# Enhanced Flocculation Efficiency in a High-Ionic-Strength Environment by the Aid of Anionic ABA Triblock Copolymers

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<b>ABSTRACT:</b> The flocculation efficiency of polyelectrolytes in a high-ionic- strength environment is often affected and reduced due to shielding of the active ionizable functional groups, as well as changes in the surface chemistry	Random Copolymer ABA Triblock Copolymer

of the solid slurry. To address this problem, a series of well-defined novel ABA triblock copolymers were employed for the flocculation of high-ionicstrength kaolin slurries at three different  $Ca^{2+}$  concentrations (0.05, 0.10, and 0.50 M). The primary focus was on the advancement in the polymer architecture, where the anionic functionalities were localized at the terminal ends. Typical commercial flocculants tend to have anionic functionalities randomly distributed throughout the polymer chain and hence a higher propensity toward condensed conformation and formation of insoluble



species. In comparison to a control random copolymer, the ABA triblock copolymers were able to flocculate kaolin slurries to give faster settlement rates, particularly at the high  $Ca^{2+}$  concentrations of 0.10 and 0.50 M. In addition, these polymers had significantly better clarification ability at higher  $Ca^{2+}$  concentrations compared to the control random copolymer. The ABA triblock copolymer architecture may therefore have potential as a flocculant in high-ionic-strength applications.

## INTRODUCTION

Rapid growth in population and technologies has led to increased generation of wastewater and industrial effluents. The processes employed to produce potable water from these waste streams require continuous development to satisfy current demands and increasingly stringent regulations. These waste effluents can contain large fractions of suspended solid particles, as well as metal ions and microorganisms.<sup>1,2</sup> The removal of suspended particulates is difficult due to their size and surface charge,<sup>1,3-5</sup> particularly for clay minerals such as kaolin and bentonite, causing substantial environmental concerns.<sup>6,7</sup> Several types of solid–liquid separation processes are utilized in industrial applications to overcome this colloidal effect. Polymer-bridging flocculation, in which fine particles are aggregated to achieve a much larger effective size, is generally the most practical process to enhance settling of colloidal suspensions.<sup>8</sup>

The flocculation process is dependent on a variety of factors, such as the type and concentration of the solid substrate, pH, the type and structure of the polymeric flocculant, and the molecular weight and charge density of the polymer.<sup>9-12</sup> The solution ionic strength has a major impact on the flocculation efficiency of a polymer, generally evaluated from the settlement rate of the suspended particles and/or subsequent supernatant clarity.<sup>1</sup> Recent practices have directly employed seawater (or diluted seawater) as the aqueous medium during flocculation.<sup>10,13</sup> The tailings from mineral processing also often

contain considerable quantities of inorganic ions,  $^{14,15}$  and their interaction with polyelectrolytes or clay minerals can lead to complications.  $^{8}$ 

At a very low ionic strength, the ionizable functionalities of the polyelectrolyte provide charge repulsions that extend the solution conformation of the polymer chain.<sup>16</sup> In addition, these ionizable groups can contribute to polymer adsorption through electrostatic interactions or salt linkages with metal ions available at the particle surface.<sup>3</sup> As ionic strength increases, reduced intramolecular electrostatic repulsions promote polymer adsorption onto surfaces, which can favor flocculation.<sup>10,17–19</sup>

Multiple studies have demonstrated an increase in settlement rate and/or a decrease in supernatant turbidity with higher salinity.<sup>10,20,21</sup> However, at high ionic strength, the shielding of active functional groups results in a condensed polymer conformation that is typically exhibited in the neutral structure of polyacrylamide (PAM).<sup>16,19,22,23</sup> This directly affects both the adsorption and bridging capacity, with the potential to greatly limit flocculation. The solution viscosity, solvency, and dispersion capability of the polymer are also

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Figure 1. Schematic for the flocculation mechanism of the ABA triblock copolymers where the A and B blocks adsorb onto colloidal particle surfaces via salt linkages and hydrogen bonding, respectively.

affected, which impact the makeup, transportation, and distribution of the flocculant throughout colloidal suspensions.<sup>16,19</sup>

The negative impact of cations on flocculation efficiency with acrylamide (AM) and acrylate copolymers is well known.<sup>16,19,21–25</sup> This effect was amplified for multivalent cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) compared to that for monovalent cations (Na<sup>+</sup> and K<sup>+</sup>).<sup>16,21,22</sup> In some cases, precipitation of the polyelectrolyte can occur due to complexation between cations and carboxylate functionalities.<sup>22,26,27</sup> Boisvert et al. concluded that insoluble precipitate formation was dependent on the hydration energy of the cation; a stronger interaction between a polymer and a cation was observed when the latter possessed a lower magnitude hydration energy.<sup>26</sup> Consequently, Ca<sup>2+</sup> generally has a stronger effect on flocculation relative to Mg<sup>2+,16,26</sup> Little has been done to overcome this problem, as interactions between ionizable functional groups and multivalent cations are considered unavoidable.

Commercial flocculants with ultrahigh molecular weight (UHMW) are often synthesized by copolymerization of AM and its derivatives.<sup>1,3</sup> The synthesis of these UHMW polymers is typically limited to free radical polymerization, with little control over the polymer architecture.<sup>3</sup> Consequently, these flocculants may be more negatively impacted at high ionic strength due to the random distribution of ionizable functionalities throughout the polymer chain.

Reversible deactivation radical polymerization (RDRP) techniques can synthesize polymers with precise molecular weights and advanced architectures while maintaining good control over the molecular weight distribution. However, the synthesis of UHMW polymers using these techniques remains difficult with limited advances toward complex architectures.<sup>28</sup> Several studies have reported the synthesis of well-defined UHMW polymers using reversible addition–fragmentation chain transfer (RAFT) polymerization,<sup>28–35</sup> atom transfer radical polymerization (ATRP),<sup>32,36–41</sup> and single-electron

transfer living radical polymerization (SET-LRP).<sup>42–44</sup> Most have focused on linear homopolymers and AB diblock copolymers, the exception being ABA triblock copolymers of dimethylacrylamide and *N*-isopropylacrylamide having molecular weights of up to 500 kDa.<sup>31</sup>

Recently, our group synthesized a series of UHMW ABA triblock copolymers from acrylic acid (AA) and AM as the A and B blocks, respectively.<sup>28</sup> The lengths of the terminal A block for these eight ABA triblock copolymers ranged from 5.21 to 173 kDa. These were the first of their kind with the total overall molecular weight being approximately 1000 kDa and well-controlled dispersity (D) remaining below 1.70.<sup>28</sup> In comparison to typical statistical copolymers of AM and AA, ABA triblock copolymers are hypothesized to have better solubility at high ionic strength due to the long and highly water-soluble B block. The terminal A blocks may still allow for polymer chain elongation due to electrostatic repulsion, as well as a competitive attachment onto particle surfaces by hydrogen bonding through the B block, even if the anionic functionalities are compromised. Figure 1 is a proposed schematic mechanism for flocculation with ABA triblock copolymers, where the terminal anionic A blocks are responsible for bridging via salt linkages with cations on the particle surfaces, while the neutral B block is able to bridge via hydrogen bonding. The unique architecture and high molecular weight of these polymers may therefore offer strong potential for flocculation at high ionic strength.

