Tuneable collector/depressant behaviour of xanthate-functional temperature-responsive polymers in the flotation of copper sulfide: Effect of shear and temperature

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ABSTRACT

Recent studies of temperature-responsive polymers, such as poly(*N*-isopropyl acrylamide) (PNIPAM), have revealed opportunities to utilise the smart materials to enhance the flotation recovery of valuable fines. PNIPAM undergoes a hydrophilic-to-hydrophobic transition when heated above a lower critical transition temperature (LCST), acting as a flocculant and collector. This study investigates the effect of shear and temperature on the flotation behaviour of a xanthate-functional temperature-responsive polymer, P(NIPAM-*co*-ethyl xanthate methacrylate (EXMA)), in the recovery of copper sulfide from a natural mixed-mineral ore. The results were compared with a conventional xanthate collector, potassium amyl xanthate (PAX). In a high-shear mechanical cell, P(NIPAM-*co*-EXMA) improved coarse grades and fine recoveries upon heating above the LCST, through the aggregation of valuable fines into larger sizes more amenable to flotation, while limiting hydrophobic slimes coating on gangue particles. Flotation using the polymer in a column cell produced little improvement relative to PAX, despite the formation of larger particle aggregates under reduced shear. P(NIPAM-*co*-EXMA) behaved as a sulfide depressant at temperatures below the LCST, where it renders the surface hydrophilic, displaying tuneable collector/depressant properties. Addition of polymer to suspension above the LCST improved concentrate grades, attributed to enhanced selectivity relative to addition below the LCST prior to heating.

1. Introduction

Temperature-responsive polymers are smart materials that exhibit an interesting set of properties, able to undergo rapid and distinct changes in conformation following a switch in temperature (Aguilar and San Román, 2014; Brisson et al., 2016; Jochum and Theato, 2013; Liu et al., 2009; Roy et al., 2013). A well-studied example is poly(*N*-isopropyl acrylamide) (PNIPAM), which transitions rapidly from a water soluble, hydrophilic coil to an insoluble, hydrophobic globule when heated in an aqueous solution above a lower critical solution temperature (LCST) of 32 °C (Schild, 1992; Sun et al., 2004). This property has led to a wide range of applications including drug delivery (Hoffman, 2013; Priya James et al., 2014; Saunders et al., 2009), tissue engineering (Aguilar et al., 2007; Custódio et al., 2014; Koetting et al., 2015), and gel actuation (Huck, 2008; Ionov, 2014; Karg et al., 2008). Furthermore, these polymers are able to induce particle aggregation (Guillet et al., 1985; Li et al., 2007; Long et al., 2011; O'Shea et al.,

2011, 2012; Sakohara et al., 2002; Vedoy and Soares, 2015), through steric and hydrophobic interactions with the PNIPAM homopolymer (Burdukova et al., 2010b), as well as bridging mechanisms with PNIPAM copolymers incorporating a surface-selective moiety (Ng et al., 2017a).

In recent years, our group has been developing novel flotation techniques using temperature-responsive polymers as selective collectors in the treatment of fine particles (Forbes et al., 2011; Franks, 2005; Franks et al., 2009; Li and Franks, 2008; Ng et al., 2015). The presence of fine particles is typically detrimental to flotation performance, due to issues with particle-bubble attachment, slimes coating, and gangue entrainment (Phan et al., 2003; Sivamohan, 1990; Somasundaran, 1980; Trahar and Warren, 1976). The addition of temperature-responsive polymers can alleviate some of these difficulties by selectively aggregating the valuable fine particles into hydrophobic aggregates at temperatures above the LCST, which are larger and more amenable to recovery by flotation. Previous work has demonstrated that the use of
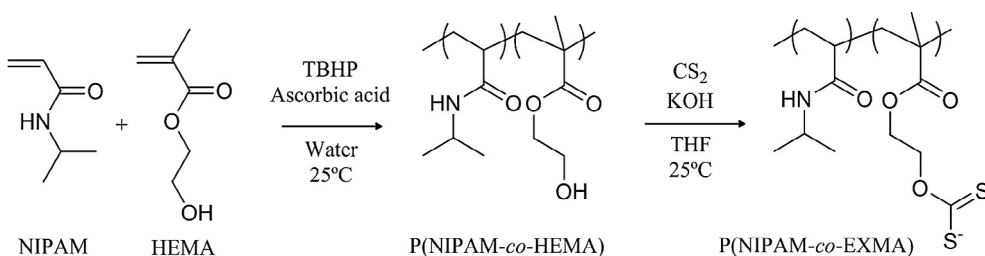

Fig. 1. Schematic pathway for the synthesis of a xanthate-functional temperature-responsive polymer, P(NIPAM-*co*-EXMA).

anionic PNIPAM can be used to enhance the recovery of hematite fines in iron ore flotation (Forbes and Franks, 2013; Ng et al., 2015). The flotation performance of xanthate-functional PNIPAM has also been shown to be comparable to small molecule xanthates, in the recovery of chalcopyrite from a synthetic feed comprised of a mixture of liberated minerals (Ng et al., 2016a).

