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Cationic hydrolytically degradable flocculants with enhanced water recovery for oil sands tailings remediation

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Micellar radical polymerization of a short-chain polyester macromonomer, polycaprolactone choline iodide ester methacrylate (PCL_nChMA), is used to produce a new cationic flocculant that becomes more hydrophobic in response to hydrolytic degradation. The cationic tips of the comb-like poly(PCL_3ChMA) accelerate the settling rate of oil sands tailings, while hydrolytic degradation of the polyester grafts reveals the hydrophobic segments that reduce capillary suction time by 30 %. This technology combines the material properties of polyesters with the productivity of radical polymerization to make dual functional flocculants with characteristics that can be easily tuned to control flocculation performance, such as polymeric cation density, hydrophobic content, and polymer architecture.

1. Introduction

During the last 50 years of oil sands mining operations in Canada, approximately 830 million cubic meters of tailings have accumulated in ponds that cover an area of approximately 176 km².^[1] Oil sands tailings comprise the by-product slurry from the bitumen extraction process, which is discharged as an aqueous suspension of pH 8-9 containing coarse sands, fine solids, clays, and fugitive bitumen.^[2-4] These tailings ponds pose two serious environmental concerns: they hold a substantial amount of unrecovered process water, and the vast area of land they occupy cannot be reclaimed.

Typically, oil sands tailings are treated with high molecular weight (MW) water-soluble polymers that flocculate and dewater the resulting sediment.^[5-7] Current polymeric flocculation technologies are centered on commercially available polyacrylamide (PAM) grades, as these exhibit reasonably high settling rates, and have been extensively employed in other industries (e.g. paper making, mining, *etc.*).^[1] However, the resulting sediments are difficult to dewater because PAM is hydrophilic and forms loosely-packed flocs.

Thus, there is the need to develop improved technology. Cationic polymers can settle the negatively charged clay species found in oil sands tailings more effectively because their quaternary ammonium groups play two roles in remediation: charge neutralization and bridging flocculation (aggregation of multiple clay particles induced by a single polymer chain).^[8,9] However, an optimum cation density must be determined, as too high of a cation concentration may redisperse the clay particles;^[10,11] in addition, the dewatering problem still persists. To improve sediment dewatering, other researchers are exploring the use of temperature-sensitive poly(*N*-isopropyl acrylamide) (PNIPAM) to exploit the temperature-activated hydrophilic/hydrophobic transition.^[6] Although these value-added materials for the remediation of oil sands tailings offer significant promise, many associated optimization challenges remain.

Our aim is to develop a new family of dual functional flocculants that can be easily adapted to field conditions from a library of building-block materials. In this communication, we present the methodology and proof of concept for a dual functional polymer with tunable cationic density for rapid settling, and modifiable polyester units that are passively degraded by hydrolysis to reveal hydrophobic segments that further expel water from the sediment. As illustrated by **Scheme 1**, comb-like high MW polymer chains are produced via the grafting through approach of new short-chain polyester cationic macromonomers, thus combining the hydrolytic degradability of polyesters with the high production rates and industrial familiarity of free-radical polymerization (FRP).

The simplicity and effectiveness of this approach to tune final material properties such as degradation rates by adjusting the average number n (e.g. $n=2, 3, 5$) of units in the polyester side chain has been demonstrated in the biomedical field for hydroxyl functionalized macromonomers.^[12,13] Changing the cyclic monomer from ϵ -caprolactone (CL) to lactide (LA)) in the bulk ring opening polymerization (ROP) step provides another means to tune degradation rates, since polycaprolactone (PCL) is more hydrophobic than polylactic acid (PLA).^[12,13] For our application, the density of the polymeric cations per hydrophobic content is also adjusted by controlling the stoichiometric ratio of cyclic monomer to initiator in the bulk ROP step. In addition, branched architectures may be achieved by changing from a methacrylate to an acrylate macromonomer, with further control of cation density and hydrophobicity achievable through copolymerization with a water-soluble monomer such as acrylamide (AM).

