopolymers with molecular weights up to 113 900 with narrow polydispersities (∼1.13) using methanol as the solvent of choice.

Introduction

Poly(methacrylic acid) (pMAA) is a versatile polymer that can be employed in many processes. One of the most attractive characteristics of this amphiphilic macromolecule is its unique responsiveness to pH and ionic strength. These properties can be applied to many applications, including particle and micelle formation[1,2] and hydrogel fabrication.[3]

One of the major challenges in polymer synthesis is the control of molecular weight with narrow polydispersity indices (PDI), defined as the ratio of the weight-average molecular weight (M_w) to the number-average molecular weight (M_n). Several techniques have been employed to synthesize MAA homopolymers and MAA-containing block copolymers, including free radical polymerization (FRP)[4] and atom transfer radical polymerization (ATRP).[5] FRP tends to produce uncontrolled polymerizations giving rise to high PDI values. In the case of ATRP, direct polymerization of the acidic form is challenging,[6] and thus the salt form or other derivatives, such as sodium methacrylate[7] and *n*-butyl methacrylate,[8] are typically used.

Reversible addition−fragmentation chain transfer (RAFT) polymerization, developed by Rizzardo and collaborators,[9] has risen to become a resourceful technique that can potentially address the limitations that other radical polymerizations encounter in MAA polymerizations. RAFT is a controlled/living free-radical polymerization method that uses both a radical initiator (I) and a chain transfer agent (CTA). RAFT possesses many synthetic advantages, including applicability to a wide range of monomers, flexibility of reaction conditions (including water as the solvent), and the ability to produce complex architectures.[10] The selection of the monomer−initiator pair and the polymerization conditions are critical factors that directly influence the outcome.[11,12] RAFT polymerization of MAA has been previously shown for block copolymers, such as poly(MAA-*block*-methyl methacrylate)[10,13] and poly(MAA-*block*-benzyl methacrylate).[10] Additionally, RAFT homopolymerization of MAA has been reported by Yang et al.[14] They performed the synthesis and characterization, as well as a kinetics analysis, of methacrylic acid and *N*-(isopropylacrylamide) homopolymers and poly(*N*-isopropylacrylamide)-*block*-poly(methacrylic acid) block copolymers using the commercially available CTA, carboxylmethyl dithiobenzoate. For MAA homopolymers, they reported a kinetic analysis based on a single set of reaction conditions (methanol, $T = 60$ °C, $[MAA]_0 = 1.90$ mol L^{-1} and $[MAA]_0:[I]_0:[CTA]_0 = 100:0.25:1$) that generated MAA homopolymers with M_n up to 13 300 and PDI = 1.3. However, carboxylmethyl dithiobenzoate degraded during the polymerization, which limits the polymerization control affecting particularly the PDI. On the basis of their initial report, we sought to identify a synthetic method to create relatively high-M_n MAA homopolymers with narrow PDI.

Herein we report the synthesis and characterization of relatively high M_n with narrow PDI pMAA by RAFT polymerization using 4-cyanopentanoic acid dithiobenzoate[15] (CPA-DB) as the CTA under a range of synthesis conditions. The system employs 4,4′-azobis(4-cyanopentanoic acid) (A-CPA) as a radical initiator, which in conjunction with CPA-DB, is an efficient RAFT initiator pair for several polymers including methacrylates[9,16] and methacrylamides.[17,18] Recently, the group of Guillaneuf[19] reported the RAFT synthesis of MAA oligomers and oligo(MAA)-*b*-poly(methyl methacrylate) in the presence of CPA-DB as a chain transfer agent. However, their analysis covered low-M_n polymers with degree of polymerization of ∼10. In our analysis, we evaluated the effect of $[MAA]_0$:$[CTA]_0$ and$[CTA]_0$:$[I]_0$ ratios as well as two different solvents, methanol and water/1,4-dioxane, initial monomer concentration, and pH on MAA homopolymerization in order to obtain well-controlled polymerization that achieves relatively high-M_n pMAA with narrow PDI. We report the relationship of M_n with conversion as well as a kinetic analysis of the polymerization under these conditions. In addition, we highlight the conditions that achieve a range of M_n with narrow PDI of MAA homopolymers up to a M_n of 113 900 with PDI ∼ 1.13.

