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A Stimuli-responsive Hybrid Polymer for Enhanced Solid-liquid Separation of Industrial Effluents

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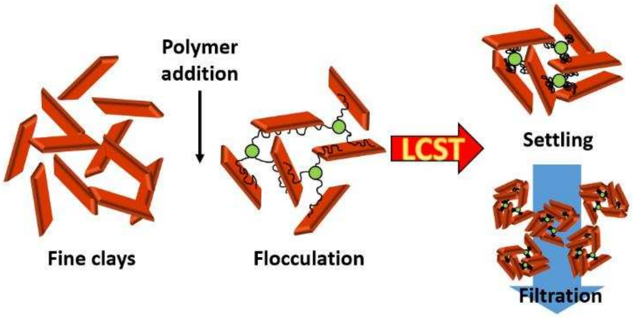
Abstract

In the current study, a novel stimuli-responsive hybrid polymer with aluminium hydroxide colloids incorporated into a cationic copolymer of N-isopropylacrylamide and N-[3-(dimethylamino)propyl] methacrylamide was synthesized to enhance the settling and filtration performance of fine clay suspensions. The conformation of the synthesized hybrid copolymer was shown to respond to changes in both temperature and pH. Compared with a cationic copolymer of similar structure without aluminium hydroxide colloids, settling and filtration rates were significantly enhanced using the hybrid copolymer, which is attributed to the synergy between the inorganic aluminium hydroxide cores and organic copolymer. While the ideal treatment protocol for the hybrid polymer involved the addition of the polymer at room temperature, followed by heating to 45°C for enhanced settling and dewatering, the synergistic effect between colloidal cores and polymer also allowed the hybrid polymer to perform well when added at temperatures above the LCST, demonstrating the robustness of the hybrid polymer to the process environment. The ideal treatment protocol resulted in optimal polymer-clay adsorption before inducing a coil-globule transition to form large and dense flocs, resulting in a porous filter cake.

Abstract Art



1. Introduction

Effective solid-liquid separation of fine particles, such as the treatment of fluid-fine sludge (e.g. bioreactor wastes) or mineral processing tailings, is an on-going environmental challenge for a number of process industries. Addition of polymeric flocculants to enhance fine particle aggregation produces fast-settling particles, but the loosely-packed flocs retain a significant amount of trapped water and the resulting soft sludge remains undesirable for long-term containment. Fine clays, typically less than 2 μm, are often difficult to settle and consolidate, producing voluminous wastes that are discharged to tailings ponds.[1,2] Between the 1960s and

2000s, tailings production increased from tens to hundreds of thousands of tons per day,[3] a direct consequence of increased demand for minerals and metals coupled with exploitation of lower grade ores. Such rapid growth in tailings generation has led to many large volume tailings ponds being constructed around the world.[1] While the significant amount of water retained in the tailings can be considered a critical commodity for industry and certain global regions, tailings ponds are an environmental hazard and an eyesore.[2] The 2019 incident in Brumadinho, Brazil once again highlights the catastrophic damage that results from the failure of a tailings dam. Not being an isolated incident in recent times, more efforts are needed to provide new strategies to rapidly dewater tailings, ensuring that the mined waste is stored in a more stable form to reduce the hazard associated with tailings disposal.[4]

Water recovery from fine tailings is necessary to reduce the volume of waste discharged and increase water recycled. Chemical treatment using coagulants and polymeric flocculants is often used by industry to accelerate the settling and dewatering of fine tailings.[5] While commercial flocculants such as polyacrylamides (PAM) generally produce large flocs which improve settling, these flocs are porous forming a low density sediment with a substantial amount of water retained. It is therefore highly desirable if not necessary to improve the floc characteristics by controlling the polymer chemical structure and functionality.[6,7]

Responsive polymers have distinct chemistry that enables conformational changes under the influence of a stimulus.[8,9] Temperature and pH responses are often preferred due to their ease for implementation in industrial processes. Poly(N-isopropylacrylamide) (pNIPAM) is a temperature-responsive polymer which exhibits a sharp temperature-induced transition from hydrophilic (extended coils) to hydrophobic (globules) as the temperature surpasses its lower critical solution temperature (LCST) of ~32 °C.[10] By exploiting this conformational change, the polymer can aggregate fines in the extended-state before densifying to form tightly-packed aggregates for settling and dewatering.[11-14] Incorporating polyelectrolytes via copolymerization can further increase the polymer-particle interaction.[15,16] Deng and Pelton used a copolymer of NIPAM and (methacrylamido)-propyltrimethylammonium chloride (MAPTAC) to flocculate TiO_2,[17] with enhanced consolidation demonstrated using a copolymer of N, N-dimethylaminopropylacrylamide (DMAPAA) and NIPAM.[18,19] Franks and coworkers incorporated dimethylaminoethylacrylate quaternary ammonium (DQA) into their NIPAM copolymer to flocculate silica particles.[20]

Hybrid polymers of organic and inorganic components at the molecular level represent an area of significant interest.[21] These hybrid polymers offer new opportunity to treat complex systems and outperform their individual counterparts. Recent research has demonstrated that hybrid polymers such as $Al(OH)_3$-polyacrylamide (Al-PAM) and $Fe(OH)_3$-polyacrylamide (Fe-PAM)[22-27] readily flocculate fine clays, with increased aggregation performance attributed to the combined effect of coagulation and flocculation by the inorganic and organic components, respectively.

In the current study, a novel inorganic-organic hybrid polymer with stimuli-responsive properties was synthesized. The novel hybrid polymer consists of the temperature- and pH-responsive cationic copolymers of NIPAM and N-[3-(dimethylamino)propyl]methacrylamide (DMAPMA), incorporated with aluminum hydroxide colloids. The research objective was to systematically evaluate the flocculation performance of the stimuli-responsive hybrid polymer and corresponding cationic copolymer of similar molecular weight and composition.

