

Review of stimuli-responsive polymers application as stabilization agents in solid-liquid dispersion systems

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Abstract: Although the flocculation process was invented a half century ago, the novel methods of suspension destabilization are still of great interest of both scientific community and industry. The goal of this work is to review the current state of application of stimuli-responsive polymers as stabilization agents in solid-liquid dispersion systems.

Keywords: aggregation, flocculation, stimuli-responsive polymers.

Polimery reagujące na bodźce zewnętrzne jako czynniki stabilizujące w układach dyspersyjnych ciało stałe-ciecz

Streszczenie: Proces flokulacji opracowano pół wieku temu, ale metody destabilizacji zawiesin nadal cieszą się dużym zainteresowaniem zarówno środowiska naukowego, jak i przemysłu. Artykuł stanowi przegląd aktualnego stanu wiedzy na temat zastosowania polimerów reagujących na bodźce zewnętrzne jako czynników stabilizujących układy dyspersyjne typu ciało stałe-ciecz.

Słowa kluczowe: agregacja, flokulacja, polimery reagujące na bodźce zewnętrzne.

Nowadays, one of the goals of chemical and process engineering is not only to achieve the highest possible efficiency but also to precisely control the process in order to obtain highly defined structure of the final product. This tendency can be seen in the field of aggregation and breakage phenomena. Although the flocculation process is used for decades, still new solutions are proposed like application of dual polymer systems [1–4], biodegradable macromolecules [5] or ultrasonic wave [1]. Yet, there are still many issues that have to be dealt with. For example, optimum flocculation and suspension separation is considered to occur at the lowest dose of polymer which produces the best combination of rapid sedimentation, clear supernatant and dense sediment. These three criteria are often mutually exclusive, *e.g.* rapid settling leads to the low density of sediment during its primary consolidation [6]. Thermosensitive flocculants may be a universal solution for the industry, mainly because they may act as selective and extremely efficient flocculants and simultaneously, due to the hydrophilic/hydrophobic transition, as flotation collectors [7–9]. Poly(*N*-isopropylacrylamide) (PNIPAM), as a most common example of

thermosensitive polymer, is a non-toxic polymer which can be used as environmentally friendly substitute to industrial agents [5, 10]. Moreover Forbes [7] indicates that PNIPAM may be more efficient than conventional flotation agent. Its copolymers can be used for selective removal of a desired mineral [11]. At the present moment one may find papers where thermosensitive polymers were used for suspension flocculation [2, 3, 5–7, 9, 12–30], nanoparticles stabilization [31, 32] or heavy metal ions removal [33]. Savage *et al.* [34] used temperature sensitive surfactant micelles to control colloidal crystallization.

In this paper a literature overview concerning application of thermosensitive polymers as stabilization agents is presented. Although the primary stimuli of these macromolecules is temperature they also exhibit reaction to many other factors like pH, heating method, salt concentration and others.

THERMOSENSITIVE AGGREGATION MECHANISM

The first application of thermosensitive polymers was reported by Guillet *et al.* in their patent [15] in 1985. Presently one may find numerous reports of research concerning properties of PNIPAM [35–39]. Vast and extensive review concerning different kinds of stimuli-responsive polymers is presented by Dimitrov *et al.* [40]. Standard flocculation process runs in four steps. Firstly, solid particles are mixed with flocculant. Then, the polymer chains are adsorbed on the surface of solids and undergo reformation achieving equilibrium state. The fourth