Materials and Methods

Materials. Methacrylic acid (99%), 4,4′-azobis(4-cyanopentanoic acid) (98.0%, Fluka), and 1,4-dioxane, anhydrous (99.8%), were

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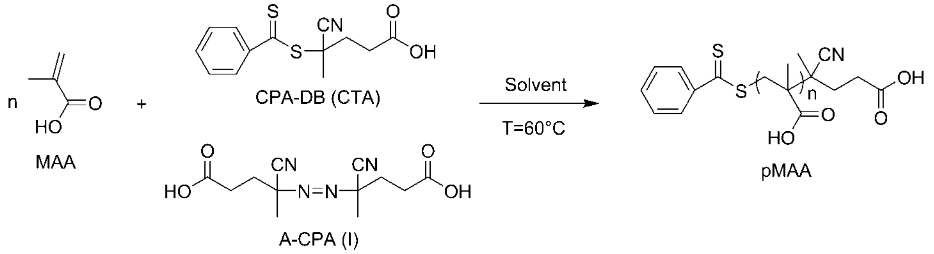

Figure 1. Synthesis schematic of poly(methacrylic acid) by RAFT polymerization.

purchased from Sigma-Aldrich and used as received. Poly(methacrylic acid), sodium salt standards were purchased from Polysciences, Inc. (Warrington, PA), and Polymer Standard Services (Mainz, Germany). Elemental analysis was performed by Quantitative Technologies Inc. (Whitehouse, NJ). Melting points were obtained using a Fisher-Johns melting point apparatus. 4-Cyanopentanoic acid dithiobenzoate (CPA-DB) was synthesized as previously described by Mitsukami et al.[20] Characterization: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.95 (s, 3H), δ 2.40−2.78 (m, 4H), δ 7.40 (m, 2H), δ 7.58 (t, 1H), δ 7.91 (d, 2H). Elemental analysis: Calcd ($C_{13}H_{13}NO_2S_2$): C, 55.89%; H, 4.69%; N, 5.01%. Found: C, 56.15%; H 4.72%; N 4.86%. Melting point: 97.0 °C. Unless otherwise stated, all other chemicals were purchased from Fisher Scientific at the highest purity available.

Characterization of pMAA. M_n and PDI for pMAA were obtained using a Waters gel permeation chromatography (GPC) system equipped with two Ultrahydrogel columns (Waters) in series (500 and 250 Å), a 1515 isocratic HPLC pump, and a 2414 refractive index detector. Temperature throughout the system was controlled at 30 °C. The mobile phase employed was phosphate buffer saline (pH = 7.4) at a rate of 0.8 mL min^{-1} calibrated with six individual poly(methacrylic acid), sodium salt standards with peak molecular weights ranging from 1670 to 110 000 Da and PDI from 1.02 to 1.11. ^{1}H NMR was performed using a Mercury 300 MHz spectrometer with deuterium oxide (D_2O) as the solvent and 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt (DSS) as an internal reference. Resonances were referenced to DSS at 0 ppm and HOD at 4.81 ppm.

MAA RAFT Polymerization. Prior to every experiment, all liquid reagents were purged under argon for at least 10 min. Individual stock solutions of the radical initiator (A-CPA) and CTA (CPA-DB) were prepared with the respective solvent to ensure accurate reactant ratios for a set of reactions at a given condition. A representative example for MAA polymerization in methanol is as follows: in a 1 mL glass ampule equipped with a magnetic stir bar, MAA (0.170 mL, 2 mmol) and CPA-DB (3.72 mg, 13.3 mmol; in 0.5 mL of MeOH) were transferred using a fixed volume pipettor. After 5 min of purging under argon, A-CPA (0.93 mg, 3.3 mmol; in 0.170 mL of MeOH) was added to the ampule using a 250 μL Hamilton syringe. The solution was purged under argon for an additional 2 min. The ampule was flame-sealed and inserted in a 60 °C oil bath under continuous stirring. The reaction was stopped at 24 h by inserting the ampule in an ice bath and exposing the solution to air. The polymer was recovered by precipitation in a generous amount of stirring diethyl ether (~50 mL), filtered, and dried under vacuum overnight. M_n and PDI calculated by GPC for this particular sample were 12 900 Da and 1.19, respectively, and the percent conversion estimated by gravimetric analysis was 91%. ^{1}H NMR (D_2O, ppm): δ 1.07 (br s, 3H), δ 1.98 (br s, 2H).