2. Materials and Methods

2.1. Materials

Kaolinite (K2-500) was purchased from Fisher Scientific. The d_{50} particle size was determined using a particle size analyzer (Malvern Mastersizer 2000, UK) to be 3.8 μm with a uniformity coefficient (d_{60}/d_{10}) of 31.5, confirming a broad particle size distribution (d_{90} = 15.6 μm).

To synthesize the desired responsive organic-inorganic hybrid polymers, monomer N-isopropylacrylamide (NIPAM) (99%) was purchased from Fisher Scientific, while monomer N-[3-(dimethylamino)propylmethacrylamide (DMAPMA) (> 99%), accelerator N, N, N', N'-tetramethylethylenediamine (TEMED), initiator ammonium persulfate (APS), aluminum chloride (99%) and ammonium carbonate (> 99%) were purchased from Sigma-Aldrich. All chemicals were used without further purification.

2.2. Synthesis of p(NIPAM-co-DMAPMA)

The cationic copolymer p(NIPAM-co-DMAPMA) (abbreviated to CP) was synthesized by free radical polymerization in the presence of redox initiators, as described by Sakohara and Nishikawa.[19] CP was synthesized in-house where p($NIPAM_{95}$-co-$DMAPMA_5$) (CP05) contained 5 mol.% DMAPMA. 5 g of monomers were used for the synthesis of the copolymer. In a 100 mL 3-necked glass flask, monomers were dissolved in 50 mL Milli-Q water (resistivity of 18.2 MΩ.cm) with 45 μL of TEMED added as a reaction accelerant. The mixture was continuously sparged with nitrogen (grade 5.0) and stirred at 250 rpm, while the reactor flask was kept dark to prevent unwanted light exposure to the reactants. After 1 h of N_2 purging, 2.3 mL of APS dissolved in Milli-Q water (10 g/L) was added to the mixture at a rate of 1 mL/min to initiate polymerization. N_2 purging and mixing were stopped 10 min after initiator addition. The reactor flask was then sealed, and the polymerization reaction was allowed to proceed for 2 h at room temperature. The synthesized polymer was in the form of a transparent gel which was diluted to 0.5 g/L using Milli-Q water. The polymer solution was then purified using seamless cellulose dialysis tubing (Fisher Scientific) with Milli-Q water for 48 h, which retained material with molecular weights higher than 12,000 Da. The purified solution was freeze-dried to obtain the final product.

2.3. Synthesis of $Al(OH)_3$-p(NIPAM-co-DMAPMA) Hybrid

Aluminum hydroxide colloids were prepared by adding solutions of ammonium carbonate to aluminum chloride under vigorous mixing.[22] 25 g of 0.1 M $AlCl_3$ solution and 50 g of 0.1 M $(NH_4)_2CO_3$ solution were prepared in two separate 250 mL beakers. Using a peristaltic pump, 36 g of $(NH_4)_2CO_3$ solution was added to the $AlCl_3$ solution at a rate of 0.5 g/min, with the mixture being stirred continuously at 500 rpm. Following addition, the mixture was stirred at 300 rpm for 1 h to complete the reaction. The $Al(OH)_3$ colloids were prepared one day prior to synthesis of the desired hybrid polymer, $Al(OH)_3$-p(NIPAM-co-DMAPMA). Particle size and zeta potential of the prepared aluminum hydroxide colloids were measured using a ZetaSizer Nano ZS (Malvern, UK), before synthesizing the inorganic-organic hybrid polymer, see Table 1.

Table 1. Physical properties of aluminum hydroxide colloids.

pH	5.58
Intensity-averaged particle size (nm)	34.2
PDI	0.224
ζ-potential (mV)	39.3

The hybrid polymer, $Al(OH)_3$-p($NIPAM_{95}$-co-$DMAPMA_5$) (Al-CP05) (Figure 1), was synthesized using the procedures described for CP, with a slight difference of replacing Milli-Q water with 50 mL of the prepared $Al(OH)_3$ colloidal suspension (0.3 wt.%).[22] Following polymerization, the white gel of the formed hybrid polymer was diluted with Milli-Q water to 0.5 g/L and purified by dialysis. The final polymer product was obtained by drying the product at 45°C.

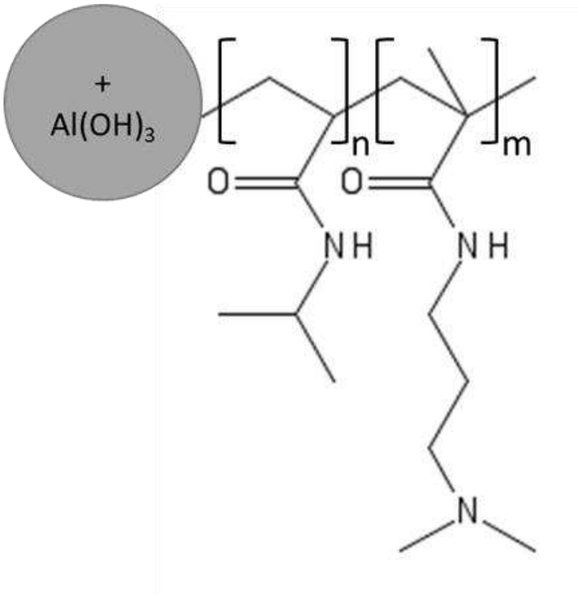


Figure 1. Molecular representation of Al-CP05.

2.4. Molecular Weight Determination of Synthesized Polymers

The molecular weights of the synthesized polymers were estimated using an Ubbelohde viscometer (CANNON Instrument Company, USA) to measure the intrinsic viscosity (as a function of the polymer concentration) of the polymer in tetrahydrofuran solution at 27 °C. The viscosity-average molecular weight ($\overline{M}_v$) is then related to the intrinsic viscosity ($[\eta]$) by:[28]

$$[\eta] = 9.59 \text{ x } 10^{-3}\overline{M}_v{}^{0.65} \tag{1}$$

The measured intrinsic viscosities and polymer molecular weights are summarized in Table 2, along with the aluminum content measured by atomic absorption spectrometry (Varian SpectrAA 220FS, Australia).

