



## Rapid Communication

# *In situ* study of aggregate sizes formed in chalcopyrite-quartz mixture using temperature-responsive polymers

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## ABSTRACT

An interesting property of temperature-responsive polymers, such as poly(*N*-isopropylacrylamide) (PNIPAM), is the ability to behave as flocculants above a lower critical solution temperature (LCST). This study examines the aggregation of a chalcopyrite-quartz mixture using a sulfide-selective temperature-responsive polymer, P(NIPAM-*co*-ethyl xanthate methacrylate (EXMA)) in a continuously-sheared suspension, relative to polyacrylamide (PAM). The investigation was carried out *in situ* using imaging and Focused Beam Reflectance Measurement techniques to obtain real-time chord length distributions. While particle aggregates were observed in the presence of PNIPAM only upon heating above the LCST, P(NIPAM-*co*-EXMA) induced particle aggregation below the LCST, due to the attraction between the xanthate moiety and the sulfide surfaces. The largest aggregates were observed with P(NIPAM-*co*-EXMA) (1.5 MDa), followed by PNIPAM, PAM, and P(NIPAM-*co*-EXMA) (115 kDa). Particle aggregates formed with PAM did not exhibit further breakage under increasing shear to 1100 s<sup>-1</sup>, while large-scale fragmentation was observed with the PNIPAM-based flocculants. Unlike PNIPAM, addition of P(NIPAM-*co*-EXMA) to suspension above the LCST was able to yield particle aggregation, attributed to the formation of charge-stabilised micelles. The influence of the shear rate on the size of the aggregates formed with P(NIPAM-*co*-EXMA) is unaffected by the polymer addition and measurement temperature below or above the LCST.

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## 1. Introduction

Temperature-responsive polymers are a fascinating class of smart materials that are able to undergo sharp, rapid, and reversible changes in conformation modulated by temperature [1–6]. The unique temperature switch of these polymers has enabled a host of potential applications in multiple fields, ranging from drug delivery [7–11], to tissue engineering [12–14], and gel actuators [15–17]. One of the most well-characterised examples is poly(*N*-isopropyl acrylamide) (PNIPAM), which transitions from a hydrophilic coil to a hydrophobic globule when heated above a lower critical solution temperature (LCST) of 32 °C [4,18]. The hydrophilic-hydrophobic transition of PNIPAM across the LCST is driven by the breakage of hydrogen bonds between the polymer and surrounding water, and the formation of new bonds between

the amide and carboxyl segments of the polymer, exposing the hydrophobic hydrocarbon backbone [19].

Our interest in temperature-responsive polymers lies in exploring new methods of utilising these materials to tackle a series of challenges in minerals processing. Previous studies have demonstrated that hydrophobic and steric attractive interactions formed between surface-adsorbed PNIPAM chains above the LCST are sufficiently strong to induce particle aggregation [20–27]. Below the LCST, the loss of the attractive forces results in a dispersed suspension, stabilised by the steric repulsion between the adsorbed polymer chains. An area that stands to benefit from the particle aggregation and hydrophobic transition properties of these smart materials is froth flotation, one of the most common separation techniques used in the treatment of valuable minerals.

Froth flotation involves the selective conditioning of valuable minerals such as copper, zinc, and nickel with surfactants called collectors to impart a hydrophobic surface [28,29]. The valuable particles can then be separated from the unwanted hydrophilic

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gangue by attachment to bubbles introduced into the vessel. Nevertheless, froth flotation suffers from several shortcomings, one of which is impaired performance when treating fine particles below 20  $\mu\text{m}$  in size [30,31], resulting in reduced recoveries and low-grade product. A promising approach is to utilise temperature-responsive polymers to selectively aggregate the valuable fines into larger sizes that are more amenable to recovery by flotation, while acting as a collector at temperatures above the LCST [20,26,32–34]. The multi-functional aspect of temperature-responsive polymers represents an advantage, as selective flocculants are typically hydrophilic and require the addition of other collectors as surface modification agents in the flotation of valuable minerals.