For the water/1,4-dioxane solvent (4:1 v/v) system, a water/HCl stock solution (pH = 4) was prepared. A representative example for MAA polymerization in water/1,4-dioxane is as follows: to a 1 mL glass ampule with a magnetic stir bar containing MAA (0.170 mL, 2 mmol), water/HCl (0.536 mL) at pH = 4 and CPA-DB (3.72 mg, 13.3 mmol; in 0.074 mL of 1,4-dioxane) were transferred using a fixed volume pipettor. The solution was purged with argon for 5 min followed by the addition of A-CPA (0.93 mg, 3.3 mmol; in 0.060 mL of 1,4-dioxane) with a 250 μL Hamilton syringe. The ultimate pH of the solution was 2.8. Following the addition of all reactants, the ampule was purged under argon for an additional 2 min, flame-sealed and inserted in a 60 °C oil bath for 4 h under continuous stirring. The product was purified with dialysis using Spectra/Por regenerated cellulose dialysis tubing (3.5 kDa MWCO) against deionized water for 3 days and lyophilized for 24 h. For the case of small molecular mass polymers (M_n < 7000 Da), purification was performed using Spectra/Por regenerated cellulose dialysis tubing (1 kDa MWCO). M_n and PDI calculated by GPC for this particular sample were 24 100 Da and 1.18, respectively, and the percent conversion estimated by gravimetric analysis was 90%.

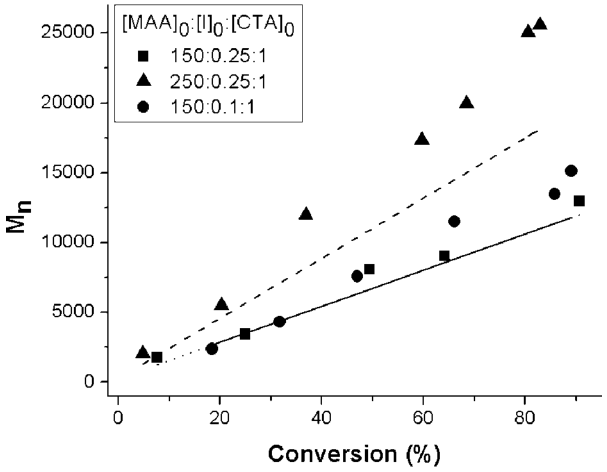

Figure 2. Relationship of M_n(GPC) and M_n(theory) with monomer conversion of MAA RAFT polymerization using A-CPA as the radical initiator and CPA-DB as the chain transfer agent. Three initial reactant ratios ($[MAA]_0$:$[I]_0$:$[CTA]_0$) were selected: 150:0.25:1 (■), 250:0.25:1 (▲), and 150:0.1:1 (●). The polymerization was conducted in methanol at 60 °C with $[MAA]_0$ = 2.4 mol L^{-1}. M_n(theory) was calculated using eq 1 for the three $[MAA]_0$:$[I]_0$:$[CTA]_0$: 150:0.25:1 (•••), 250:0.25:1 (---), and 150:0.1:1 (—). Data points were generated from an average of two repetitions that had an error of less than 18%.

Results and Discussion

Effect of $[MAA]_0$:$[I]_0$:$[CTA]_0$ Ratios on MAA Polymerization. PMAA was synthesized via RAFT polymerization using A-CPA as the radical initiator and CPA-DB as the chain transfer agent (Figure 1). Two different $[MAA]_0$:$[CTA]_0$ ratios (150:1 and 250:1) as well as two $[I]_0$:$[CTA]_0$ ratios (0.25:1 and 0.1:1) were evaluated and compared. The selection of reactant ratios is of vital importance for the polymerization control and directly impacts the final molecular weight.

Figure 2 shows the relationship of M_n with conversion for pMAA under the selected reactant ratios in methanol at 60 °C. Experimental M_n as determined by GPC were compared with theoretical M_n calculated using eq 1,[21] where $[m]_0$ and $[RAFT]_0$ are the initial monomer and CTA concentrations, respectively, x is the fractional monomer conversion, M_0 is the molar mass of the monomer, and M_{RAFT} is the molar mass of the CTA.

$$\bar{M}_{\mathrm{n,th}} = \frac{[\mathrm{m}]_0 M_0 x}{[\mathrm{RAFT}]_0} + M_{\mathrm{RAFT}} \qquad (1)$$

For all three conditions, M_n linearly increases with conversion, characteristic of controlled/living polymerizations. The higher $[\mathrm{MAA}]_0$:$[\mathrm{CTA}]_0$ ratio yields higher M_n due to more free monomer available relative to the CTA initially present. Maintaining $[\mathrm{MAA}]_0$:$[\mathrm{CTA}]_0$ constant and lowering the $[\mathrm{I}]_0$:$[\mathrm{CTA}]_0$ ratio (from 0.25:1 to 0.1:1) has a small increasing effect on the M_n throughout the reaction. This behavior has also been distinguished in methacrylamide-based homopolymers employing the same CTA/I RAFT system.[17]

