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# A review of temperature-responsive polymers as novel reagents for solid-liquid separation and froth flotation of minerals

Wei Sung Ng[a,b], Luke A. Connal[c], Elizaveta Forbes[b], George V. Franks[a,*]

[a] Chemical Engineering, University of Melbourne, Parkville, VIC 3010, Australia
[b] CSIRO Mineral Resources, Clayton, VIC 3168, Australia
[c] Research School of Chemistry, Australian National University, Acton, ACT 2601, Australia

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ABSTRACT

Over the past few decades, the study of temperature-responsive polymers has unlocked a vast array of potential applications in various research areas, including biological systems, wastewater treatment, and gel actuation. These dynamic materials are able to exhibit reversible hydrophilic-hydrophobic transitions in a sharp and rapid manner, under a change in temperature in aqueous solutions. This property can be used to reversibly change particle-particle interactions between attractive and repulsive states. Recent studies have demonstrated that the temperature-responsive properties of these materials can be utilised to enhance water recovery and increase solids concentration in dewatering processes, as well as improve the recovery of minerals in flotation operations. This review explores the nature of temperature-responsive polymers, and the mechanisms behind their use as flocculants in solid-liquid separation and tuneable collector/depressants in froth flotation. The polymers and minerals investigated will be considered in detail, as well as the factors influencing the dewatering and flotation capabilities of thermo-responsive materials. The challenges and considerations in the development of new temperature-responsive polymers and their potential applications in minerals processing will also be discussed.

## 1. Introduction

Temperature-responsive polymers are a class of materials that are able to exhibit different behaviours depending on the temperature (Aguilar and San Román, 2014; Liu et al., 2009; Roy et al., 2013). When heated or cooled across a known transition point, these polymers undergo a sharp and rapid change from a hydrophilic state to a hydrophobic conformation, or vice versa, in aqueous solutions (Halperin et al., 2015; Lowe and Roth, 2016; Schild, 1992). The study of these materials over the past several decades has revealed a host of potential applications in a wide array of industries, including drug delivery systems (Hoffman, 2013; Hunter and Moghimi, 2017; Priya James et al., 2014; Saunders et al., 2009), tissue engineering (Aguilar et al., 2007; Custódio et al., 2014; Koetting et al., 2015), gel actuation (Huck, 2008; Ionov, 2014; Karg et al., 2008), and the manufacturing of textiles (Hu and Lu, 2014). In recent years, several studies examining the use of temperature-responsive polymers in minerals processing have also emerged. These investigations are largely centred on the use of the polymers in solid-liquid separation and froth flotation, exploiting the responsive and switchable nature of the materials to enhance our current treatment practices.

Conventional flocculants, such as copolymers based on polyacrylamide (PAM), induce attraction between particles to produce aggregates that have increased sedimentation rates compared to the individual fine particles. Once the aggregated particles form a sediment bed, this bed resists consolidation and compacting due to the strong bond between particles induced by the polymeric flocculant (Hunter, 2001; Israelachvili, 2011). Nevertheless, the bed, or thickener underflow, contains a significant amount of water trapped within and between the flocs. Conversely, well-dispersed particles will eventually settle to form sediments that consolidate to high density under low applied pressure. The use of thermo-responsive reagents allows for the switching of interactions between polymer-adsorbed particles, between attraction when fast sedimentation is required, and repulsion when sediment consolidation is desired. In contrast, conventional flocculants can only produce attraction between particles, making it difficult to recover additional water and achieve high sediment densities. Furthermore, conventional flocculation results in paste-like underflow rheology, while temperature-responsive flocculants can be used to reduce the yield stress and viscosity of the underflow (Franks et al., 2014).

In froth flotation, fine valuable particles are problematic, because

* Corresponding author.
*E-mail address:* gvfranks@unimelb.edu.au (G.V. Franks).

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they are difficult to recover (Sivamohan, 1990; Trahar and Warren, 1976) and can form hydrophobic slime coatings on larger gangue particles, resulting in grade dilution (Attia and Deason, 1989). There is potential for thermo-responsive polymers to alleviate these issues, by selectively aggregating the fine particles into larger, hydrophobic flocs through the hydrophilic-hydrophobic transition of the polymer. In addition, the polymer is able to function as both a depressant and a collector depending on the temperature, due to the responsive nature of the material and the ability to switch between hydrophilic and hydrophobic states.

In the following sections, the nature of the temperature-responsive polymers will be introduced, along with the mechanisms allowing the polymers to act as dewatering aids in solid-liquid separation and surface modification agents in froth flotation. This will be accompanied by a comprehensive review on the current state of the technology, followed by a discussion on its future prospects and opportunities. The scope of this review will be limited to studies involving the treatment of minerals, and will not enter much detail on the use of temperature-responsive polymers as flocculants in other industries, such as wastewater treatment and biological settings.

## 2. Behaviour of temperature-responsive polymers

Temperature-responsive polymers typically express one, or both, of two general behaviours. Polymers that become insoluble with heating are known to display lower critical solution temperature (LCST) behaviour, where the LCST refers to the transition temperature at which the material changes from a hydrophilic state to a hydrophobic globule (Liu et al., 2009; Roy et al., 2013). Conversely, polymers that become soluble at elevated temperatures possess upper critical solution temperature (UCST) properties, whereby the material undergoes a hydrophobic-to-hydrophilic transition upon heating above the UCST (Hoogenboom, 2014; Marcelo et al., 2017).