The crux of the proposed application is that the particle aggregates formed in the presence of the temperature-responsive polymers need to lie within the optimal flotation size range when exposed to typical flotation shear conditions, which need to be sufficiently high to encourage particle-bubble attachment [35,36]. Previous studies on the aggregation of iron ore particles using a hematite-selective anionic PNIPAM copolymer have established that a substantial drop in aggregate size occurs with increasing shear, due to large-scale fragmentation [37], although the aggregates remain large enough for recovery at typical flotation shear rates of  $1000\text{ s}^{-1}$  and above [38]. In this study, we direct our attention to the particle aggregation properties of a series of sulfide-selective temperature-responsive polymers on a chalcopyrite-quartz mixture as a synthetic copper ore under typical flotation shear conditions. The xanthate-functional PNIPAM copolymers used in this work, P(NIPAM-co-ethyl xanthate methacrylate (EXMA)), have been shown in prior studies to exhibit a high degree of selectivity towards sulfide surfaces [33,34], due to the presence of the xanthate moiety [39–42], and displays the necessary properties for the proposed application as a selective flocculant and collector in flotation. It is therefore of interest to examine the relationship between shear rates and the size of aggregates formed using the polymer to optimise its properties in the proposed application.

Here, we introduce a series of real-time measurements on the aggregation of a mixture of chalcopyrite and quartz particles in the presence of PNIPAM homopolymer and xanthate-functional PNIPAM copolymers, under continuous shear. Chord length distributions of the particles and aggregates in the suspension were recorded *in situ* using a Focused Beam Reflectance Measurement (FBRM) probe [43–45], while images of the aggregates in the slurry were captured using a Particle Vision and Measurement (PVM) probe. This study will also investigate the effect of the polymer molecular weight, shear rates, and dosage temperature on the size of the aggregates formed in the presence of the temperature-responsive polymers, in comparison to conventional polyacrylamide (PAM) flocculants.

## 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 ( $\text{CS}_2$ , Aldrich), potassium chloride (KCl, VWR) and potassium hydroxide (KOH, VWR) were used as supplied. Poly(*N*-isopropyl acrylamide) (PNIPAM) homopolymer used in this study was synthesised in our laboratories, following procedures as described by O'Shea [23], with an LCST of  $32.0\text{ }^\circ\text{C} \pm 0.5\text{ }^\circ\text{C}$  and a number-average molecular weight of 6 MDa. Polyacrylamide (PAM, Magnafloc 800 HP) used in this work was obtained from BASF®. The number-average molecular weight was 6 MDa as derived from the intrinsic viscosity values provided by BASF®. The PAM sample was checked by  $^1\text{H}$  Nuclear Magnetic Resonance (NMR, Varian Unity 400 spectrometer) and found to have undergone minimal (<1%) hydrolysis to acrylic acid groups. High purity quartz (sized below  $300\text{ }\mu\text{m}$ ) and chalcopyrite particles (assayed at 60%Cu, sized below  $212\text{ }\mu\text{m}$ ) particles used in the particle aggregation tests were provided by CSIRO.

### 2.2. Methods

#### 2.2.1. Synthesis of xanthate-functional PNIPAM copolymers

A temperature-responsive random copolymer of PNIPAM featuring xanthate functionality was synthesised under two different methods to produce two samples with similar chemical structures at different molecular weights. The high molecular weight sample was produced following a 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 [46]. 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 ( $25\text{ }^\circ\text{C}$ ) for 24 h to yield P(NIPAM-co-HEMA), which was then purified and isolated through precipitation in DEE.  $^1\text{H}$  NMR characterisation confirms that the product contains 95% NIPAM units and 5% HEMA units by moles. Subsequently, the synthesised P(NIPAM-co-HEMA) was reacted with carbon disulfide (10 times stoichiometric excess) in the presence of KOH (1.0 M, 1.5 times the stoichiometric amount of HEMA groups present) in THF. The solution was then reacted at room temperature ( $25\text{ }^\circ\text{C}$ ) for 24 h to yield P(NIPAM-co-ethyl xanthate

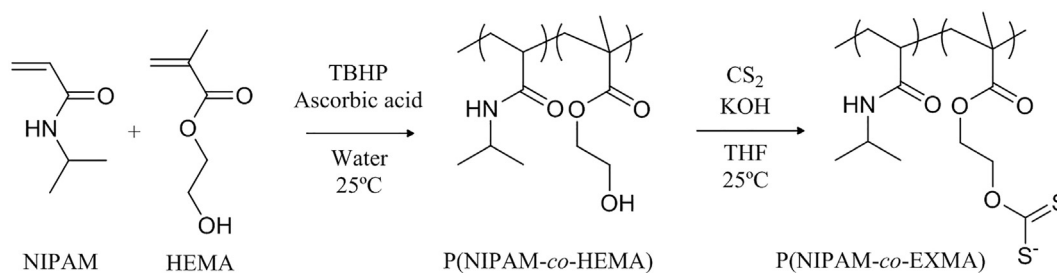


Fig. 1. Schematic pathway for the synthesis of a xanthate-functional temperature-responsive polymer, P(NIPAM-co-EXMA).

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