It is usually desired to minimize the radical initiator species concentration (particularly $[\mathrm{I}]_0 \ll [\mathrm{CTA}]_0$) to favor polymer chain growth exclusively from the CTA species, which can give greater polymerization control and generate lower PDI.[11] However, reducing the radical initiator concentration 2.5-fold did not have a significant impact on the PDI, which only at high conversions (>88%) were under 1.20. At low conversion, PDI has relatively high values, and it gradually decreases as M_n increases (Figure 3). In particular, for $[\mathrm{MAA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CTA}]_0$ = 150:0.25:1 in methanol, PDI decreased from 1.52 at 8% conversion to 1.19 at 91% conversion. Similar continuously decreasing behavior was observed for all other conditions analyzed. For $[\mathrm{MAA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CTA}]_0$ = 250:0.25:1, a PDI of 1.17 was achieved at 80% conversion, and for $[\mathrm{MAA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CTA}]_0$ = 150:0.1:1, a PDI of 1.20 was achieved at 88% conversion. It is important to note that changes in the solution color were not observed even at high times, suggesting that the CTA remained undegraded throughout the reaction.

Experimental M_n for the lower reactant ratios ($[\mathrm{MAA}]_0$:$[\mathrm{CTA}]_0$ = 150:1) were very consistent with theoretical M_n calculated based on actual monomer conversion data demonstrating a controlled polymerization behavior. Higher reactant ratios ($[\mathrm{MAA}]_0$:$[\mathrm{CTA}]_0$ = 250:1) experienced slightly higher experimental M_n than theoretical M_n (~1.3 times higher) relative to lower reactant ratios. Still, high reactant ratios maintained good agreement with theoretical values. For the current system, the effectiveness of the chosen chain transfer agent with a good free-radical leaving group was demonstrated by the controlled polymerizations achieved that generated polymers with narrow PDI and M_n consistent with theoretical values.

Effect of Solvent Selection on MAA Polymerization. Solvent selection has a dramatic effect on the M_n profiles as well as on the polymerization kinetics. A variety of solvents, including different organics (i.e., benzene, dimethylformamide, ethyl acetate, and methanol) in addition to water-based solvent systems, have been employed in many RAFT polymerization.[10,12,14,22] The potential applicability of water-based solvents to RAFT polymerizations offers many advantages mainly due to their stability, low cost, and ease of use. In particular, pMAA has higher solubility in alcohols and water than in most organics, and its previous synthesis was performed in methanol.[14] Therefore, we investigated the effect of solvent on the polymerization progression by comparing an alcohol (methanol) with an aqueous system (water/1,4-dioxane) while maintaining all other parameters constant (i.e., temperature, concentration and reactant ratios). Because CPA-DB is not readily soluble in water at room temperature, the addition of a water-miscible organic solvent, in this case 1,4-dioxane, was used to further enhance solubility. The cosolvent issue could have been avoided by selecting a CTA with higher water solubility (i.e., trithiocarbonate), a subject of ongoing studies.

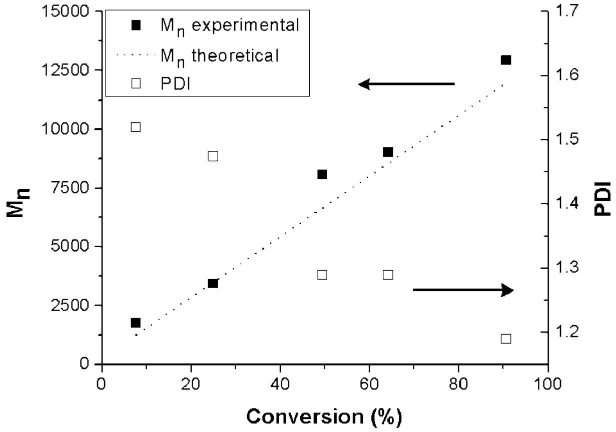

Figure 3. Relationship of M_n(GPC) (■), M_n(theory) (•••), and PDI (□) with conversion of MAA RAFT polymerization using A-CPA as the radical initiator and CPA-DB as the chain transfer agent. M_n(theory) was calculated using eq 1. The polymerization was conducted at $[\mathrm{MAA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CTA}]_0$ = 150:0.25:1 in methanol at 60 °C with $[\mathrm{MAA}]_0$ = 2.4 mol L^{-1}. Data points were generated from an average of two repetitions that had an error of less than 13%.