2.5. Lower Critical Solution Temperature (LCST) of Synthesized Polymers

For the temperature-responsive polymers the solution was clear below the LCST and became turbid as the temperature exceeded the LCST, confirming the hydrophilic-hydrophobic transition of the synthesized polymers. A turbidimeter (DRT-15CE, HF Scientific, USA) was used to accurately determine the LCST of each polymer, which in the current study was defined as the mid-point of the transition zone of the turbidity-temperature dependence curve (see Table 2). The turbidity was expressed in Nephelometric Turbidity Unit (NTU). Further characterization of the two synthesized polymers, including the conductivities of the polymer solutions (Figure S4) and IR spectra (Figure S5) was performed with the results being provided in the Supporting Information.

Table 2. Polymer composition, intrinsic viscosity, molecular weight, LCST and aluminium content of CP05 and Al-CP05.

Polymer	Abbreviation	$[\eta]$ (mL/g)	$\bar{M}_v$ (MDa)	$LCST_{pH8.5}$ (°C)	Al content (wt.%)
p(NIPAM$_{95}$-co-DMAPMA$_5$)	CP05	135	2.4	38	-
Al(OH)$_3$-p(NIPAM$_{95}$-co-DMAPMA$_5$) hybrid	Al-CP05	125	2.1	37	0.09

Note: monomer subscript represents molar percentage.

2.6. Settling and Filtration Testing

Clay suspensions at 5 wt. % (95 g) solids were prepared by dispersing kaolinite in pH adjusted Milli-Q water of 8.5. A 2000 ppm flocculant solution was prepared one day prior to its use. For each experiment (settling and filtration), the 5 wt.% suspension was mixed using a mechanical overhead stirrer (IKA RW20, Germany) with a four-blade axial flow impeller attachment (3.8 cm dia. and 45° pitched). To fully disperse the particles the suspension was mixed for 5 min at 500 rpm at the desired temperature. The agitation speed was then adjusted to the pre-determined value for each flocculant, 350 to 400 rpm for CP05 and 300 rpm for Al-CP05, with the optimum mixing speed determined by the highest initial settling rate (ISR) obtained by adding 50 ppm polymer at temperatures below or above the LCST. The flocculant solution was then added at 0.1 mL/s using a micropipette.

For settling tests, the flocculated suspension was adjusted to the target temperature before transferring the suspension to a 100 mL graduated cylinder for visual assessment of the settling rate. The settling cylinder was inverted five times and placed in a water bath of equivalent temperature. The settling rate was determined by observing the time-dependent position of the mudline (supernatant-suspension interface). The ISR was determined from the slope of the mudline height versus time curve. Following settling, the turbidity of the supernatant was measured using the DRT-15CE turbidimeter. For consistency, the supernatant was sampled and measured 15 min after the settling test.

For filtration tests, the flocculated suspension was adjusted to the target filtration temperature and transferred to a laboratory filter press (Fann Instrument Company LPLT 300, USA) with a filtration area of 45.8×10^{-4} m^2. For high temperature filtration the elevated temperature was maintained by a band heater enclosing the filter press. Special hardened filter paper (N87000, Fann Instrument Company) with particle retention of 2-5 µm was used as the filter medium. Filtration was conducted under a constant gauge pressure of 15 kPa using compressed air and the mass of filtrate was monitored as a function of time by an electronic balance to obtain the filtration curve. The filtration rate was determined by the slope of the filtration curve dm/dt which remained almost constant during the initial stages of filtration. After 100 s of filtration the wet cake was dried in a well-ventilated oven at 110 °C to a constant mass such that the final moisture content of the filter cake could be determined. For a better comparison to previously published data, the specific resistance to filtration (SRF) in m/kg was calculated as a measure of the filterability of a suspension. Assuming the cake is incompressible at constant pressure drop, the integrated form of Darcy's cake filtration equation with boundary condition of V = 0 at t = 0 can be expressed as:[29]

$$\frac{t}{V} = \frac{\mu_f\ c\ SRF}{2A^2\Delta P}V + \frac{\mu_f\ R_m}{A\Delta P} \tag{2}$$

and the slope (b) of the t/V versus V plot can be used to determine the SRF:[23]

$$SRF = \frac{2\Delta P A^2}{\mu_f c}b \tag{3}$$

where ΔP is the pressure drop in Pa; R_m the resistance of filter medium; A the area of filter in m^2, μ_f the viscosity of filtrate in Pa·s, c the mass of dry cake solids per filtrate volume in kg/m^3, and b the slope of t/V versus V plot.

Different mixing and settling protocols were considered to demonstrate the switching potential of the synthesized hybrid polymer. For room temperature mixing and room temperature settling/filtration (RM-RS/F), both polymer-suspension mixing and settling/filtration were conducted at room temperature (23 °C). For room temperature mixing and high temperature settling/filtration (RM-HS/F), mixing was conducted at room temperature (23 °C) and settling/filtration at 45 °C. Both mixing and settling/filtration were conducted at 45 °C in the high temperature mixing and high temperature settling/filtration (HM-HS/F) protocols.

The flocculation performance of the synthesized polymers was assessed by the ISR and turbidity of the supernatant, while the dewatering performance was quantified by the filtration rate, SRF and final moisture content of the filter cake. Each experiment was repeated three times with the averaged data reported.