2. Results and Discussion

The macromonomer synthesis is summarized in **Scheme 2** with further details reported in the Supporting Information. Briefly, in the presence of stannous octoate ($\text{Sn}(\text{oct})_2$)

catalyst, deanol (De) is used to initiate the bulk ROP of CL to produce polycaprolactone 2-(*N,N*-dimethylamino)ethyl ester (PCL_nDe) which is then reacted with methacryloyl chloride to yield polycaprolactone 2-(*N,N*-dimethylamino)ethyl ester methacrylate (PCL_nDeMA). The tertiary amine is methylated using methyl iodide to afford the final macromonomer, herein termed polycaprolactone choline iodide ester methacrylate (PCL_nChMA, with *n*=3 for this synthesis), whose structure as well as those of its corresponding intermediate species were confirmed by the proton nuclear magnetic resonance (¹H-NMR) characterizations presented in **Figure S1, S2, and S3**.

PCL_nChMA macromonomers can be classified as tail-type polymerizable surfactants (surfmers) because they are amphiphiles that possess a cationic head and contain a vinyl group within the hydrophobic tail.^[14,15] In general, the micellar structure undergoes extensive reorganization during surfmer polymerization,^[16,17] and the resulting polyelectrolytes have high MW due to compartmentalization of the polymerizable group.^[14,18] As depicted by Scheme 1, PCL_nChMA surfmers form micelles in aqueous solution (critical micelle concentration determined via **Figure S4**); the rapid consumption of 10 wt.% PCL₃ChMA during a batch radical homopolymerization in D₂O was demonstrated in situ using ¹H-NMR, with 90 % conversion reached almost twice as fast as AM under identical conditions (see **Figure S5**). The transmission electron microscopy (TEM) image in **Figure 1** confirms a worm-like morphology for the poly(PCL₃ChMA) product, while preliminary MW analysis using multi-angle light scattering indicates the material has a weight-average MW greater than 1 million Da. These two characteristics are beneficial for oil sands tailings remediation because they promote bridging flocculation which ultimately improves settling performance.^[11]

In **Figure 2**, the performance of poly(PCL₃ChMA) flocculant in fluid fine tailings from the Alberta oil sands is compared to commercial PAM. The better clarity of the supernatant and compactness of the resulting sediment after only 10 minutes of settling demonstrates that poly(PCL₃ChMA) is a more effective flocculant than PAM due to its cationic groups. Following flocculation, poly(PCL₃ChMA) undergoes hydrolytic degradation to reveal a more hydrophobic polymer which expels water from the sediment. This important second aspect of our flocculant design is demonstrated in **Figure 3**; phase separation was achieved after several days of an ex situ accelerated degradation study corresponding to the cleavage of ester linkages, as confirmed by the ¹H-NMR spectra in **Figure S6**.

Next, capillary suction time (CST) was used to quantify the effect of poly(PCL₃ChMA) degradation on the in situ dewaterability of a 2 wt.% kaolin clay model tailings sediment. Since CST measures the filtration rate of free water, a lower CST value indicates improved permeability of the sediment. Under accelerated degradation conditions, the sediments produced using 500 ppm poly(PCL₃ChMA) (relative to solids) had a 30 % lower CST value, whereas the change in CST was negligible for the 0 and 500 ppm PAM controls (see **Figure S7**). This result verifies that the in situ degradation of the flocculating agent leads to increased consolidation of the clay solids. Although the change in final material properties following hydrolysis of polyesters has been well-documented,^[19,20] poly(PCL₃ChMA) is, to the best of our knowledge, the first reported polymeric material which becomes more hydrophobic in response to hydrolysis. Moreover, the increased dewaterability of poly(PCL₃ChMA) is advantageous because it does not depend on the input of external energy to trigger a hydrophilic to hydrophobic transition (in contrast to PNIPAM-based flocculants), and the polyester hydrolysis byproducts are widely regarded as biodegradable.^[21]