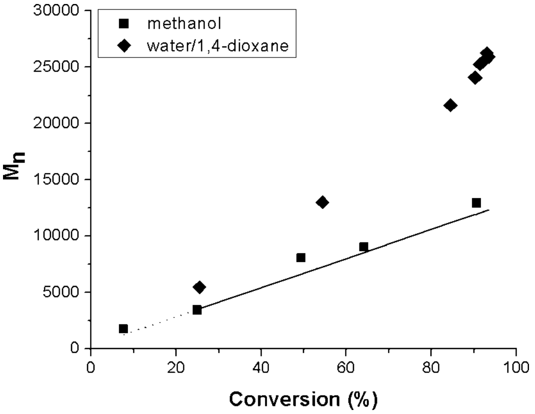

Figure 4. Relationship of M_n(GPC) and M_n(theory) with monomer conversion of MAA RAFT polymerization using A-CPA as the radical initiator and CPA-DB as the chain transfer agent in two different solvent: methanol (■) and water/1,4-dioxane (4:1 v/v) (◆). Solid line (—) represents M_n(theory) of MAA RAFT polymerization in water/1,4-dioxane, and dotted line (•••) represents M_n(theory) of MAA RAFT polymerization in methanol, both calculated using eq 1. The polymerizations were conducted at $[\mathrm{MAA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CTA}]_0$ = 150:0.25:1 at 60 °C with $[\mathrm{MAA}]_0$ = 2.4 mol L^{-1}. Data points were generated from an average of two repetitions that had an error of less than 16%.

As seen in Figure 4 for the water/1,4-dioxane solvent system, M_n increases linearly with conversion obtaining much higher values (~2 times higher) than both the theoretical M_n calculated using eq 1 and the methanol system under the same reaction conditions. A remarkable increase in viscosity after 4 h (90% conversion) which increased until 30 h (93% conversion) in addition to a change in color after 30 h was observed. Interestingly, like methanol, the water-based solvent system achieved low PDI values at high conversion (PDI < 1.20 at conversions >85%). The apparent rapid increase in M_n could be attributed to many factors such as a faster reaction rate due to higher propagation rate coefficient in this particular solvent system. However, the deviation from theoretical M_n and change in solution color indicates poorer stability of the reactants in aqueous solutions than in methanol, suggesting that the latter is a better solvent choice to achieve greater polymerization control.

One of the undesirable effects associated with water-based systems is the potential hydrolysis of the dithioester group of the CTA, which is temperature and pH dependent.[22,23] CTA hydrolysis leads to its inactivation, generating fewer reactive species than originally introduced into the system leading to higher M_n than the initially calculated. Therefore, the pH of the solution was maintained at ~3, since for this particular CTA,

Table 1. Experimental and Theoretical Number-Average Molecular Weights, Polydispersity, and Monomer Conversion Data for Aqueous MAA RAFT Polymerizations Conducted at Different pH[a]

entry	pH	M_n(GPC)[b]	PDI (M_w/M_n)[b]	conversion[c] (%)	M_n(theory)[d]
1	2.8[e]	24100	1.18	90	11900
2	4.8[f]	10700	1.39	54	7300
3	6.7[f]	5000	1.41	25	3500
4	12.8[f]	8600	1.95	12	1800

[a] MAA RAFT polymerizations were conducted in water/1,4-dioxane (4:1 v/v) at 60 °C for 4 h using A-CPA as radical initiator and CPA-DB as chain transfer agent with $[\text{MAA}]_0:[\text{I}]_0:[\text{CTA}]_0 = 150:0.25:1$ and $[\text{MAA}]_0 = 2.4$ mol L^{-1}. Data were generated from an average of two repetitions that had an error of less than 5%. [b] As determined by gel permeation chromatography calibrated with poly(methacrylic acid) standards with PBS (pH = 7.4) as mobile phase. [c] As determined by gravimetric analysis. [d] As determined using eq 1. [e] pH of solution was adjusted by HCl additions. [f] pH of solution was adjusted by NaOH additions.

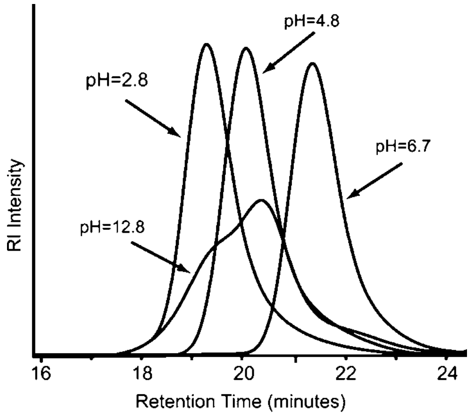

Figure 5. Molecular weight distributions for MAA RAFT polymerizations using A-CPA as the radical initiator and CPA-DB as the chain transfer agent, conducted at 60 °C with $[\text{MAA}]_0:[\text{I}]_0:[\text{CTA}]_0 = 150:0.25:1$ and $[\text{MAA}]_0 = 2.4$ mol L^{-1}. Polymerizations were carried out in water/1,4-dioxane (4:1 v/v) at different pH.