2.7. Quartz Crystal Microbalance with Dissipation (QCM-D)

QCM-D (Q-Sense E4, Sweden) was used to study the temperature response of CP05. The working principles of QCM-D can be found elsewhere.[30] A silica QCM sensor was cleaned using 2% SDS solution, UV-ozone for 20 min and rinsed thoroughly with Milli-Q water. With the temperature at 20°C, a solution of 500 ppm CP05 in Milli-Q water at pH 8.5 was pumped in to the QCM cell to adsorb on the silica sensor. With a deposited CP05 layer formed (determined by a plateau in frequency and dissipation signals), Milli-Q water was then pumped through the QCM cell to remove excess polymer. Once a new equilibrium had been reached the flow of Milli-Q water was stopped and the experiment re-started (find new f and D) with the resonance properties set to zero values. With no fluid flow, the QCM cell was then heated from 20 to 50°C at 5°C increments, ensuring that the resonance properties had stabilized before each step change. A second QCM cell was run in parallel as a control experiment with the frequency and dissipation signals of a blank QCM silica sensor (no deposited CP05) recorded for the same temperature sweep. Changes in polymer confirmation resulting from a 5°C step increase were inferred from $\Delta f_{CP05} - \Delta f_{water}$ and $\Delta D_{CP05} - \Delta D_{water}$ signals, with the water-only signal correcting for changes in fluid viscosity and density.

3. Results and Discussion

3.1. CP05 Cationic Copolymer

The coil-globule transition of the temperature-responsive cationic polymer (CP05) was measured by QCM-D. Figure 2 shows the relative changes in frequency ($\Delta f_{CP05} - \Delta f_{water}$) and dissipation ($\Delta D_{CP05} - \Delta D_{water}$) caused by the adsorbed CP05 on QCM-D sensor and successive increase in temperature of the QCM-D measurement cell. In the low temperature range (20 – 35°C), $\Delta f_{CP05} - \Delta f_{water}$ and $\Delta D_{CP05} - \Delta D_{water}$ values are close to zero with a slight decrease in ΔD, indicating a negligible change in the mass of polymer adsorbed and the conformation of the adsorbed polymer. The change observed in Δf and ΔD in response to temperature change is thus dominated by bulk fluid properties (i.e. changes in fluid density and viscosity). As the temperature approaches the LCST, changes in $\Delta f_{CP05} - \Delta f_{water}$ and $\Delta D_{CP05} - \Delta D_{water}$ become sensitive to the fluid temperature, showing an increase in $\Delta f_{CP05} - \Delta f_{water}$ and a decrease in $\Delta D_{CP05} - \Delta D_{water}$ with increasing the temperature of the fluid. Since the polymer remained adsorbed on silica sensor surfaces as shown in Figure S1, the observed increase in $\Delta f_{CP05} - \Delta f_{water}$ arises most likely from the release of the solvation water during the transition of the polymer from a hydrated swollen-state (coil) to a dehydrated dense-state (globule) as the temperature increases to above the LCST, leading to a more compact layer of adsorbed polymer as shown by a decrease in $\Delta D_{CP05} - \Delta D_{water}$.[30] The QCM-D results would suggest that the LCST for CP05 is in the range 35 – 40°C, in good agreement with turbidity measurements (LCST = 38°C, Table 2).

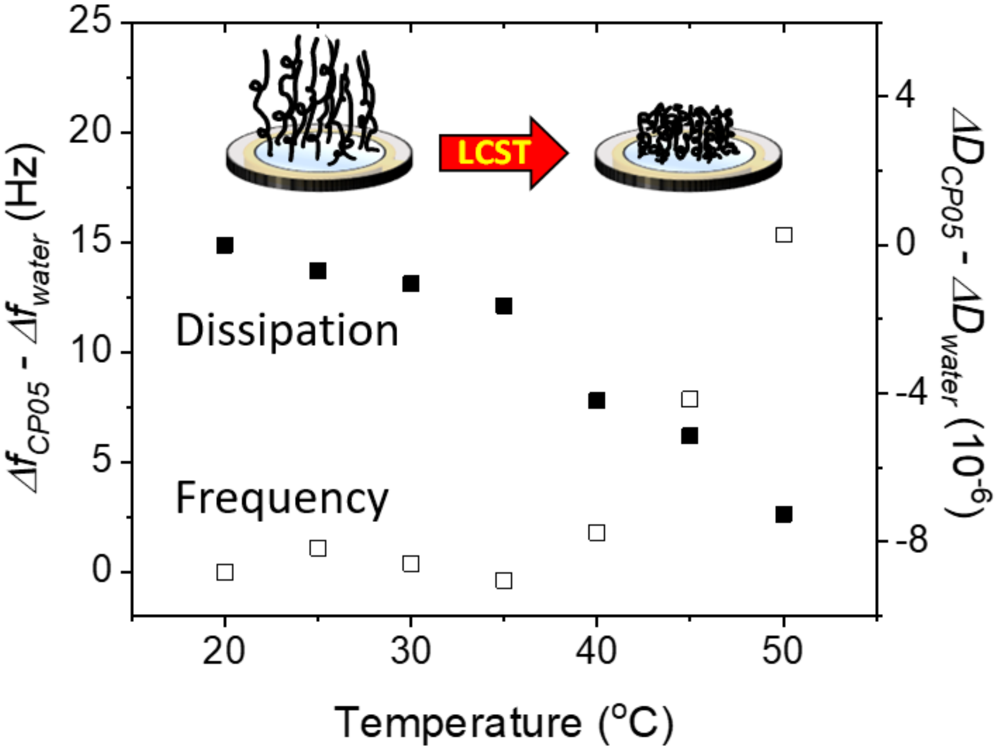


Figure 2. Relative changes in frequency and dissipation ($\Delta f_{CP05} - \Delta f_{water}$ and $\Delta D_{CP05} - \Delta D_{water}$) as a function of the QCM-D measurement cell temperature. The LCST of CP05 is in the temperature range 35 – 40°C.