In this work, we aim to evaluate the flocculation efficiency of the aforementioned UHMW ABA triblock copolymers with kaolin clay at high ionic strength induced by calcium chloride. To the best of our knowledge, this is one of the first reported studies employing polymers with advanced architectures to address the limitations of flocculation at high ionic strength. The effect of different salt concentrations (0.05, 0.10, and 0.50 M) on the flocculation efficiency (settlement rate and supernatant turbidity) of the ABA triblock copolymers is Scheme 1. Overall Reaction Pathway for the Synthesis of the UHMW ABA Triblock Copolymers Using Sequential RAFT Polymerization Followed by Aminolysis and Oxidation of the Thiocarbonylthio Functionality (Ref 28 – Reproduced by Permission of The Royal Society of Chemistry)



explored using cylinder settling tests. Comparisons against control homopolymers and statistical copolymers of AM and AA carrying similar molecular weights are conducted to contrast between the ABA triblock architecture and that representative of current commercial flocculants.

Cylinder settling tests are routinely used to quantify flocculation efficiency and compare flocculants in many applications. However, the applied mixing for these tests is often not well defined, with the potential for limited sensitivity or even misleading trends if the conditions are not well understood.<sup>45,46</sup> Settlement rate and supernatant turbidity as efficiency measures offer only indirect indications of the extent of aggregation. Flocculation in turbulent pipe flow gives control over both the intensity and duration of mixing between flocculant solutions and a slurry; a focused beam reflectance measurement (FBRM) probe can then be utilized inline to monitor the flocculated aggregate size in real time under specific shear conditions as a function of flocculant dosage.<sup>4</sup> Cylinder settling remained the primary test to determine the ultimate flocculation efficiency of a polymer, while the turbulent pipe flow approach was utilized to gain complementary information on the initial stages of aggregation under applied turbulent shear.

## MATERIALS AND METHODS

**Materials.** The following chemicals were used directly as received without further purification: acrylamide (Sigma, 99%), 3-((((1-carboxyethyl)thio)carbonothioyl)thio)-propanoic acid (Boron Molecular, 90%), ammonium persulfate (Sigma-Aldrich, 98%), sodium formaldehyde sulfoxylate dihydrate (Sigma-Aldrich, 98%), sodium nitrate (Merck, 99.9%), sodium bicarbonate (Merck, 99.9%), *n*-butylamine (Sigma-Aldrich, 99.5%), calcium chloride dihydrate (Merck, 99%), *N*,*N*-dimethylformamide (Ajax FineChem, 99.9%), and water (Milli-Q and RO grades). Acrylic acid (Aldrich, 99%) was passed through a small column of basic activated aluminum oxide

(Acros Organics) and immediately used for polymerizations. Prestige NY kaolin clay (46.7 wt % SiO<sub>2</sub>, 36.1 wt %  $Al_2O_3$ , 0.8 wt % TiO<sub>2</sub>, 0.9 wt % Fe<sub>2</sub>O<sub>3</sub>, 0.7 wt % CaO, 0.4 wt % MgO, 0.4 wt % K<sub>2</sub>O, and 0.1 wt % Na<sub>2</sub>O) was kindly donated by Sibelco Australia and used as received.

General Procedure for the Synthesis of the ABA Triblock Copolymers. The synthetic pathway of the ABA triblock copolymers is outlined in Scheme 1, and these polymers were synthesized in a three-step process based on the procedure previously reported by our group.<sup>28</sup> The first two steps involved the initial RAFT polymerization and subsequent chain extension using AA and AM, respectively. The final step in the synthetic pathway involved the aminolysis of the AB diblock copolymers to produce the ABA triblock copolymers by spontaneous formation of disulfide linkages.

In a typical RAFT polymerization reaction, the monomer (AA or AM) and the RAFT chain transfer agent were dissolved in Milli-Q water inside a sealable reaction flask. In addition, DMF was employed as the internal standard for the subsequent calculation of the monomer conversion by <sup>1</sup>H NMR. The reaction flask was sealed and subsequently charged with a stream of argon gas. Deoxygenation of the reaction mixture was performed by argon bubbling for 30 min. The temperature of the reaction mixture was kept constant at 20 °C throughout the process. The initiators (APS and SFS) were then separately injected into the reaction flask, followed by a further 5 min of argon bubbling. The reaction was left running under the stream of argon gas for 24 h. In a typical aminolysis experiment, the AB diblock copolymer was dissolved in water and charged in a sealable reaction flask. To promote an oxidative environment, the reaction mixture was bubbled with pure oxygen for 30 min prior to the addition of nbutylamine. The reaction was left running under a closed environment at 50 °C for up to 24 h. The polymers were purified by dialysis in water and freeze-dried before being used in the subsequent stage or flocculation testings. Purification was performed using a SnakeSkin dialysis tubing (Thermo Fisher Scientific) with a molecular weight cutoff of 3500 Da. Freeze-drying was performed on a Labconco FreeZone Benchtop Freeze Dry system.

General Procedure for the Synthesis of the Control Copolymers. Three different control UHMW polymers with a molecular weight of approximately 1000 kDa were employed in this study: a homopolymer of AA (PAA), a homopolymer of AM (PAM), and a random copolymer of AA and AM (RAB). These control polymers were synthesized using a free radical polymerization technique, which was previously reported by our group.<sup>48</sup> In this procedure, the appropriate amount of monomer(s) was dissolved in Milli-Q water and charged into a sealable reaction flask. The reaction mixture was deoxygenated by argon bubbling for 30 min. Aqueous solutions of the initiators (APS and SFS) were separately injected into the reaction flask, and argon bubbling was applied for a further 5 min after each injection. The reaction was left running at 20 °C for 24 h under a stream of argon flow. The resultant polymer gel samples were freeze-dried without any purification and ground into smaller particles for use as a flocculant.