low pH values have shown to reduce the hydrolysis rate of the dithioester group.[23,24]

To further investigate the behavior of MAA RAFT polymerization in water-based solvent, several experiments were performed in different pH solutions. Table 1 shows the data for aqueous MAA RAFT polymerization conducted at different pH ranging from 2.8 to 12.8. At constant reaction time (t = 4 h), the monomer conversion gradually decreases as the solution pH increases. The same behavior applies to M_n with the exception of pH = 12.8, where the bimodal molecular weight distribution shifted M_n to a higher value (Figure 5). PDI progressively increases as the solution becomes more basic, achieving PDI ~ 2 at pH of 12.8. Under this condition (pH 12.8), the loss of polymerization control was clearly observed due to the large disagreement with theoretical M_n, high PDI, pronounced solution decoloration, and formation of a bimodal molecular weight distribution, consistent with findings of Albertin et al.[25] using the same CTA agent in basic pH solutions. This behavior has been attributed to degradation of the CPA-DB due to hydrolytic instability in basic pH solutions.

Kinetic Analysis of MAA Polymerization. MAA homopolymerization is characteristic of pseudo-first-order kinetics that takes place after an initial apparent induction period which is a stage of slow reaction rate dependent on many factors including the monomer/CTA selection. The induction times were estimated to be short (<1.5 h) for all cases. As seen in Figure 6, the polymerization develops linearly with time until nearly complete monomer consumption where the rate of polymerization is minimal and cannot be accurately measured. Increasing $[\text{MAA}]_0:[\text{CTA}]_0$ causes a decrease in the polymerization rate; however, PDI is not affected, and the ultimate M_n obtained is higher. Moreover, reducing the concentration of radical initiator decreases the polymerization rate due to the lack of radical initiator species that could potentially initiate polymer chains. In agreement with Figure 4, the solvent has a dramatic effect on polymerization rate. For the aqueous system the polymerization progresses extremely rapid at very short times and slows after about 6 h, a behavior that might have been affected by the type of solvent and increase in viscosity.

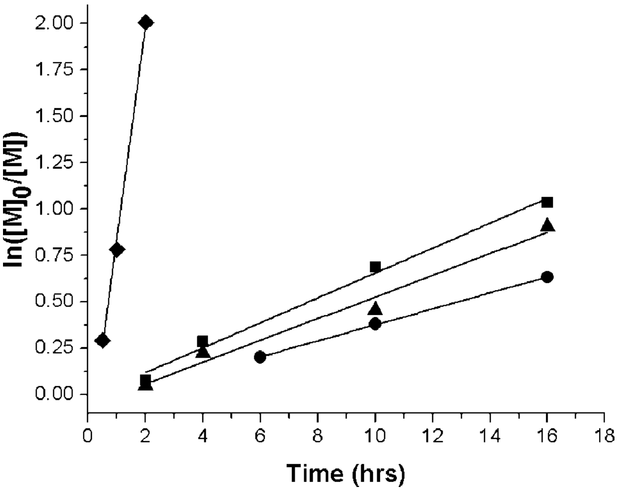

Figure 6. Relationship of $\ln([\text{M}]_0/[\text{M}])$ with time (h) of MAA RAFT polymerization using A-CPA as the radical initiator and CPA-DB as the chain transfer agent at three initial reactant ratios and two different solvents. Ratio (MAA:I:CTA), solvent → ■ 150:0.25:1, methanol; ▲ 250:0.25:1, methanol; ● 150:0.1:1, methanol; ◆ 150:0.25:1, water/dioxane (4:1 v/v). The polymerizations were conducted at 60 °C with $[\text{MAA}]_0 = 2.4$ mol L^{-1}. Solid lines (—) represent linear regressions calculated based on short times only where chain growth is linear with time (16 h for methanol and 2 h for water/1,4-dioxane). R^2 values for linear regressions >0.97 for all cases.

Several factors, including initial monomer concentration and temperature, have been found to directly impact the propagation rate coefficients in free-radical polymerizations of MAA.[26−29] For this reason, we investigated the effect of initial monomer concentration on MAA RAFT polymerizations in both solvents.