The flocculation of 5 wt.% kaolinite suspensions by CP05 and its stimuli-responsive behavior for improved performance was assessed as a function of the three testing protocols, see Figure 3. For low polymer concentration (10 ppm), all the ISRs were slow, suggesting a substantial underdose of polymer. Flocculation performance improved with increasing polymer concentration, and an optimum ISR was attained at ~100 ppm. The influence of the testing protocol was magnified at higher polymer concentrations with the flocculation performance decreasing in the order RM-HS > RM-RS > HM-HS. RM-HS immediately demonstrates the benefit of flocculating with a stimuli-responsive polymer. Details of such dependence on conformational changes are outlined in the discussion section, but good flocculation, followed by floc densification leads to higher settling rates compared to non-responsive polymers (i.e. akin to the case of RM-RS). The worst performing system HM-HS is a direct consequence of the globule conformation of CP05 not being favorable to adsorb kaolinite particles. Many of the available binding sites are inaccessible, hence flocculation efficiency is low. For homopolymers such as pNIPAM, it has previously been reported that polymer chains tend to self-aggregate rather than adsorb on particle surfaces when added at temperatures above the LCST.[20]

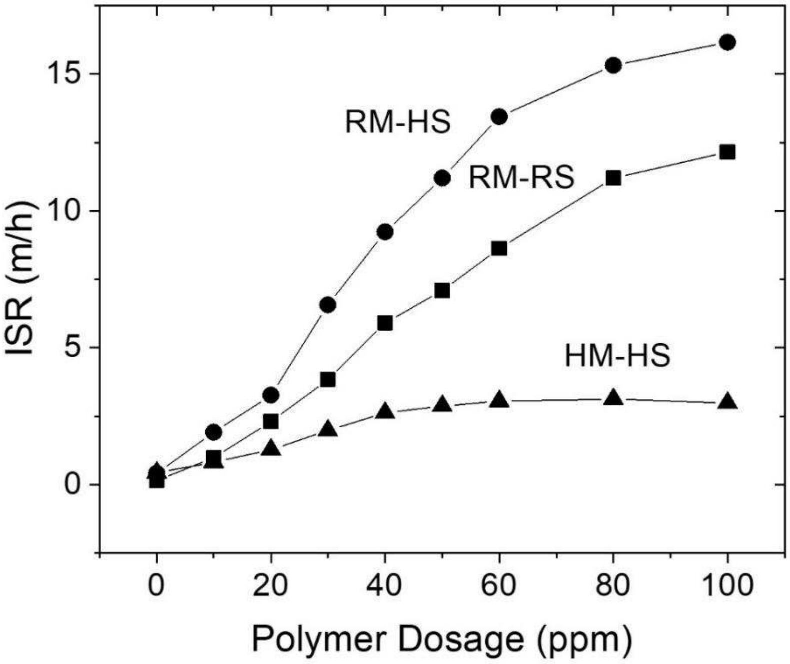


Figure 3. Initial settling rates of flocculated kaolinite suspensions (5 wt.%) as a function of CP05 dosage and testing protocol.

Incorporation of DMAPMA in the NIPAM backbone provides pH sensitivity with the ionizable functional groups of DMAPMA able to donate or accept protons. The effect of pH on CP05 LCST is shown in Figure 4a, with the LCST decreasing at higher pH (more basic). An 18°C shift in the LCST was measured between pH 8 and 11. At high pH the polymer becomes more hydrophobic due to deprotonation of the amide groups, reducing the LCST. The dual stimuli response (temperature and pH) of CP05 provides greater durability of the polymer, with the LCST tuned by controlling pH.

The ISR of flocculated 5 wt.% kaolinite suspensions was considered for the optimum testing protocol (RM-HS) and as function of pH (Figure 4b). The highest settling rate was measured at pH 8.5 with reduced performance as the pH was adjusted to more acidic and basic conditions. To better understand the pH-dependent ISRs, zeta potentials of silica particles were measured in 100 ppm CP05 solution (Figure 4c). To measure the charge on the polymer, CP05 was first adsorbed on silica at neutral pH with excess polymer being removed by washing. The adsorption of CP05 caused charge reversal of silica, suggesting not only positive charge of polymers, but also specific binding and significant adsorption of positively charged polymer on silica surfaces. The pH-dependent zeta potentials give some insights into the performance of polymers. At high pH, deprotonation of DMAPMA (pKA = 8.9) will reduce the cationic charge of CP05, and hence reduce the affinity of the polymer on negatively charged kaolinite particles (predominantly interacting with kaolinite basal planes). At pH 11 which is the LCST of the polymer at ~ 30 °C, the polymer becomes less solvated than at pH 8.5, reducing the number of binding sites available and hence resulting in poor flocculation of kaolinite particles (see previous discussion on testing protocols).

Alternatively, in acidic conditions, protonation of the amide group produces a highly hydrophilic polymer, however, flocculation performance reduces due to a weakened interaction potential between CP05 and the slightly negatively charged kaolinite. Moreover, at pH 8 the LCST is approaching 50 °C with the polymer displaying weak temperature sensitivity, thus following the protocol RM-HS (high temperature = 45 °C), only partial densification of the floc is likely to occur. Based on these findings the remaining study was conducted at pH 8.5.