Size Exclusion Chromatography (SEC). Molecular weight distributions of the polymeric flocculants were measured using a Tosoh High-Performance EcoSEC HLC-8320GPC system. Three analytical columns (TSKgel G5000PW<sub>XL</sub>, TSKgel G6000PW<sub>XL</sub>, and TSKgel GMPW<sub>XL</sub>) connected in series and a TSKgel SuperH-RC reference column were employed to analyze the polymers. In addition, the system also consisted of a dual flow pumping unit, a vacuum degasser, an autosampler, a Bryce-type refractive index (RI) detector, a UV detector set at 305 nm, and a TSKgel PW<sub>XL</sub> guard column. The polymers were measured against a series of polyacrylic acid standards with molecular weights ranging from 1 kDa to 1 MDa. Measurements were performed at 40 °C with 0.1 M NaNO<sub>3</sub> and 0.1 M NaHCO<sub>3</sub> (pH  $\approx$  8.3) in deionized water as the eluent (flow rate of 1 mL/min).

**Makeup and Preparation of Polymers for Flocculation Analysis.** A total of 11 different anionic copolymers (eight ABA triblock copolymers and three control polymers) with similar molecular weights and varying charge densities were synthesized and employed as flocculants for this study. The ABA triblock copolymers were previously synthesized by our group, and their architectures were confirmed through a series of SEC and UV-vis analyses.<sup>28</sup> The properties of these polymeric flocculants are summarized in Table 1.

Table 1. Summary of the Anionic Polymeric FlocculantsEmployed in This Study

abbreviated name	$M_{ m n,SEC}$ of A block (kDa)	overall $M_{ m n,SEC}~( m kDa)$	Đ
PAA		1220	7.73
PAM		922	8.63
RAB		960	10.4
ABA1	5.21	1040	1.63
ABA2	11.8	924	1.72
ABA3	20.9	1140	1.57
ABA4	33.9	1180	1.48
ABA5	45.7	903	1.40
ABA6	84.8	1080	1.45
ABA7	118	1020	1.93
ABA8	173	850	1.62

An initial 0.25 wt% stock solution of the polymeric flocculant was prepared by initially wetting the powdered flocculant (0.25 g) with acetone (3 mL) in a 100 mL glass bottle, subsequently followed by the addition of deionized water (97 mL). The mixture was shaken vigorously by hand for 30 s to allow for even distribution of the polymer particles and immediately mixed continuously on a benchtop tube roller mixer at 70 rpm for 2 h. At this point, the resulting solution became clear and homogeneous. This stock solution was further diluted with deionized water and mixed again at 70 rpm for 5 min on the roller to make a 0.025 wt % homogeneous working solution, which was used directly for flocculation testing. The working solution was always prepared fresh before immediate flocculation testing and discarded at the end of each day, while the concentrated stock solution was stored under refrigeration when not in use and kept for no longer than one week. The flocculant dosage in this study is expressed as grams of polymer per tonne of dry kaolin solids (g/tds).

Preparation of High-Ionic-Strength Kaolin Slurries. For cylinder settling tests, kaolin slurries were prepared fresh daily at the desired solid concentration by adding kaolin clay (3 wt % for cylinder settling tests; 1.5-6 wt % for turbulent pipe flow tests) to deionized water in a 20 L pail. The cation of interest in this study was Ca<sup>2+</sup> and therefore a high-ionic-strength environment was generated by the addition of the appropriate amount of calcium chloride to the bulk slurry in the pail. The slurry was subsequently stirred vigorously using an overhead mechanical stirrer equipped with an impeller blade at a rate of approximately 500 rpm where a vortex was observed. This high-intensity stirring was applied for 3 h to allow for uniform distribution and dispersion of the clay particles. Subsequently, the stirring rate was reduced to approximately 250 rpm, where a smaller vortex was observed, for a gentle stirring environment during flocculation testing. All flocculation measurements were performed at the neutral pH (approximately between 7 and 8) of the high-ionicstrength slurry.

For continuous flocculation tests, kaolin slurries were also prepared fresh daily at the desired solid concentration by adding kaolin clay to tap water in a 60 L pail. The kaolin slurry was stirred vigorously at 200 rpm using an overhead mechanical stirrer equipped with a large impeller blade so that a vortex was observed. The appropriate quantity of calcium chloride pellets was then slowly added into the slurry. The vigorous stirring was maintained for 1 h. Subsequently, the same stirring rate was maintained and the kaolin slurry was directly pumped into the turbulent pipe flow system with inline FBRM monitoring.

Flocculation by Cylinder Settling Tests. In a typical cylinder batch settling test, the high-ionic-strength kaolin slurry was transferred to a 1000 mL graduated cylinder (Azlon CT1000P, diameter 6.6 cm, height 44 cm). The temperatures of both the kaolin slurry and the flocculant working solution were unadjusted and maintained at room temperature. A stainless steel plunger was employed for the purpose of mixing and distributing the flocculant throughout the slurry. The diameter of the plunger was 5 cm, with five evenly distributed inner radial holes of 1 cm diameter. The plunger was used to mix the slurry vigorously for approximately 5 s, which was immediately followed by the addition of the required amount of the flocculant. Once the flocculant was added, five plunger strokes were applied to the slurry, where each stroke was considered as both a downward and an upward motion. For good consistency, a metronome was employed to allow for each plunging motion (up or down) to be performed at a rate of 45 BPM. The settlement time of the flocculated particles was measured from when the mud line passed the starting point at the 900 mL mark until it reached the 700 mL mark on the graduated cylinder (the total distance of 7 cm). At 20 min after the last stroke, approximately 10 mL of the supernatant was taken from the 800 mL mark on the graduated cylinder for turbidity analysis using a Hanna Instruments HI98703-01 Portable Turbidity Meter.