Table 2 includes the data for MAA homopolymerizations at three initial MAA concentrations, 1.0, 2.4, and 5.0 mol L^{-1}, in two solvents, methanol and water/1,4-dioxane, at 60 °C. For both systems (aqueous and methanol), it is apparent that at the same reaction time, higher $[\text{MAA}]_0$ yields higher monomer conversion which may indicate that the polymerization becomes faster as $[\text{MAA}]_0$ increases. For the aqueous systems at high monomer conversions, all three conditions demonstrated similar high deviation from theoretical M_n values calculated using eq 1. However, higher $[\text{MAA}]_0$ generated polymers with narrower PDI. For the methanol system, all three conditions achieve narrow PDI at high monomer conversion. Still, higher $[\text{MAA}]_0$ seems to have a greater deviation from theoretical values, suggesting that lower $[\text{MAA}]_0$ in methanol achieves better polymerization control.

Effect of Increasing $[\text{MAA}]_0:[\text{CTA}]_0$ Ratio on Molecular Weight. Table 3 includes experimental M_n determined by GPC, theoretical M_n calculated using eq 1, monomer conversions, and PDI values for the range of investigated $[\text{MAA}]_0:[\text{CTA}]_0$ ratios of RAFT polymerizations performed in methanol at an initial monomer concentration of 2.4 mol L^{-1} and constant reaction time of 48 h. By adjusting the $[\text{MAA}]_0:[\text{CTA}]_0$ ratio, a variety of M_n were obtained ranging from 4600 up to 113 900. In agreement with the controlled behavior of RAFT polymeriza-

Table 2. Experimental and Theoretical Number-Average Molecular Weights, Polydispersity, and Monomer Conversion Data of MAA RAFT Polymerization Conducted at Different Initial MAA Concentration in Two Solvents, Methanol and Water/1,4-Dioxane (4:1 v/v)[a]

entry	solvent	$[MAA]_0$ (mol L^{-1})	time (h)	M_n(GPC)[b]	PDI (M_w/M_n)[b]	conversion[c] (%)	M_n(theory)[d]
1	water/1,4-dioxane	1.0	0.5	4200	1.34	21	3000
2	water/1,4-dioxane	1.0	2	17600	1.38	82	10900
3	water/1,4-dioxane	2.4	0.5	5500	1.36	25	3500
4	water/1,4-dioxane	2.4	2	21600	1.17	84	11100
5	water/1,4-dioxane	5.0	0.5	3400	1.65	31	4300
6	water/1,4-dioxane	5.0	2	22200	1.18	91	12000
7	methanol	1.0	4	2000	1.32	5	900
8	methanol	1.0	24	10800	1.17	60	8000
9	methanol	2.4	4	3400	1.48	25	3500
10	methanol	2.4	24	12900	1.19	91	12000
11	methanol	5.0	4	6900	1.28	40	5400
12	methanol	5.0	24	19600	1.11	89	11800

[a] MAA RAFT polymerizations were conducted in methanol or water/1,4-dioxane (4:1 v/v) at 60 °C using A-CPA as radical initiator and CPA-DB as chain transfer agent with $[MAA]_0:[I]_0:[CTA]_0 = 150:0.25:1$. Data were generated from an average of two repetitions that had an error of less than 17%. [b] As determined by gel permeation chromatography calibrated with poly(methacrylic acid) standards with PBS (pH = 7.4) as mobile phase. [c] As determined by gravimetric analysis. [d] As determined using eq 1.

Table 3. Experimental and Theoretical Number-Average Molecular Weights, Polydispersity, and Monomer Conversion Data of MAA RAFT Polymerization Conducted in Methanol at Different Initial Reactant Ratios ($[MAA]_0:[CTA]_0$)[a]

entry	$[MAA]_0:[CTA]_0$	M_n (GPC)[b]	PDI (M_w/M_n)[b]	conversion[c] (%)	M_n (theory)[d]
1	50	4600	1.36	97	4500
2	100	8100	1.24	96	8500
3	150	16700	1.18	89	11800
4	225	21900	1.15	86	16900
5	375	35600	1.15	88	28700
6	500	42200	1.15	86	37300
7	750	56200	1.15	80	51900
8	1250	82300	1.16	77	83100
9	2500	113900	1.13	49	105700

[a] MAA RAFT polymerizations were conducted in methanol at 60 °C for 48 h using A-CPA as radical initiator and CPA-DB as chain transfer agent with $[MAA]_0:[I]_0:[CTA]_0 = 150:0.25:1$ and $[MAA]_0 = 2.4$ mol L^{-1}. Data were generated from an average of three repetitions that had an error of less than 7%. [b] As determined by gel permeation chromatography calibrated with poly(methacrylic acid) standards with PBS (pH = 7.4) as mobile phase. [c] As determined by gravimetric analysis. [d] As determined using eq 1.

tions, when M_n is normalized with conversion and plotted against $[MAA]_0:[CTA]_0$ ratios, a linear trend (Figure 7) is observed as expected, consistent with theoretical M_n values.