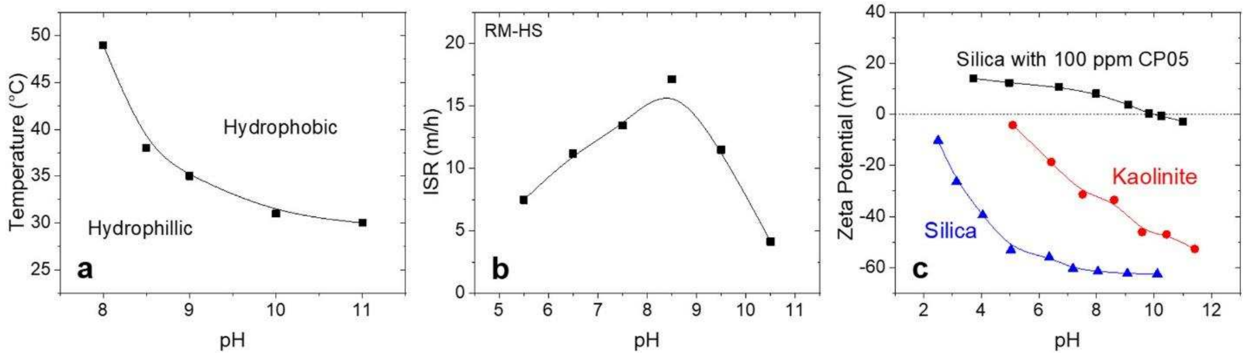


Figure 4. Effect of pH on the (a) LCST of 2000 ppm CP05 solution, (b) initial settling rate of 5 wt.% kaolinite suspensions with 100 ppm CP05, and (c) zeta potential (ζ) of kaolinite, silica and silica particles with 100 ppm CP05. ζ measured in 10 mM KCl solution at 25 °C.

3.2. Al-CP05 Hybrid Polymer

While CP05 is an effective flocculant for kaolinite suspensions, it is anticipated that the hybridization of CP05 with an inorganic coagulant ($Al(OH)_3$) can further improve flocculation performance. The temperature response of CP05 and inorganic-organic hybrid polymer (Al-CP05) were compared as shown in Figure 5a. The LCST of the hybrid Al-CP05 polymer was found to be slightly lower than that of CP05, with Al-CP05 exhibiting a more gradual transition from translucent to opaque state than CP05. The gradual change in turbidity likely arises from the formation of a more hydrophilic and/or polydispersed polymer due to the incorporation of aluminum hydroxide colloids.

The ISRs of 5 wt.% kaolinite suspensions flocculated by CP05 and Al-CP05 are shown in Figure 5b. To illustrate the synergistic role of incorporating $Al(OH)_3$ colloidal particles into the hybrid flocculation, the settling performance for the co-addition of CP05 + $Al(OH)_3$ is shown in Figure S2 for comparison. Dosing at the optimum polymer concentration (100 ppm), the ISRs of flocculated suspensions can be compared for the different testing protocols. Both polymers exhibited the same dependence on testing protocol with RM-HS and HM-HS producing the best and worst flocculation/settling results. However, the ISRs for Al-CP05 consistently exceeded those for CP05, with the ISR at 100 ppm measured to be ~100 m/h, six times greater than the ISR measured for CP05. Since Al-CP05 and CP05 were synthesized with comparable molecular weights and equivalent monomer ratio, the superior performance of Al-CP05 can be linked to the increased charge density of the hybrid polymer which promotes effective dispersion of the polymer chains around the trivalent colloid core (electrical double layer repulsion). As such, optimum interaction (maximum number of adsorption sites) of the hybrid polymer with negatively charged kaolinite particles can be achieved.[23] More interestingly, Al-CP05 was shown to maintain very high settling rates even when the polymer was added at temperatures above the LCST (HM-HS). This superior performance likely indicates that the aluminum hydroxide core increases the hydrophilicity of the hybrid-polymer (as confirmed by turbidity measurements, see Figure 5a), which in addition to the charged aluminum hydroxide core, minimizes the full extent of polymer self-aggregation. Such characteristic is a unique property of Al-CP05 compared to CP05 (see Figure 3, HM-HS) and other temperature-responsive flocculants (e.g. pNIPAM), improving the flocculant robustness and applicability to perform in challenging process environments.