Continuous Flocculation in a Turbulent Pipe Flow. Continuous flocculation experiments were conducted using an FBRM D600L probe (Mettler Toledo) and a pipe reactor, which consisted of a series of stainless steel pipes. The theories and principles associated with the FBRM technique and chord length distributions in flocculation studies were previously discussed by Heath et al. and Owen et al., respectively.<sup>49,50</sup> The coarse (C) electronics mode was employed rather than the fine (F) mode as the slower response with the former increases the probability of larger, highly porous aggregates being measured as a single object. Consequently, the sensitivity of the FBRM would be reduced for particles and fines with sizes below 10  $\mu$ m.<sup>47</sup> This was deemed to be appropriate for this study. While the probe can measure chord lengths up to 2000  $\mu$ m, for these experiments, chord length distributions were measured between 1 and 1000  $\mu$ m in 100 channels distributed logarithmically. The chord length distributions are usually presented as line graphs for ease of comparison but in reality should be column graphs. A volume-weighting is achieved by applying a squareweighting to the chord length distribution.

$$n_{i,2} = n_i M_i^2 \tag{1}$$

where  $n_i$  and  $n_{i,2}$  are the counts and square-weighted counts in a chord channel, respectively, and  $M_i$  is the midpoint of the channel. The mean of this distribution is also derived

mean square-weighted chord length = 
$$\frac{\sum_{i=1}^{k} n_i M_i^3}{\sum_{i=1}^{k} n_i M_i^2}$$
(2)

The D600L probe had an outer stainless steel casing of 25 mm in diameter and a 12 mm diameter flat sapphire window at its tip. Window cleaning was performed regularly to ensure that there was minimal adherence of fine particles on the surface, which could affect the final measured size. Therefore, cleaning was repeated before each set of measurements until a total background count of less than 150 counts per second was obtained in air.

In previous studies of flocculation kinetics in turbulent pipe flow, the internal diameter of the pipe can range up to 38 mm.<sup>51</sup> Stainless steel pipes may be linked together to achieve total reactor lengths between 1 and 50 m. For the purpose of these flocculation experiments, a small-scale pipe reactor was employed with an internal pipe diameter of 7.7 mm. A straight pipe with a length of 1 m was connected to the inlet of the pipe reactor, which was subsequently followed by a 7 m long helical coil pipe attachment. Every single coil had a total length of 1 m and therefore this section of the pipe reactor incorporated seven coils. The diameter of each coil was approximately 30 cm. Secondary flow effects can be observed in helical coils,<sup>52</sup> but computational fluid dynamics modeling on this experimental setup was able to confirm small and negligible effects for the size of the coil and low flow velocities employed.<sup>47</sup> An overall schematic of the pipe reactor is shown in Figure S1a in the Supporting Information (SI).

The inlet of the pipe reactor was designed to allow for the feed lines (slurry and flocculant) to join and mix together (Figure S1b in the SI). This design therefore allowed for the distance between the point of flocculant addition and the FBRM probe to be well defined. The flocculant feed line had an internal diameter of 3 mm. The outlet of the pipe reactor was a flow cell measurement chamber, which allowed for the insertion of an FBRM probe at a 45° angle to the slurry flow (Figure S1c in the SI). This was carefully designed to ensure that no dead zone exists and the probe window is free of any blockages.

In a typical experiment, water was initially pumped through the system to check for leaks. Subsequently, the kaolin slurry was pumped through the pipe reactor at a volumetric flow rate of approximately 2.5 L/min until the distributions and main statistics (total counts, mean chord length, and mean square-weighted chord length) directly obtained from the FBRM software were stable in real time. At this point, the flocculant was then pumped through the pipe reactor at an appropriate flow rate so that the final dosage of the flocculant reached the desired values of 17, 33, 50, or 67 g/tds. Chord length distributions between 1 and 1000  $\mu$ m were measured and recorded every 2 s. The FBRM results reported were averaged from 20 to 30 measurements when stability was achieved for the condition employed. Unweighted and length square-weighted chord length distributions and a variety of statistics were monitored and recorded by the software in real time. However, for the purpose of this study, only the mean unweighted chord length and the mean squareweighted chord length were closely examined as a function of flocculant dosage. Once measurements for all of the desired dosages and flocculants were performed, the pipe reactor was flushed with water and the FBRM probe window was cleaned before the next set of measurements with a different kaolin concentration (1.5, 3, or 6 wt %)

**Dynamic Light Scattering (DLS).** The hydrodynamic volumes (effective diameter) of the ABA triblock copolymers were analyzed through dynamic light scattering (DLS). These measurements were conducted using a Brookhaven NanoBrook Omni particle size and zeta potential analyzer, with measurements conducted in triplicate for each polymer sample. Before analysis, the polymers were prepared in

filtered deionized water at the flocculation working concentration of 0.25 wt % under ambient conditions.

## RESULTS AND DISCUSSION

The UHMW ABA triblock copolymers of AA and AM employed in this study (**ABA1–ABA8**) were the first of their kind, possessing a precise architecture and composition while maintaining such high molecular weight and low dispersities.<sup>28</sup> Better flocculation efficiency in a high-ionic-strength environment was hypothesized for these polymers solely based on the advancement in architecture compared to the current commercial random-type polymeric flocculants. However, it would be misguiding to directly compare these ABA triblock copolymers to currently available commercial anionic flocculants due to the considerable differences in molecular weight.

To primarily focus on the difference in the architecture, control polymers with a similar molecular weight to the ABA triblock copolymers were synthesized. Homopolymers of AA and AM (PAA and PAM, respectively) were synthesized using free radical polymerization at optimized conditions to achieve a target molecular weight of approximately 1 million Da. PAA and PAM were employed as control polymers; in theory, the negative effect of high ionic strength would be more significant toward the flocculation efficiency of the anionic PAA compared to the neutral PAM. A random copolymer of AA and AM (RAB) with similar molecular weights was also synthesized using the same methodology. The architecture of RAB is representative of current commercial flocculants commonly applied to clay-based tailings and thus can be directly compared against ABA1–ABA8 in Table 1.

Cylinder Settling Test Conditions. A series of cylinder settling tests were initially performed using the three control polymers (PAA, PAM, and RAB) and the eight ABA triblock copolymers (ABA1-ABA8). The cylinder settling test is one of the most common methods employed to study and evaluate flocculation. Nevertheless, there are certain negative connotations associated with this method due to the potential for a high level of standard errors typically attributed to poor mixing and variations in the solid concentrations and testing procedures.<sup>53,54</sup> The main intention of conducting these tests was to obtain a general idea of the fundamental effect of the multivalent cation and its concentrations on the flocculation efficiency of these novel polymers. These initial tests would allow for the identification and analysis of various trends among the ABA triblock copolymers or between the subject polymers and the control polymers. Therefore, this methodology was deemed to be sufficient for the initial stage of flocculation in this study.