Excluding very low $[MAA]_0:[I]_0:[CTA]_0$ ratios (50:0.25:1 and 100:0.25:1), all PDI obtained by GPC were below 1.20. In particular, high monomer conversion of low $[MAA]_0:[I]_0:[CTA]_0$ ratios (50:0.25:1) corresponds to low conversion of higher ratios (e.g., 150:0.25:1), which had previously shown to have high PDI (Figure 3). For instance, 97% of conversion ($t = 48$ h) for the 50:0.25:1 ratio will have a M_n of 4600 and a PDI of 1.36. At the same M_n of 4600, the 150:0.25:1 ratio will have had reached ~32% conversion (6 h) and have a PDI of 1.40. This is why lower reactant ratios yield higher PDI, suggesting that this particular system requires a minimal $[MAA]_0:[CTA]_0$ ratio to achieve narrow PDI for the synthesized polymers.

Though a specific M_n can be obtained by allowing the polymerization to progress until a specific monomer conversion (or a definite time), varying the $[MAA]_0:[CTA]_0$ ratio and allowing the polymerization to achieve nearly completion seems to be a more effective approach given that it can yield polymers with narrower PDI. In this case, we fixed the reaction time to have a controlled variable. However, higher $[MAA]_0:[CTA]_0$ required longer times to reach completion which is why a normalized M_n was included in the plot for molecular weights vs reactant ratios shown in Figure 7. For high reactant ratios (2500:0.25:1), M_n was as high as 113 900 at only 49% conversion with a narrow PDI of 1.13. Narrow PDIs for low-M_n polymers using this system are difficult to achieve but could be obtained by employing a CTA with much higher transfer constant. Experimental M_n obtained were slightly higher than the theoretical values calculated from conversion data since the theoretical values assume absolute polymerization control and nondegradation of the CTA which, although to a minimal extent, is inevitable even in alcohol systems.

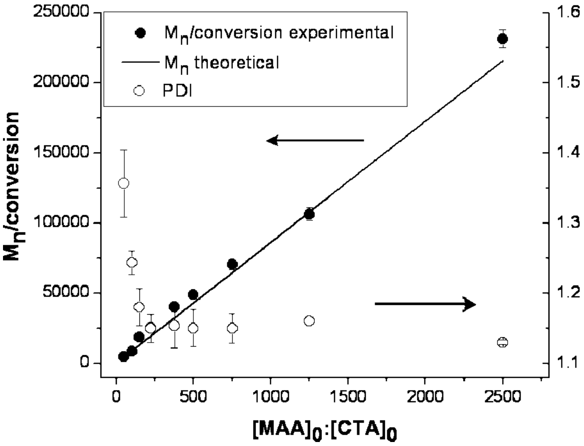

Figure 7. Relationship of M_n/conversion (GPC) (●), M_n(theory) (—), and PDI (○) with initial reactant ratio ($[MAA]_0:[CTA]_0$) of MAA RAFT polymerization using A-CPA as the radical initiator and CPA-DB as the chain transfer agent. The polymerizations were conducted at 60 °C for 48 h. For each reaction, the solvent volumes were adjusted to maintain the MAA concentration at 2.4 mol L^{-1} (0.21 g/mL). Data points were generated from an average of three repetitions that had an error of less than 7%. Error bars represents standard errors.

Conclusions

We employed the RAFT polymerization technique to synthesize pMAA with different M_n up to 113 900 with narrow PDI (~1.13). The selected I/CTA system resulted in an effective method that, for this particular monomer, produced well-controlled polymerizations under certain conditions. Two solvents (methanol and water/1,4-dioxane), initial monomer concentration, and pH were evaluated, and a kinetic analysis was performed with several variations on the reactant ratios ($[MAA]_0:[I]_0:[CTA]_0$). It was determined that methanol is a more suitable solvent for the polymerization due to higher stability of the reactants and good control throughout the polymerization under the conditions analyzed. In contrast, water-based solvent systems had poorer control over the polymerization particularly at basic pH which was attributed to CTA degradation. Nonetheless, both methanol and water/1,4-dioxane (pH ~3) systems generated polymers with narrow PDI (<1.20) at high monomer conversions. A kinetic analysis for MAA polymerizations in methanol as well as low pH water-based solvent corroborated the linear trend at short times of $\ln([M]_0/[M])$ vs time, characteristic of controlled/living polymerizations with pseudo-first-order kinetic behavior.

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