3. Conclusions

In this communication, we have presented the methodology and proof of concept for the production of a new family of cationic polyester macromonomers, termed polycaprolactone choline iodide ester methacrylate (PCL_nChMA), which become more hydrophobic in response to hydrolysis. Using micellar radical polymerization of these macromonomers, we combined the material properties of polyesters with the productivity of radical polymerization to generate dual functional comb-like polymeric flocculants, poly(PCL_3ChMA), with tunable charge density for rapid settling, and hydrolytically degradable grafts that reveal hydrophobic segments which further expel water from the sediment. A significantly clearer supernatant and more compact sediment was achieved when poly(PCL_3ChMA) was used to flocculate fluid fine tailings from the Alberta oil sands compared to commercial polyacrylamide flocculant. In addition, we demonstrated that hydrolytic degradation of poly(PCL_3ChMA) causes up to a 30 % reduction in capillary suction time (a measure of sediment permeability) for a kaolin model tailings sediment. Our future studies will systematically vary the value of n and the polyester type (PCL and PLA) to produce macromonomers with both methacrylate and acrylate functionality. Via macromonomer copolymerization with acrylamide, we will then correlate the properties of the resulting polymer (degree of branching, cationic density, hydrophobicity, and copolymer sequence distribution) with flocculation and degradation performance

4. Experimental

The synthetic procedure for PCL_3ChMA macromonomer is described below, while further details for macromonomer, polymer, and sediment preparations and characterizations are supplied in the Supporting Information.

The bulk ROP of CL was performed using $\text{Sn}(\text{oct})_2$ as catalyst and De as initiator. Briefly, CL (5.11 g, 44.6 mmol) was loaded into a 50 mL sealed round bottom flask, purged with N_2 , and heated to 110 °C. A catalyst/initiator mixture with molar ratio 1:333 was prepared separately, then 1.34 g of this mixture (corresponding to 14.9 mmol De) was added

to the CL by syringe and allowed to react for 8 hours at 110 °C to afford polycaprolactone 2-(*N,N*-dimethylamino)ethyl ester (PCL₃De) with average $n = 3.0$ and CL conversion $\approx 94\%$ (as determined by ¹H-NMR).

Next, in a sealed 3 neck 100 mL round bottom flask, PCL₃De (6.45 g, 14.9 mmol - OH) was dissolved in 26 mL tetrahydrofuran (THF) to which 20 mL triethylamine (TEA, 143.5 mmol) was then added. The solution was cooled to 0 °C using an ice bath, bubbled with N₂ for 10 minutes, and then 1.9 mL freshly distilled methacryloyl chloride (MACl, 19.4 mmol) was fed over 20 minutes using a glass syringe. The reaction mixture was maintained at 0 °C for 3 hours, filtered to remove the TEA salt, and then passed through a column of basic alumina. The solvent was evaporated in vacuo to afford 5.89 g polycaprolactone 2-(*N,N*-dimethylamino)ethyl ester methacrylate (PCL₃DeMA) in 75 % yield including MACl impurities.

PCL₃DeMA (5.89 g, 11.2 mmol) was dissolved in 160 mL diethyl ether, cooled to 0 °C in an ice bath, and kept under constant flow of N₂. Approximately 2.5 mL ICH₃ (40 mmol) was injected by syringe then the reaction was allowed to warm to room temperature and proceed for 48 hours. The white waxy precipitate was collected by filtration, washed with cold diethyl ether, and dried in vacuum oven at 40 °C overnight to afford 5.20 g polycaprolactone choline iodide ester methacrylate (PCL₃ChMA) (72 % methylation yield).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Scheme 1. Schematic representation of PCL_nChMA micellar polymerization to achieve cationic degradable flocculants.

Scheme 2. Synthetic procedure to produce cationic degradable comb-polymers.

Figure 1. Transmission electron microscopy image of poly(PCL₃ChMA) synthesized at 50 °C as 10 wt.% in D₂O with 0.22 wt.% V-50 as thermal initiator.

Figure 2. Comparison of flocculation performance for 500 ppm (a) poly(PCL₃ChMA) and (b) commercial PAM in 2 wt.% fluid fine tailings after 10 minutes of sedimentation.

Figure 3. Accelerated hydrolytic degradation test at 85 °C of 5 wt.% PCL₃ChMA in D₂O with initial pH adjusted to 9. Samples were cooled to room temperature for visual documentation.

Dual functional cationic flocculants that become more hydrophobic in response to hydrolysis to expel water and improve sediment consolidation. Micellar radical polymerization of a new cationic short-chain polycaprolactone (PCL) methacrylate macromonomer combines polyester material properties with the productivity of radical polymerization to afford a family of flocculants with highly tunable final properties.

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