Cylinder settling tests were conducted using a kaolin slurry, with calcium chloride added to create a high-ionic-strength environment. The kaolin slurry was initially maintained at a solid concentration of 3 wt % throughout. Three different calcium chloride concentrations of 0.05, 0.10, and 0.50 M were targeted. The large increments in the concentration of  $Ca^{2+}$  allow for any significant changes or trends in the flocculation efficiency of the anionic flocculants to be observed. Solutions of the polymeric flocculants were introduced into the slurry at four different dosages ranging from approximately 17 to 67 g/tds, and the flocculation efficiency was determined. Efforts were made during the cylinder settling test to reduce the standard errors by having the same operator, accurate solid and salt concentrations, and consistent quantity and rate of plunger strokes throughout.

**Effect of Ca<sup>2+</sup> on Settlement Rate.** The settlement rates of all 11 polymers as a function of dosage are shown in Figure 2. The most efficient strategy to assess these flocculation



Figure 2. Settlement rate of the kaolin slurry (3 wt %) as a function of flocculant dosage for the ABA triblock copolymers (ABA1–ABA8) and the control polymers (PAA, PAM, and RAB) obtained by cylinder settling tests with varying  $Ca^{2+}$  concentrations at (a) 0.05 M, (b) 0.10 M, and (c) 0.50 M.

efficiency plots is to track the changes associated with polymer **RAB** (the solid blue line with circle markers) while comparing it to the ABA triblock copolymers (dashed lines with square markers).

At the lowest  $Ca^{2+}$  concentration of 0.05 M (Figure 2a), RAB remained effective in flocculating the kaolin slurry. Increments in dosage resulted in considerably larger increases in settlement rate compared to that of the ABA triblock copolymers. With the exception of ABA7, the overall settlement rates of the ABA triblock copolymers were lower compared to those of RAB, particularly at the highest dosage of 67 g/tds. This first set of data indicated that RAB was somewhat unaffected by the concentration of  $Ca^{2+}$  targeted, and its settlement rate would in all likelihood be superior compared to that of the ABA triblock copolymers if higher dosages were employed. Note that PAM consistently gave lower settlement rates at all dosages, reflecting the more coiled conformation of the nonionic polymer. The settlement rates were marginally lower for PAA flocculation, with adsorption via salt linkages possibly being less effective due to the influence of such adsorption being limited by a degree of polymer complexation.

A twofold increase in the concentration of Ca<sup>2+</sup> to 0.10 M led to a substantial drop in the settlement rate for RAB (Figure 2b). At this concentration, the settlement rates achieved with RAB were now observed to be inferior compared to those for polymers ABA4-ABA7. Concurrently to this decline in activity, the settlement rates obtained for the ABA triblock copolymers remained in a similar range where no notable changes were observed. This stability in settlement rates was observed yet again when the concentration of Ca<sup>2+</sup> was further increased fivefold from 0.10 M. This indicated that the flocculation efficiency of the ABA triblock copolymers remained relatively unaffected by the changes in the ionic strength, contrary to that of RAB. At the highest Ca<sup>2+</sup> concentration of 0.50 M (Figure 2c), the overall settlement rates obtained with RAB were lower than that with all of the eight ABA triblock copolymers. The polymer RAB went from being initially better than seven of the ABA triblock copolymers to being the most compromised by the 10-fold increase in  $Ca^{2+}$  concentration.

Any further increase in Ca<sup>2+</sup> concentration from 0.50 M would perhaps result in similar settlement rates being observed from flocculation with both RAB and PAM. This is attributed to the near-complete shielding of the anionic groups on RAB, leading to a pseudo-PAM structure and hence a condensed polymer conformation that is typically observed in unmodified PAM.<sup>16</sup> Closer observation showed minimal changes in the settlement rates with PAM across all three Ca2+ concentrations. These results were expected, as the neutral amide functionality on the polymer backbone would be unaffected by the cations present in the solution. Slight increases in settlement rates were generally observed for PAM and the ABA triblock copolymers when the Ca<sup>2+</sup> concentration was increased. High concentration of multivalent cations would lead to compression of the electrical double layer (EDL), which destabilized the unflocculated colloidal suspension and hence assisted with the subsequent flocculation process.

In contrast to those from **PAM**, the settlement rates obtained from **PAA** flocculation were significantly influenced by the presence of calcium cations. A notable drop in the settlement rates was observed with a stronger ionic strength, until a near-plateau response curve was observed at 0.50 M  $Ca^{2+}$ , indicating effective deactivation as a flocculant. These results were expected, as anionic functionalities across the entire polymer chain would interact with the cations available in the kaolin slurry, and hence, heightened negative effects at higher ionic strength were observed.

Based on the settlement rates obtained from the control polymers alone, it would be concluded that polymers with a higher fraction of anionic functionalities were more susceptible to undesirable interactions with multivalent cations. However, examination of the measured settlement rates from just the ABA triblock copolymers indicated the opposite. Longer A blocks for these polymers generally corresponded to faster settlement rates. Overall, **ABA5–ABA8** were able to flocculate to faster settlement rates, particularly at the highest Ca<sup>2+</sup> concentration of 0.50 M. At each concentration of Ca<sup>2+</sup>, the settlement rate was observed to decrease once the A block passed a threshold molecular weight. For all three concentrations of Ca<sup>2+</sup> employed, **ABA7** with the second longest A blocks was able to induce the formation of aggregates with the highest settlement rates in comparison to those for **ABA8**.

Relatively inferior settlement rates obtained from using ABA1-ABA4 can be attributed to the lower concentration of anionic functionalities present, which led to inadequate polymer chain elongation and consequently resulted in inefficient polymer-particle bridging. This effect was amplified particularly in higher-ionic-strength environments due to shielding of the active anionic groups. Nevertheless, these differences in the settlement rates among the ABA triblock copolymers were very minor across all three concentrations of Ca<sup>2+</sup>. To verify this elongation effect, DLS was employed for the determination of the hydrodynamic volumes of the ABA triblock copolymers. The results were able to confirm this hypothesis, which showed an increase in the hydrodynamic volume in correspondence to the increase in the chain length of the anionic block (Table S1 in the SI), ranging from 19.5  $\mu$ m up to 35.8  $\mu$ m for polymers ABA1 and ABA7, respectively. However, these values were significantly higher than the values expected for a singular polymer chain with a molecular weight of approximately 1 MDa. These results plausibly indicated that micelles or other forms of self-assembly were present at the working flocculant concentration of 0.25 mg/mL. While these polymer solutions were transparent to the naked eye at this concentration, it was observed that a higher concentration of 2.5 mg/mL exhibited a small degree of cloudiness. This further supported that the formation of self-assemblies was a strong possibility, which arose from the slight difference in solubility between the anionic and nonionic blocks. Consequently, these DLS results indicated that the ABA triblock copolymers were introduced to the kaolin slurry, where chain elongation was more pronounced for those with longer anionic blocks and thus were able to flocculate particles at a relatively higher efficiency.