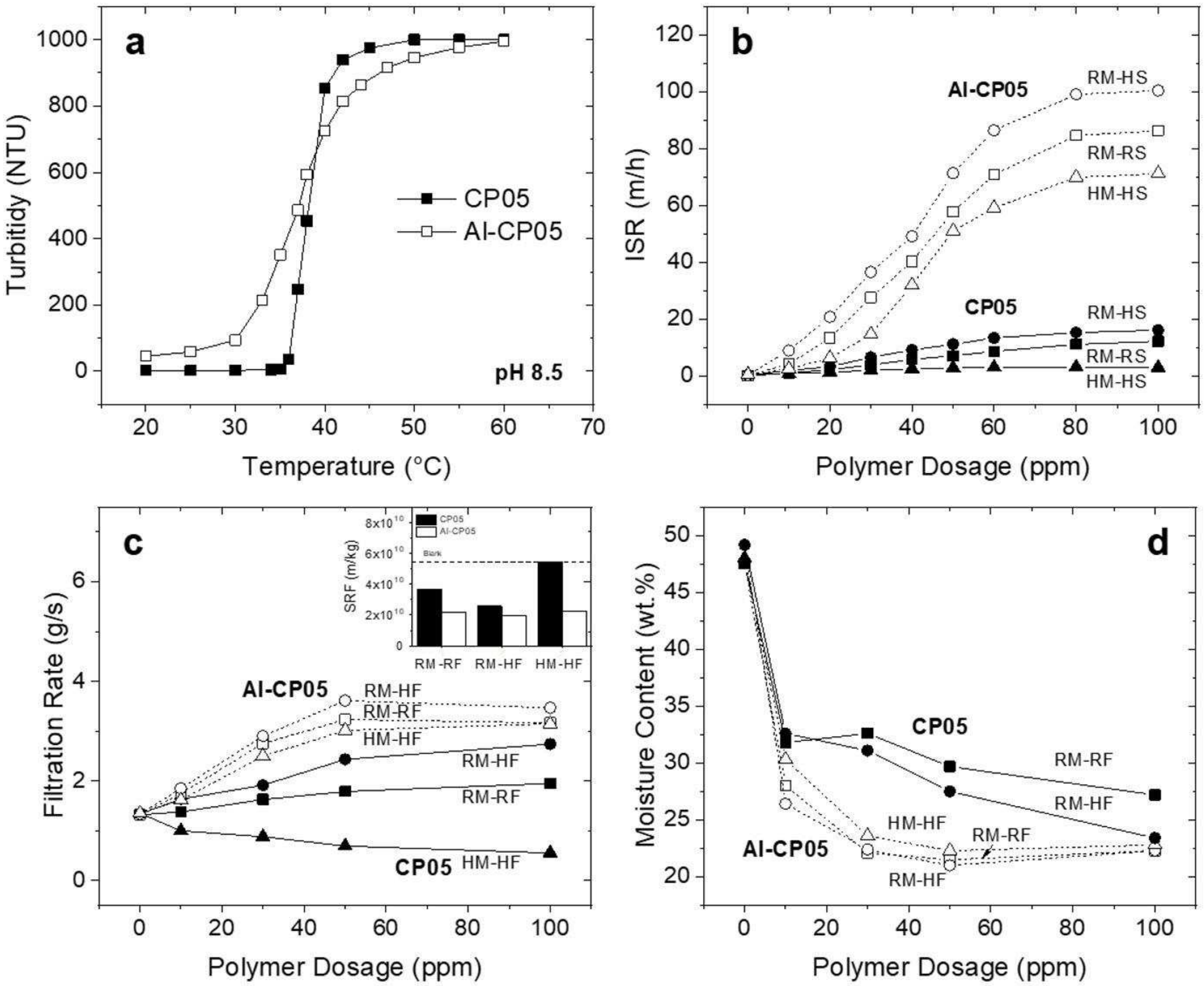


Figure 5. Performance comparison of CP05 and Al-CP05: LCST of polymer determined by turbidity-temperature curves (a); initial settling rate of 5 wt.% kaolinite suspensions (b); filtration rates of flocculated sediments with the specific resistance to filtration shown inset (dash line represents no polymer addition) (c); and moisture content of filter cakes after 100 s filtration time (d).

Supernatant turbidities were measured following 15 min settling. Without polymer addition the supernatant appeared as a murky brown suspension. Following flocculation by either CP05 or Al-CP05 the clarity of the supernatant significantly improved (Figure S3). For testing protocols RM-RS and RM-HS the difference in turbidities for both polymers was negligible, suggesting good flocculation performance. Those differences in ISR (Figure 5b) would have been mitigated by sampling the supernatant after 15 min settling. While HM-HS increased the supernatant turbidity of a CP05 flocculated suspension, the robust performance of Al-CP05 at high temperature was again demonstrated by very low turbidities comparable to those measured for room temperature flocculation. The effectiveness of Al-CP05 to flocculate ultra-fines in all conditions tested can partly be attributed to the electrostatic interaction between the aluminum hydroxide colloid and kaolinite particles, and the previously discussed increased charge density of the polymer.

Sediments formed by flocculating with CP05 and Al-CP05 were then filtered and the filtration rate, specific resistance to filtration (SRF) and filter cake moisture content compared, see Figure 5c and d. Similar to the settling tests, the filtration performance was sensitive to the testing protocol, and the filtration rate improved in the order HM-HF < RM-RF < RM-HF (observed for both CP05 and Al-CP05). Regardless of the testing protocol, Al-CP05 outperformed CP05 (filtration rate and SRF). An optimum filtration rate of 3.6 g/s was measured for 50 ppm Al-CP05 by protocol RM-HF. This corresponded to a SRF of 2.0×10^{10} m/kg, lower than the SRF of a dispersed (no flocculant added) 5 wt.% kaolinite suspension (5.5×10^{10} m/kg). For comparison, SRFs of 8.2×10^{10} and 1.5×10^{12} m/kg have been reported for tailings containing 4.2 and 40.1 wt.% fines, respectively.[23] A lower SRF confirms a more permeable filter cake and thus improved filtration. For CP05 polymer, the treatment protocol was shown to have a marked effect on filtration performance, unlike Al-CP05, with performance diverging as the polymer dosage increased. In particular, HM-HF for CP05 showed a worsening performance with increasing polymer concentration.

As anticipated, the moisture content of the filter cake corresponded to those changes in filtration rate, where increased filtration rates produced drier sediments. The protocol RM-HS produced the driest sediments as the hydrophobic nature of the flocs facilitated dewatering. The Al-CP05 hybrid polymer outperformed CP05, producing the lowest moisture content of 21 wt.% at 50 ppm Al-CP05, reduced from ~48 wt.% without polymer addition. At 50 ppm, the moisture content of Al-CP05 treated sediment was ~6 wt.% lower than the CP05 treated sediment, although the moisture content of the CP05 treated sediment could be lowered to 23.5 wt.% by doubling the polymer concentration. As shown in Figure 5c, the filtration protocol HM-HF for CP05 produced extremely poor filtration rates, progressively worsening from zero polymer addition. Reduced performance resulted from poor flocculation of ultra-fines and increased blinding of the filter medium, as such the moisture content for this system was not considered.

