ABSTRACT
A continuous stirred-tank reactor (CSTR) model is developed for the production of arborescent polyisobutylene via carbocationic copolymerization of isobutylene and an inimer using multi-dimensional method of moments. An inimer is a molecule that contains a functional initiating group and vinyl monomeric group (Initiator-Monomer) forming a T-shaped branching point. The model is used to predict dynamic changes in average branching level ($Br$) and number-average and weight-average molecular weights ($Mn$ and $Mw$). Simulations of this self-condensing vinyl copolymerization (SCVCP) show a tendency toward higher polydispersity and higher $Br$ compared to batch reactor simulations conducted using the same recipes and residence times. At high inimer feed concentration and/or long residence time, the model predicts that a CSTR does not reach steady-state operation due to $Mw$ increasing toward infinity. There is only a narrow operating range in which the inimer feed concentration can be adjusted to achieve a desired steady-state $Mw$. If SCVCP is to be conducted in a CSTR, it will be important to ensure that residence times and inimer feed concentrations are selected within the permissible stable operating window.
ABSTRACT

Starch is a biologically-derived polymer which has attracted attention as a substitute for conventional synthetic polymers. Previous work investigated the use of starch in paper coating latexes for increased sustainability. However, the addition of large amounts of native starch to synthetic paper coating latex lead to high viscosity and separation during printing. This was due to the hydrophilic nature of the starch. To increase the compatibility, we therefore proposed to make the starch more hydrophobic through nitroxide mediated polymerization (NMP). NMP would be used to grow small amounts of synthetic polymer from the starch, making it more hydrophobic and offering a high degree of control during the polymerization step. In this work, the surface hydroxyl groups of a cold water soluble starch (CWS) were first modified with reactive vinyl groups using methacrylic anhydride and 4-vinylbenzyl chloride. The vinyl groups were then reacted with the alkoxyamine BlocBuilder® for use in future NMP studies. The modified CWS was characterized using Fourier Transform Infrared Spectroscopy, Thermogravimetric Analysis, and proton (H\(^1\)) and solid-state carbon (C\(^{13}\)) nuclear magnetic resonance. The analysis showed successful addition of vinyl groups to the CWS and subsequent successful attachment of the BlocBuilder® mediator.
**ABSTRACT**

We have studied the use of a bio-sourced Pickering emulsifier based on cellulose nanocrystals (CNC) grafted with less than 25% of synthetic, CO$_2$-responsive polymer for the reversible emulsification/demulsification of oil and water. Following functionalization of the CNC surface with glycidyl methacrylate, CO$_2$-switchable poly(N,N-(diethylamino)ethyl methacrylate) (PDEAEMA) and poly(N-3-(dimethylamino) propyl methacrylamide) (PDMAPMAm) macroalkoxyamines with low dispersities, high livingness and chain end functionalities were grown through nitroxide-mediated polymerization (NMP) and grafted to the nanocrystals. Two different tertiary amine polymers were selected to investigate how differences in their pK$_{aH}$ and $T_g$ affected the final properties of the graft-modified CNC and the resulting Pickering emulsions. The graft molecular weight and graft density was shown to have an influence on the surface and interfacial properties of the Pickering emulsifiers, which were characterized by surface and interfacial tensiometer measurements. The resulting droplets obtained from oil in water emulsions were visualized using optical microscopy. The emulsification/demulsification process was found to be responsive to N$_2$ and CO$_2$, reversible and easily repeatable. The Pickering emulsifiers could be recovered after application, which would make this technology particularly interesting for oil water separation and enhanced oil recovery. The pK$_{aH}$ of the grafted polymer and the polarity were correlated to the CO$_2$ bubbling time required to break the emulsion and to the emulsion stability (lifetime). The effects of chain length of the grafted polymer, graft densities, total amount of CO$_2$-switchable groups on the CNCs surface, and concentration of Pickering stabilizer on the properties of emulsions were investigated.
ABSTRACT
Polymers from renewable resources have gained significant attention in recent decades due to environmental issues and the realization of limited petroleum resources. Among the natural polymers, polyhydroxyalkanoates (PHAs) comprise a group of natural biodegradable polyesters that are synthesized by microorganisms. This work investigated the effect of the chain structure of medium chain length polyhydroxyalkanoates (MCL PHA) on their thermal properties, and developed a simple chemical modification approach to improve their crystallization kinetics. Chemical modification through peroxide-mediated grafting of a trifunctional coagent (trialyl trimesate-TAM) was done to induce branching, and altered the crystallization properties of Poly(3hydroxydecanoate) P(3HD).
In recent years there has been increased interest in the production of furans as a potential feedstock for biofuel production, as well as for use in the chemical industry. Carbohydrates can be efficiently converted to 5-hydroxymethylfurfural (HMF), a precursor to biojet fuel. Previous research in the field has shown that CO$_2$ can be utilized to catalyze the conversion of fructose to HMF. We report that high pressure CO$_2$ can be used in biphasic reactions to increase total furan yields. A yield of 64% was achieved when preforming the reaction using glucose as a feedstock under 7 MPa of CO$_2$ with pentanol as a secondary phase. Yields of 20-50% were observed when preforming the reaction using other polysaccharides (e.g., starch, cellulose). In addition, it was found that the introduction of acetone as a co-solvent can improve total furan yields. It also allows for the synthesis the HMF aldol adduct, which is an important intermediate for biojet fuel production.
ABSTRACT
The biological production of biofuels through fermentation has become increasingly important due to the heightened need for sustainable energy sources. Butanol and ethanol fermentation processes, conducted by *Clostridium acetobutylicum* and *Saccharomyces cerevisiae*, respectively, suffer from end-product inhibition, leading to low final product concentrations and reduced volumetric productivity. As microbial cytotoxicity within a fermentation hinders effectiveness, *in-situ* product recovery methods can be implemented, via the use of two-phase partitioning bioreactor (TPPB) technology. This work involves the synthesis and introduction of a polyelectrolyte absorbent phase, poly(vinylidodecylimidazolium bromide) [P(VC$_{12}$ImBr)], in TPPB systems for sorption of the target molecules, butanol and ethanol. P(VC$_{12}$ImBr) was found to have a high partition coefficient and selectivity for both ethanol and butanol, along with favourable diffusivity for this application. When implemented in a TPPB system, P(VC$_{12}$ImBr) can increase substrate conversions and volumetric productivity through sorption of the target molecule, reducing ethanol or butanol inhibition.
ABSTRACT
Oil sands mining operations in Canada produce considerable amounts of waste tailings that have proven difficult to dewater effectively using commercial polyacrylamide based flocculants. We have developed a novel polymer, synthesized from short chains polyester cationic macromonomers of polycaprolactone choline iodide ester methacrylate (PCL2ChMA), that hydrolytically degrades after flocculation; the increased hydrophobicity improves the dewaterability of the sediments as they age, as characterized by an 85% decrease in capillary suction time (CST). We are now systematically investigating the relationship between flocculant performance and macromonomer structure to optimize the polymer design. The first modification is to change the polyester repeating unit from caprolactone to lactic acid, with the resulting poly(lactic acid) choline iodide ester methacrylate (PLA4ChMA) expected to accelerate the in situ degradation rate after application. The other two new macromonomers synthesized are acrylate analogs of the methacrylate materials, and are expected to yield flocculants of higher molar masses and hence improved performance. The materials are assessed based on the initial settling rates induced when added to oil sands mature fine tailings, the turbidity of the resulting supernatants, and the CST of the resulting sediments.