Effect of  $Ca^{2+}$  on Supernatant Turbidity. The supernatant turbidity of the kaolin slurry was measured consistently at 20 min after the addition and homogenization of the polymeric flocculant. Turbidity results obtained with the 11 polymers as a function of dosage are shown in Figure 3, presented in the exact same format as that for the settlement rates for ease of examination. Lower turbidity values (lower NTU) are desirable, as this indicates that the polymeric flocculants are more efficient at clarifying the supernatant.

At the lowest Ca<sup>2+</sup> concentration of 0.05 M, it could be clearly observed that all eight ABA triblock copolymers were



Figure 3. Supernatant turbidity of the kaolin slurry (3 wt %) as a function of flocculation dosage for the ABA triblock copolymers (ABA1–ABA8) and the control polymers (PAA, PAM, and RAB) obtained by cylinder settling tests with varying  $Ca^{2+}$  concentrations at (a) 0.05 M, (b) 0.10 M, and (c) 0.50 M.

able to induce much lower turbidity compared to RAB and the control polymers PAA and PAM. For example, the turbidity obtained from using ABA2 at a dosage of 50 g/tds was very

These results essentially indicated that the clarification performance of all eight ABA triblock copolymers was considerably better than that of RAB, irrespective of the Ca<sup>2+</sup>concentration. Given that little work had previously been done on the flocculation efficiency of well-defined ABA triblock copolymers, the reason behind this phenomenon in turbidity remains unclear, with the interpretation complicated by the fact that capture of fines after flocculation can be influenced by a range of factors.<sup>46</sup> At very low solid concentrations, such as in the study of wastewater clarification, supernatant turbidity can mostly be a reflection of the reagents used to promote fine particle aggregation or the applied mixing during aggregation.<sup>55-57</sup> At higher solid concentrations, differences in the viscosity of the dosed flocculant solutions can influence mixing and the efficiency of aggregation;<sup>58</sup> however, in this case, the polymers used are not of a high enough molecular weight and are sufficiently diluted before dosing such that this is not likely to be a factor. Turbidity can also increase as a consequence of aggregate breakage from excessive mixing during the flocculation process,<sup>59</sup> but this is more likely to be an issue when high settlement rates (i.e., >20 m/h) are sought; settlement rates in this study were <10 m/h, and the applied mixing was considered moderate. It is known that immediately after such mixing, there is often the potential for further aggregate growth to occur before settling commences.<sup>50</sup> While such growth is not expected to lead to the further capture of free fines within aggregate structures, supernatant turbidity is still then influenced by hindered settling in batch testing as free fines can be dragged down with the bulk solids, in particular with flocculated clays.<sup>46</sup> Any variation in the size and density of the aggregates thus formed could then impact the resultant turbidity.

A closer inspection of the supernatant turbidity results did not show any obvious trends among the ABA triblock copolymers. All eight ABA triblock copolymers produced similar performance, particularly at the two lowest Ca<sup>2+</sup> concentration of 0.05 and 0.10 M. At the highest concentration of 0.50 M, the differences in the results obtained for the ABA triblock copolymers were slightly more significant and noticeable. The effect of anionic chain length on the supernatant turbidity was unclear. Unlike the results obtained for the settlement rates, the supernatant turbidity generally did not increase after the molecular weight of the A blocks had passed a certain threshold. Across the three different concentrations of the salt used, turbidity results obtained using ABA triblock copolymers with long terminal A blocks were slightly higher compared to those with shorter A blocks. This was in agreement with the previous comparison between polymers PAM, RAB, and PAA.

As mentioned previously, the control polymers were synthesized using a standard free radical polymerization method to allow for better comparison with industry-based polymeric flocculants. These flocculants are typically synthesized in large batches using free radical polymerization and thus can demonstrate significantly broad molecular weight distributions. The uncontrolled synthesis of the control polymers consequently led to large dispersity values. The effect of dispersity on the flocculation efficiency of a polymer was deemed to be of interest and thus two additional homopolymers with low dispersities derived from AA or AM (D of 1.42 and 1.38, respectively) were synthesized. This was achieved using a three-stage method similar to that employed to synthesize the ABA triblock copolymers, to allow for direct comparison with their higher-dispersity counterparts PAA and PAM (D of 7.73 and 8.63, respectively). The molecular weight distribution and flocculation data are shown in the SI.

The change from high to low dispersity did not significantly alter the flocculation efficiency. The changes in either the settlement rate or the supernatant turbidity as a function of the flocculant dosage were minimal for the low-dispersity polymers. In contrast, their high-dispersity counterparts generally showed larger changes with higher dosages. This was attributed to the likely presence of some high-molecularweight polymer chains within the higher-dispersity samples and thus had a larger influence on the flocculation efficiency. The chain length of the low-dispersity samples would be more consistent and thus minor changes were observed with higher dosages. The settlement rates obtained from the low-dispersity samples were therefore generally slower, particularly with an increase in the flocculant dosage. Supernatant turbidities obtained from using low-dispersity polymers were also generally higher compared to that of the high-dispersity polymers, most likely caused by the same molecular weight distribution effect. Based on these results, the dispersity of the polymers was deemed to be a relatively minor factor, with the architecture of the ABA triblock copolymers having a much bigger role in improving flocculation efficiency in a high-ionicstrength environment.

**Measuring Aggregate Dimensions in Real Time by FBRM.** Polymer comparisons from batch cylinder testing inevitably involve performance measures made on the products of a series of partially overlapping steps. These include the distribution of the polymer solution through the slurry, adsorption of the polymer to particle surfaces during this mixing step, subsequent aggregate growth (with possible concurrent breakage), and the likelihood of additional aggregate growth occurring in the milder shear conditions after plunger mixing has ceased. The latter steps represent the well-known concept of "tapered shear", with the conditions considered most conducive for optimal aggregation involving a short duration of higher shear to favor reagent distribution and initial aggregate growth, followed by reduced shear that then enables larger aggregates to be formed.<sup>50,60</sup>

A pipe reactor was employed in conjunction with an FBRM probe to provide inline monitoring of the flocculated aggregate size while under turbulence. This supplementary methodology was employed to gain a better understanding of the aggregation response due to the unique supernatant turbidity results. However, these tests were not considered as the primary means to determine the flocculation efficiency of the polymeric flocculants, as the cylinder settling tests alone were sufficient. The mean shear rate examined (1270 s<sup>-1</sup>) ensures that conditions remained turbulent throughout all testing and matches that used this experimental configuration previously,<sup>47</sup> with the fixed reaction time (9.2 s) considered to be definitely after any dosed polymer has been well mixed through the slurry flow.