A polymer can exhibit both LCST and UCST properties, albeit at different temperatures. Furthermore, while the transitional behaviours of the polymers are reversible, the rate and temperature range of the temperature-responsive behaviour will vary depending on the material. The behaviour of these polymers originates from a balance of the enthalpy of mixing/solvency compared to the entropic cost of polymer-solvent interactions required for solvency (Bischofberger et al., 2014; Halperin et al., 2015). Temperature-responsive properties are present when these values are close, and a slight change in temperature shifts the balance from solvency to insolubility, whereby the polymer segment-to-segment interactions are now more favourable relative to polymer-solvent interactions.

The LCST and UCST behaviours of a thermo-responsive polymer can be influenced by a variety of factors, including the pH, salt concentration, salt type, polymer molecular weight, and polymer concentration (Furyk et al., 2006; Halperin et al., 2015; López-León et al., 2014; Okada and Tanaka, 2005). In the context of minerals processing, another consideration is that the presence of solids can potentially influence the LCST and UCST of the polymers, as the polymer chains now have the option to adsorb onto the solid surfaces. Mineral surfaces containing water-soluble groups can also introduce different ions and salts into the solution, altering the thermo-responsive behaviour of the polymers. One caveat for the use of LCST and UCST concepts is that these measures are typically described in solids-free solutions, neglecting the presence of solid surfaces. A comprehensive study and modelling of the thermo-responsive behaviour of these polymers in a solvent with suspended solids and/or air bubbles (in flotation, for instance) would need to take into account not just the polymer-polymer and polymer-solvent interactions, but also the interactions with the solid surfaces and air. In this review, these interactions will be considered and discussed where a specific relationship exists between the polymer and the surface.

While a huge library of different temperature-responsive polymers exists, the most well-known example is arguably poly(*N*-isopropyl acrylamide) (PNIPAM), which has been known to be thermo-responsive since before 1968 (Heskins and Guillet, 1968). PNIPAM has an LCST of 32 °C, where it turns from a water-soluble, hydrophilic coil into an insoluble, hydrophobic globule (Halperin et al., 2015; Schild, 1992). This transformation is reversible, and the polymer can be observed to precipitate out of solution when heated above the LCST. As one of the earliest discovered thermo-responsive polymers with an LCST close to biological temperatures, PNIPAM has received the most attention in terms of characterisation and industrial applications. This familiarity has been somewhat reflected in the choice of temperature-responsive polymers investigated for minerals processing purposes, with the bulk of the studies being performed using PNIPAM-based copolymers. As we shall see in the next section, in theory, any temperature-responsive polymer with a sufficiently high molecular weight should be capable of acting as a temperature-responsive flocculant. A list of the temperature-responsive polymers discussed in this review is as shown in Table 1 and Fig. 1.

**Table 1**
List of abbreviations for the polymers described in this review.

| Abbreviation | Polymer name |
|---|---|
| PAA | Poly(acrylic acid) |
| PAEMA | Poly(2-aminoethyl methacrylamide hydrochloride) |
| PAM | Poly(acrylamide) |
| PAOPA | Poly(3-acryloyloxypropanoic acid) |
| PBAAM | Poly(*N*-*tert*-butylacrylamide) |
| PDADMAC | Poly(diallyldimethyl ammonium chloride) |
| PDMAPAA | Poly(*N*,*N*-dimethylaminopropyl acrylamide) |
| PDMAPMA | Poly(*N*,*N*-dimethylaminopropyl methacrylamide) |
| PDQA | Poly(dimethylamino ethyl acrylate quartenary chloride) |
| PMAAB | Poly(5-methacrylamido-1,2-benzoboroxole) |
| PNIPAM | Poly(*N*-isopropyl acrylamide) |
| PNVCL | Poly(*N*-vinyl caprolactam) |
| PTBA | Poly(*tert*-butyl acrylate) |

## 3. Temperature-responsive polymers in solid-liquid separation

### 3.1. Mechanism of temperature-responsive flocculants

Similar to its response as a “free” polymer in solution, a temperature-responsive polymer adsorbed on a mineral surface is able to change between hydrophilic and hydrophobic states, depending on the suspension temperature with respect to the transition temperature (Burdukova et al., 2010b; Franks, 2005; Franks et al., 2010). The flocculant activity of the thermo-responsive polymers comes from the attractive hydrophobic forces and attractive steric interactions of the polymer in the hydrophobic state above the LCST (or below the UCST), encouraging the formation of particle aggregates. A complementary process is the surface deposition or precipitation of polymer onto pre-adsorbed polymer, due to hydrophobic attraction, further increasing the surface adsorption of polymer (O’Shea et al., 2011). Below the LCST (or above the UCST), the polymer exhibits hydrophilic behaviour, and in some cases induces steric repulsion between particles. This eliminates the attractive interactions holding the aggregates together, “switching off” the flocculating capabilities of the polymer. Thermo-responsive polymers could therefore act as multi-functional, switchable flocculants and dispersants, controlled by the process temperature. It should be noted that, while the thermo-responsive polymers may not necessarily fall into the category of dispersants in a traditional sense (which are either small molecules or low molecular weight polymers), our use of the term “dispersant” here is more general, and simply describes the ability of the polymer to disperse and stabilise the suspension.

The use of temperature-responsive polymers as dewatering aids was initially explored by Guillet et al. (1985), as well as Deng et al. (1996),