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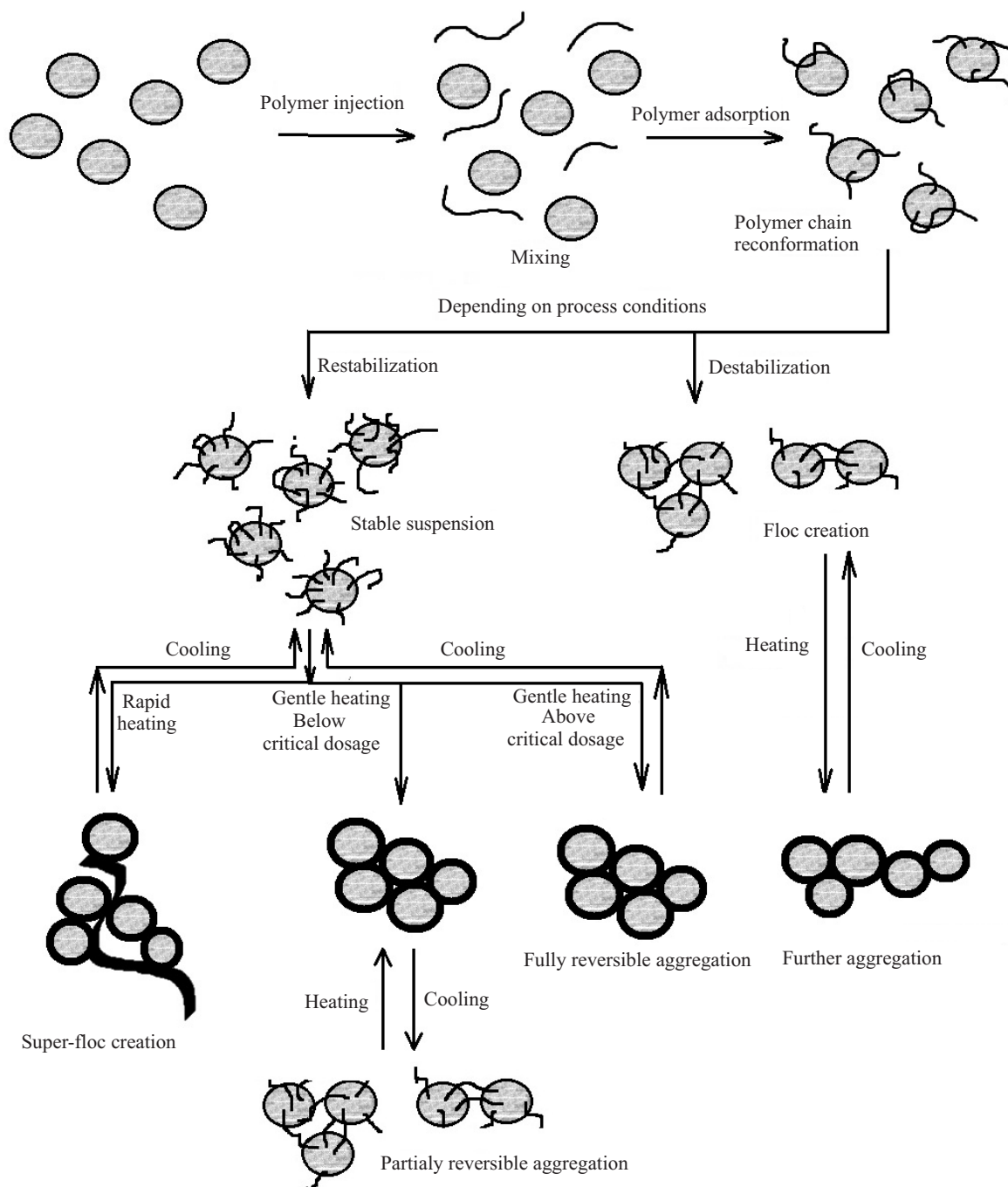


Fig. 1. Flocculation mechanism using thermosensitive polymers

step, *i.e.* the aggregation, may run via three different mechanisms: charge neutralization, charge patching or bridging [41]. There exists a range of flocculant concentration, so called flocculation window, within which aggregates are created. When this concentration is exceeded an effect of suspension stabilization is observed – particles covered with polymer cannot aggregate because of repulsive forces between the hydrophilic chains. On the other hand, when a thermosensitive polymer is used a different mechanism needs to be postulated (Fig. 1).

At a certain temperature polymer chains change their character from hydrophilic to hydrophobic. This transi-

tion results in a change of polymer chains' shape from straight and long strings into small coils. When the flocculant concentration is within the flocculation window, the polymer undergoes transition to a hydrophobic form and makes the particles' surface hydrophobic as well. The presence of a hydrophobic surface restricts the natural structuring tendency of water, simply by imposing a barrier which prevents the growth of clusters in a given direction. Therefore, water confined in a gap between two such surfaces would not form clusters larger than a certain size. For a narrow gap, this could be a serious limitation and results in the increase of free energy of the water in relation to bulk water. There is an attrac-

tion between hydrophobic surfaces, as a consequence of water molecules migrating from the gap to bulk water, where there are unrestricted hydrogen-bonding opportunities and a lower free energy [16].

In the newly formed aggregates primary particles are much closer together than in the case of particles created via bridging mechanism. When the suspension is cooled down and the polymer chains change their properties back to hydrophilic, the bridging mechanism occurs again but this time it is more effective – the particles are already covered with the polymer and the distance between them is smaller. However, if the flocculant concentration is above the flocculation window the situation is different. In this case, when the suspension is cooled down, polymer starts to straighten and changes properties back from hydrophobic to hydrophilic. An effect called steric stabilization appears. Since the chains become hydrated once again, overlap of the adsorbed polymer layers would cause some dehydration and hence an increase in free energy and repulsion between particles [16]. Part of polymer has to be desorbed back to the solution and the rest stabilizes particles. Bava *et al.* [42] proved that application of thermosensitive polymers not only changes the aggregation mechanism but also influences the breakage of flocs. They investigated kinetics of dispersion using PNIPAM and silica particles in poly(dimethylsiloxane) as a model suspension. The temperature of suspension determined the breakage mechanism from rupture at low temperature to erosion at high temperature.