To appreciate how the FBRM chord length distributions respond to flocculation, it is useful to first examine results obtained separately for a kaolin slurry flocculated with a



Figure 4. (a) Unweighted and (b) length square-weighted chord length distributions for the flocculation of the 2 wt % kaolin slurry with BASF Magnafloc 336 (reaction time 9 s, mean shear rate  $1270 \text{ s}^{-1}$ ).

commercial anionic flocculant (BASF Magnafloc 336) at a very low ionic strength; in this case, 0.03 M Ca<sup>2+</sup> is added to ensure stable dispersion of the kaolin particles. This flocculant has a nominal molecular weight in excess of 15 MDa, i.e., more than an order of magnitude higher than that of RAB. Figure 4 shows chord length distributions obtained from pipe flocculation at different dosages, contrasted to results for the unflocculated kaolin slurry. The unweighted chord length distributions (Figure 4a) offer sensitivity to the number of particles or aggregates within the slurry, and as increasing dosages of flocculant are introduced, aggregation leads the distribution to reduce in intensity and shift to larger chord lengths. The flocculated distributions can display some bimodal character, particularly at the lower dosages, with shoulders or peaks at short chord lengths (<10  $\mu$ m), indicative of some fines not being captured in aggregates.

Large aggregates provide only a small number of counts to such distributions. The length square-weighted chord length distributions (Figure 4b) represent a volume-weighting and better reflect the extent of aggregation, although any fines then essentially become invisible. With each increment in dosage, the volume-weighted peak shifted to larger sizes and a higher intensity. Previous studies have shown that the sizes attained can be limited by the solid concentration and the applied shear conditions.<sup>50</sup> The importance of considering both unweighted and volume-weighted distributions toward fully understanding a flocculation response can therefore be seen.

Based on the results obtained from the cylinder settling tests, the most prominent differences between the ABA triblock copolymers and **RAB** were observed at the highest  $Ca^{2+}$ concentration of 0.50 M. **ABA7** was one of the top-performing flocculants among the ABA triblock copolymers and was therefore selected for direct comparison against **RAB** in continuous pipe flow flocculation, with the aggregate chord length distributions determined in real time as a function of flocculant dosage at three different solid concentrations in 0.50 M  $Ca^{2+}$  (Figure 5). Similar to that for the cylinder settling tests, four dosages ranging from 17 to 67 g/tds were employed. The axes for the unweighted and square weight counts in each plot were kept constant to allow for ease of analysis and direct comparison between the two polymers **ABA7** and **RAB**.

A comparison of the unweighted chord length distributions for the unflocculated kaolin distributions in Figure 5 shows that the presence of 0.50 M Ca<sup>2+</sup> clearly induces a level of aggregation. While the shift in size is not large (the mean unweighted chord length rose from 46 to 51  $\mu$ m across the dosage range), it would still represent a substantial reduction in the available surface area exposed to the dosed polymers and in part explains why polymeric flocculants with a molecular weight of 1 MDa were able to induce sedimentation rates larger than 5 m/h at quite low dosages.

The unflocculated distributions in Figure 5 also display an increase in counts as the kaolin concentration is raised, although it should be noted that FBRM counts will rarely give a linear relationship with concentration.<sup>49</sup> At the same time, the peak position clearly shifts to the left; this apparent detection of shorter chords at high solid concentrations would initially appear counterintuitive. The lower detection limit for FBRM is 1  $\mu$ m and is typically not very sensitive to particles <2  $\mu$ m, with the kaolin slurry expected to contain a significant fraction of particles of colloidal sizes. The signal processing algorithm requires reflected light pulses to rise and fall quickly before and after each particle, and higher solid concentrations may then increase the probability of overlapping particles that might otherwise be invisible to FBRM being measured as single chords, leading to the apparent shift in the peak to shorter chord lengths.<sup>c</sup>

Figure 5b represents the unweighted (solid lines) and length square-weighted (dashed lines) chord length distributions for the flocculation of 3 wt % kaolin slurries containing 0.50 M Ca<sup>2+</sup>, matching the cylinder setting conditions in Figures 2 and 3. Immediately obvious is that the magnitude and form of the observed responses to the applied dosages are very different from those in Figure 4. There is still a reduction in the unweighted counts, but they remain high, with only small shifts to longer chord lengths. The peaks in length square-weighted distributions do not shift at all (consistently around 45  $\mu$ m); instead, they just increase in intensity. Together, these observations are consistent with the polymers increasing the



Figure 5. Unweighted (solid lines) and length square-weighted (dashed lines) chord length distributions for the flocculation of the kaolin slurry with 0.50 M  $Ca^{2+}$  using polymers RAB and ABA7 (reaction time 9.2 s, mean shear rate 1270 s<sup>-1</sup>) at varying solid concentrations of (a) 1.5 wt %, (b) 3 wt %, and (c) 6 wt %.

capture of the finest particles within the slurries into small aggregates, but the size of such aggregates that can be attained

is limited by the polymer molecular weight and the applied shear.



**Figure 6.** Plausible schematic representation of (a) how the solution conformation of a random copolymer of AA and AM would be restricted by complexation with  $Ca^{2+}$  and (b) how high concentrations of  $Ca^{2+}$  are postulated to impact the activity of conventional anionic and ABA triblock copolymers.

The chord length distributions for **RAB** flocculation of 3 wt % kaolin slurries (Figure 5b) showed distinct changes with each increment in the flocculant dosage. In the case of **ABA7**, the response to dosage followed a similar general trend, but the change with each increment was slightly smaller. However, while the unweighted distributions did shift toward larger chord lengths, there was a greater growth in counts at approximately 20  $\mu$ m at the expense of the higher counts seen in the 30–80  $\mu$ m range with **RAB**. As a consequence, applying a length square-weighting to these distributions led to much smaller peak increases with dosage when compared to those for **RAB**.