In the current work, we seek to investigate the influence of shear and temperature on the flotation performance of the temperature-responsive polymers. Based on real-time size measurements of the particle aggregates formed in the presence of PNIPAM under constant mixing, the shear rates experienced by the aggregates have been found to play a substantial role in the particle aggregation properties of the polymer, where increasing shear rate results in decreasing aggregate sizes (Ng et al., 2017a; Ng et al., 2017b). Hence, flotation using the polymer in a low-shear environment, such as in a column cell, is expected to result in the formation of larger particle aggregates relative to flotation in a high-shear mechanical cell (Deglon et al., 2000), which may have a substantial impact on recoveries. Thus far, flotation studies with temperature-responsive polymers have all been conducted in mechanical cells. A series of column flotation studies are therefore necessary, to understand how a low-shear system in a different cell type affects the flotation performance of the temperature-responsive materials.

Furthermore, despite the tuneable properties of the polymer in solution, the main focus of previous studies has been on exploiting the hydrophobic behaviour of temperature-responsive polymers above the LCST. Limited flotation work has been performed using these materials at temperatures below the LCST, where the polymer is expected to remain hydrophilic and hence act as a depressant (Franks et al., 2009). Here, we report the first instance of a flotation study using selective PNIPAM copolymers that compares the performance at temperatures below and above the LCST, to demonstrate the ability to control the collector/depressant activity of the polymer by using a simple temperature switch. This offers potential advantages in multi-stage flotation, where a particular mineral may need to be depressed in one stage of flotation prior to being activated in another stage. Thermo-switchable surface properties would remove the need to add multiple depressants, activators and collectors, by acting as a single multi-functional reagent serving all three roles. Addition of polymer at temperatures above the LCST is also of interest, as this would be more convenient than addition of the polymer at room temperature followed by heating.

In this study, the flotation performance of a synthesised xanthate-functional temperature-responsive polymer, P(NIPAM-*co*-ethyl xanthate methacrylate (EXMA)) in the recovery of copper sulfide from a real mixed-mineral ore sample has been investigated, in comparison with a conventional small molecule xanthate collector, potassium amyl xanthate (PAX). P(NIPAM-*co*-EXMA) is selective towards copper sulfide surfaces, and capable of imparting surface hydrophobicity to adsorbed surfaces at temperatures above the LCST (Ng et al., 2016a), due to the xanthate functionality (Fuerstenau et al., 2007; Shergold, 1984; Wills and Finch, 2016; Woods, 1996). The flotation tests were performed under different conditions, in a mechanical cell and a column cell, to understand the influence of cell type and shear on flotation recoveries. The current work also examines the effect of preconditioning and

flotation temperature on mineral recoveries, to demonstrate the thermo-switchable collector/depressant activity of the smart polymer.

2. Experimental

2.1. Materials

N-isopropyl acrylamide (NIPAM) monomer (98%, Tokyo Chemical Industry) was twice recrystallised using a 40:60 mixture of toluene:*n*-hexane. 2-hydroxyethyl methacrylate (HEMA) monomer (98%, Aldrich) was filtered through a column of basic aluminium oxide (Scharlau) to remove the hydroquinone inhibitors. tert-Butyl hydroperoxide (TBHP, Aldrich) was used as received as a 70% aqueous solution. Tetrahydrofuran (THF, VWR), diethyl ether (DEE, Chem-Supply), L-ascorbic acid (99,% Aldrich), carbon disulfide (CS_2, Aldrich), potassium chloride (KCl, VWR) and potassium hydroxide (KOH, VWR) were used as supplied. Potassium amyl xanthate (PAX, Tall Bennett) was used as received. Cataflot P40 was obtained from CECA (Colombes, France) as a low molecular weight polyacrylate dispersant (Bulatovic, 2010), while methyl isobutyl carbinol was obtained from Orica Chemicals (Melbourne, Australia) for use as a frother. Copper ore samples (assayed at 0.67%Cu) used in the flotation tests were obtained from Northparkes Mines. The main copper-bearing minerals are chalcopyrite and bornite, with the majority of the non-copper gangue present as silica.

2.2. Methods

2.2.1. Synthesis of xanthate-functional PNIPAM copolymers

A temperature-responsive random copolymer of PNIPAM featuring xanthate functionality was synthesised following the two-step schematic pathway as depicted in Fig. 1. The first step involves redox-initiated free radical polymerisation under an argon atmosphere using a general procedure as described elsewhere (Bernard et al., 2006). Although our previous work with analogous polymers utilised thermal-initiated polymerisation (Ng et al., 2016a), redox-initiation was used in the current work to produce polymers of higher molecular weight, as a higher molecular weight has been shown to improve the flotation performance of temperature-responsive materials (Burdukova et al., 2010a).

TBHP was used as an initiator, with ascorbic acid as an oxidising agent. The NIPAM and HEMA monomers were present in a 95:5 M ratio in deionised water. The solution was reacted at room temperature (25 °C) for 24 h to yield P(NIPAM-*co*-HEMA), which was then purified and isolated through precipitation in DEE. [1]H Nuclear Magnetic Resonance (NMR, Varian Unity 400 spectrometer) characterisation confirms that the product contains 95% NIPAM units and 5% HEMA units by moles. Due to the molecular weight of the polymer product, dynamic light scattering (DLS, Wyatt DynaPro NanoStar light scattering detector) was used instead of Gel Permeation Chromatography to approximate the molecular weights, based on the measured hydrodynamic radius in comparison with analogous copolymers of known molecular weight. DLS measurements were conducted on polymers samples of 1 mg/mL in deionised water, with the solutions being filtered through 0.45 µm Teflon filters at room temperature prior to