3.3 Comparison of Polymer Performances

The benefit of using Al-CP05 has been demonstrated with the optimum performance to treat suspended fine solids in water achieved by utilizing the temperature switch of the hybrid polymer, see Graphical Abstract. Based on the QCM-D and flocculation results, the hybrid polymer is to be added at temperatures below the LCST so that the polymer chains are fully extended, exposing the aluminum hydroxide core and maximizing the number of polymer-particle binding sites. Following flocculation, the floc can be densified by increasing the temperature above the LCST. Under such conditions the extended polymer structure recoils towards the aluminum hydroxide core, densifying the floc and squeezing retained water from the floc. The effective increase in floc density promotes higher suspension settling rates. In a similar study using a temperature-responsive inorganic-organic hybrid polymer, Al-NIPAM which incorporates the $Al(OH)_3$ core with pNIPAM (major component of the CP05 and Al-CP05 polymers), the floc size measured by focused beam reflectance measurement (FBRM) was shown to be almost unchanged at temperatures below the LCST of the polymer (34°C). At temperatures above the LCST, the measured floc size was found to decrease with further increasing the temperature. Despite this decrease in floc size, an increase in ISR was observed, which resulted from densification of the formed flocs.[31]

Due to similarities in initiating the polymerization, it is expected that Al-CP05 exhibits a similar star-like structure to Al-PAM. The star-like polymer structure produces improved filtration performance from induced pelleting flocculation and the formation of mushroom type flocs.[23,32] Such structures are also thought to form with Al-CP05, with the temperature switch producing enhanced floc densification and filtration governed by fluid flow through the network of pellet-like flocs.

Optimal polymer dosages were evaluated based on the two performance criteria: settling and filtration. For CP05, a polymer concentration in excess of 100 ppm was required to result in the best settling and filtration rates. For Al-CP05, the optimal polymer concentrations were lower with the maximum settling and filtration rates measured for 100 ppm and 50 ppm dosages, respectively. Although there is slight discrepancy in the optimum Al-CP05 dosage, 50 ppm can be considered the optimum since the settling rate was shown to be in excess of 70 m/h, already quadruple the settling rate of CP05 at 100 ppm.

A summary of performance properties of Al-CP05, other conventional and pNIPAM-based flocculants is provided in Table 3. While the comparison is interesting, direct comparison of the settling and filtration data should be carefully considered because flocculation and dewatering performances can be dependent on test conditions. When compared to conventional polymers such as anionic HPAM and non-ionic polyethylene oxide (PEO), hybrid polymers (Al-PAM and Al-CP05) have the added advantage of producing larger flocs of controllable floc structure due to contributions from the organic flocculant and inorganic coagulant. This has been exemplified by the low supernatant turbidity and enhanced filtration performance when using Al-PAM.[23,24]

Table 3. Flocculation performance of previously studied polymers.

Polymer (Mw)	Susp. (pH)	Dosage	ISR	Turbidity	Filtration	Refs.
PEO (2.5 MDa)	8 wt.% kaolinite (7.5)	500 g/t	12.5 m/h (40 °C)	-	-	(33)
HPAM (2.7 MDa) 30% Anionic	8 wt.% kaolinite (7.5)	500 g/t	~5.7 m/h	-	-	(33)
PEO (2.5 MDa)	8 wt.% kaolinite (7.5)	1000 g/t	65 m/h	-	-	(34)
HPAM (2.7 MDa) 30% Anionic	8 wt.% kaolinite (7.5)	1000 g/t	~10.8 m/h	-	-	(34)
HPAM (17.5 MDa) ~27% Anionic	13.5 wt.% oil sands tailings, 40.1% solids < 44 µm (8.5)	30 ppm	~42.8 m/h	470 (10 min)	No filter cake formed	(23)
HPAM (17.5 MDa) ~27% Anionic	10 wt.% mature fine tailings, 96% solids < 44 µm (8.5)	100 ppm	8.8 m/h	162 NTU (5 min)	0.1 g/s (75 ppm)	(24)
Al-PAM (2.0 MDa)	10 wt.% mature fine tailings, 96% solids < 44 µm (8.5)	75 ppm	6.25 m/h	156 NTU (5 min)	0.6 g/s, 23 wt.% (10 min)	(24)
pNIPAM (3.2 MDa)	10 wt.% kaolinite (8.6)	500 ppm	2 m/h (40 °C)	N/A	-	(12)
pNIPAM (0.324 MDa)	10 wt.% mature fine tailings (8)	750 ppm	~3.6 m/h (50 °C)	~410 NTU (24 h)		(35)
p(AEMA-st-NIPAM) (0.961 MDa)	10 wt.% mature fine tailings (8)	1000 ppm	4.7 m/h (50 °C)	~170 NTU (24 h)	-	(35)

Al-CP05* (2.1 MDa) 0.09 wt.% Al	5 wt.% kaolinite (8.5)	50 ppm	71 m/h (45 °C)	5.6 NTU (15 min, 60 ppm)	3.6 g/s, 21 wt.% (100s)	N/A

*current study

Flocculation studies using pNIPAM have shown enhanced floc densification when the temperature was raised above the LCST, following flocculation at temperatures below the LCST.[12,36] However, dosages were generally high and polymer addition was limited to temperature conditions below the LCST due to the non-ionic nature of pNIPAM. The current Al-CP05 polymer overcomes that issue with excellent performance characteristics observed at substantially lower flocculant dosages regardless of the temperature protocol. The dual stimuli response, plus the inorganic-organic structure produced excellent performance characteristics when compared to alternative hybrid and homopolymers. The outstanding performances of Al-CP05 can be attributed to the hybrid polymer structure that modulates the polymer conformation and provides a dual effect of coagulation and flocculation to capture and retain fines. As demand for wastewater treatment continues to grow,[37] the development of novel flocculants, such as Al-CP05, is essential to meet and exceed environmental standards.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publication website at DOI:

S1. Steady state frequency and dissipation values from adsorption of CP05 onto silica; S2. Initial settling rate of 5 wt.% kaolinite suspensions by a blend of CP05 and $Al(OH)_3$; S3. Turbidity of supernatants after 15 min settling of 5 wt.% kaolinite suspensions with (a) CP05 and (b) CP05+Al and (c) Al-CP05; S4. Conductivity of (a) CP05, (b) CP05+Al and (c) Al-CP05 in DI water at varying polymer concentrations; S5. IR spectra of CP05 and Al-CP05: (a) from 500 to 4000 cm^{-1} and (b) from 500 to 1200 cm^{-1}.

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Notes

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