To gain a better understanding of these responses, the above experiments at 3 wt % kaolin were repeated with the same flocculants and dosages at lower (1.5 wt% in Figure 5a) and higher (6 wt % in Figure 5c) solid concentrations and still maintaining a Ca<sup>2+</sup> concentration of 0.50 M. At 1.5 wt %, the trends for each dosage increment for both flocculants were effectively identical to those observed at 3 wt % kaolin. At 6 wt %, the unweighted counts were still reduced with increasing dosage but to a much smaller degree, and it can be seen that the peak in the unweighted chord length distributions were closer to 10  $\mu$ m, compared to 20  $\mu$ m at 1.5 and 3.0 wt %. This reflects the highly porous nature of the aggregates formed with the platelike kaolin particles, leading to a very high effective

volume fraction at quite low solid concentrations.<sup>50</sup> The efficient distribution of the polymers throughout the slurry becomes more difficult at higher solid concentrations.

An important observation is that the peak in the volumeweighted chord length distributions did not shift for any kaolin solid concentration for flocculation with **ABA7** or **RAB** at any dosage. This indicated that the limitation in aggregate size under the applied shear conditions is a consequence of the polymer molecular weight rather than the solid concentration; the latter a common factor for higher-molecular-weight polymers.<sup>47</sup>

**Implications.** It is important to emphasize that the two different experimental methods represent different aspects of the flocculation process. The cylinder settling tests determined the flocculation efficiency of the polymeric flocculants through settlement rate and supernatant turbidity as overall performance measures. The FBRM chord length distribution obtained from flocculation with the pipe reactor method captures the growth of aggregates under selected shear conditions to assist in understanding the unique performance characteristics of the ABA triblock copolymers. The latter essentially provides a snapshot of the aggregation state under turbulent shear conditions, whereas the former represents not only the initial turbulent mixing of the polymer and initiation of aggregation but also the subsequent further aggregate growth that takes

place under a milder shear. Considering these results together (i.e., contrasting the FBRM results under turbulence in Figure 5 with the overall performance data in Figures 2 and 3), it appears that the main advantages of the ABA triblock copolymers mainly manifest through still being able to provide additional growth under mild shear at higher  $Ca^{2+}$  concentrations.

For commercial anionic flocculants, it has been noted that the initial dissolution of powder products in solutions containing even low concentrations of  $Ca^{2+}$  severely impacts their activity.<sup>16</sup> While the dilution of optimally prepared flocculants into  $Ca^{2+}$  solutions immediately before dosing did have a detrimental effect, the diluted flocculant solutions could still form small aggregates and the restriction in activity only prevented larger sizes from being attained. This may provide useful insights into how flocculation progresses with the ABA triblock architecture and under which conditions its advantages may be fully realized.

Figure 6a represents how the solution conformation of a conventional flocculant similar in composition to **RAB** may be restricted by complex formation with  $Ca^{2+}$ , thereby reducing the potential for particle bridging.<sup>62</sup> In Figure 6b, this is also shown in terms of how the adsorbed conformation on a surface may be affected, with a high  $Ca^{2+}$  concentration limiting the extension away from the surface of polymer tails that provide the capacity to bridge among particles. The decline in settlement rates observed for flocculation with **RAB** in Figure 2c is then likely to be due to a significant reduction in further aggregate growth under reduced shear immediately after the last plunger stroke.

In contrast, the nonionic block within ABA7 may lead to a flatter overall adsorbed conformation at a low Ca<sup>2+</sup> concentration with the anionic tails ensuring that there is some extension away from the adsorbed surface. At a high Ca<sup>2+</sup> concentration, there will inevitably be complexation of the anionic tail blocks, but they remain a minor proportion of the full polymer chain length, and the nearest nonionic sections remain away from the adsorbed surface and are able to then provide bridging. Consequently, this characteristic led to decent settlement rates observed throughout the cylinder settling tests. In addition, based on the pipe reactor results, the ABA triblock copolymers were more selective toward capturing the fine particles within the slurry, thus resulting in very low turbidity values across all three concentrations of Ca<sup>2+</sup> employed. This characteristic is atypical of commercial polymeric flocculants and was proven to be beneficial toward clarifying the supernatant.

It can therefore be seen that the ABA triblock architecture can maintain flocculation efficiency, despite a high level of multivalent cations within a slurry. This demonstrates that such polymers may have considerable potential as tailing flocculants when there is a need for or a preference to undertake mineral processing in seawater or other highly saline liquors. Of course, this would require synthetic procedures to produce higher molecular weights than have been achieved in this study. There is also a need to extend the flocculation studies to establish the impact of using such flocculants on the structure of aggregates formed and how downstream properties (rheology, sediment compaction) may be affected.

# CONCLUSIONS

A total of eight novel ABA triblock copolymers (ABA1-ABA8) were employed in the flocculation of high-ionic-

strength kaolin slurries. The performance of these polymers was compared against that of three control polymers (PAA, PAM, and RAB) with similar molecular weights to understand how the polymer architecture affects flocculation efficiency in high-ionic-strength environments. Polymer RAB possessed a random copolymer architecture that is representative of current commercial flocculants and thus could be directly compared to the eight polymers bearing well-defined ABA triblock architectures.

A series of cylinder settling tests were performed at three  $Ca^{2+}$  concentrations (0.05, 0.10, and 0.50 M), where the settlement rate and the supernatant turbidity were evaluated as a function of flocculant dosages (ranging from 17 to 67 g/tds). The ABA triblock copolymers were able to consistently flocculate the kaolin slurry to achieve acceptable settlement rates, whereas the performance of **RAB** declined significantly at the highest  $Ca^{2+}$  concentration of 0.50 M, indicating that it was certainly compromised by the multivalent cations.

Turbulent pipe flocculation with an inline FBRM probe for real-time monitoring of flocculated aggregate sizes was used to contrast **RAB** with the best-performing ABA copolymer (**ABA7**) at a high calcium concentration. Both could form only small aggregates under turbulence, a reflection of their relatively low molecular weights. That both could still achieve useful settlement rates is an indication of the importance of additional aggregation that took place during cylinder settling after turbulent mixing; such aggregation for **RAB** was detrimentally affected by higher calcium concentrations, but the ABA copolymers appear largely unaffected. With further development, polymers bearing the ABA triblock architecture have strong potential for implementation into current industrial flocculation applications, particularly for high-ionicstrength environments.

## ASSOCIATED CONTENT

## **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.9b03689.

Overall schematic of the pipe reactor employed for the FBRM experiments; inlet design of the pipe reactor; cross section of the flow cell measurement chamber at the pipe reactor outlet; hydrodynamic volumes of the ABA triblock copolymers; and flocculation comparison among control polymers with different dispersities (PDF)

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#### Notes

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