IMPACT OF DIFFERENT FACTORS ON THERMOSENSITIVE AGGREGATION

Molecular weight

Burdukova *et al.* [10] proved that in case of thermosensitive flocculation the zeta potential of treated particles depends both on temperature of suspension and molecular weight of polymer. In the first case, for temperatures above the Lower Critical Solution Temperature (LCST), the zeta potential is lower than for temperatures below LCST. In the second case, zeta potential value decreases with increasing molecular weight of PNIPAM. Moreover the molecular weight increases significantly the probability of particle/bubble attachment during flotation. It also influences greatly the polymer hydrophobicity for temperatures both below and above the LCST [10, 11, 24]. However at temperature above LCST the increase in hydrophobicity is significantly greater [11].

Franks *et al.* [9] noticed that molecular weight as well as polymer dosage greatly influences the sedimentation process. The higher molecular weight of PNIPAM, the higher initial settling rate of suspension was noticed. Similar findings were reported by Li *et al.* [19]. High molecular weight PNIPAM created larger and denser aggregates of silica particles. On the other hand, in the case of

low molecular weight polymer, higher dosages were required. A strong trend of polymer adsorption with molecular weight below LCST was demonstrated by O'Shea *et al.* [21]. Moreover authors indicate that adsorbed PNIPAM provides nucleation sites on the surface of particles for hydrophobic association and hence further deposition of the polymer onto the particle surface at temperatures above the LCST. Similar conclusions were made in recently published papers [22, 24, 26]. Finally, it is worth to emphasize that the LCST of PNIPAM does not vary significantly with molecular weight for polymers of molecular weight greater than $100 \cdot 10^3$ [11] ($50 \cdot 10^3$ according to O'Shea *et al.* [21]).

Molecular structure

There are basically two methods of nanoparticles stabilization using polymers, physical adsorption and covalent grafting techniques. As an example of the first case Budgin *et al.* [31] used amphiphilic block copolymers as well as PNIPAM homopolymer in order to encapsulate iron oxide nanoparticles. In result, the submicron particles were created which were responsive not only to temperature but to magnetic field as well. On the other hand, grafting techniques was used by Gong *et al.* [32]. They created TiO₂-PNIPAM nanoparticles using polymer of low molecular weight and narrow molecular weight distribution. That allowed one to freely switch between temperature triggered aggregation and photocatalytic effect. On the other hand, Bayliss *et al.* [43] performed research on colloidal phase separation using PNIPAM microgel particles, hydroxyethyl cellulose and polystyrene particles in water.

Ghimici and Constantin [5] indicated that commercial forms of synthetic flocculants have some drawbacks like very slow biodegradation in soil or water and toxicity of residual monomers which are usually present in small amounts. They developed a thermosensitive flocculant based on pullulan which was biodegradable. It was successfully used in clay powder flocculation. Nichifor and Zhu [20] proved that molecular structure of thermosensitive polymers has influence on the separation of emulsions and suspensions. They used different copolymers of *N,N*-dimethylacrylamide (DMA), *N*-ethylacrylamide (EA), acrylamide with *t*-butylacrylamide and styrene (St). The copolymers based on DMA and St led to effective separation of dodecane in water emulsion. On the other hand, EA and St copolymers were ineffective. Authors attribute this difference to the different hydrophobicities which can influence their adsorption. O'Shea *et al.* [23] indicate that counterionic random copolymers of PNIPAM afford selective flocculation even when added at a temperature above the LCST. Unfortunately, the charge patch and bridging mechanisms produce strongly and irreversibly flocculated sediments which persist even upon cooling. Therefore, they propose to use block-copolymers which may enable selectivity in ad-

sorption and simultaneously fully reversible aggregation of particles. In their research it was proven that adsorption of polymers increases with increasing charge density due to the electrostatic interactions. Sakohara and Nishikawa [28] investigated the impact of cationic component (*N,N*-dimethylaminopropylacrylamide) mole fraction onto TiO₂ flocculation efficiency. They proved that ionic copolymer significantly influences the LCST of the thermosensitive flocculant which in turn affects sedimentation tests. Generally speaking, the higher molar fraction of the ionic component, the higher was LCST. What is interesting, in the reported research [28] it was stated that hydrophobic interaction induced by adsorbed nonionic polymer above LCST was too weak to overcome electrostatic repulsion force between particles. Employment of ionic polymer was therefore necessary.

Influence of pH

Deng *et al.* [13] proved that adsorption of thermosensitive polymers depends on pH and temperature. In their experiments they used poly(*N*-isopropylacrylamide-*co*-diallyldimethylammonium chloride) and titanium dioxide in water as model suspension. Moreover, a reversible flocculation was observed under conditions where the copolymer concentration was so high that the TiO₂ particles were sterically stabilized at room temperature (Fig. 1). The dependence of polymer adsorption on the pH was used by Qiu *et al.* [26]. They employed double responsive poly(vinyl caprolactam) to aggregate silica particles and proved that increasing the pH at temperatures above LCST decreased adsorption, reversing on lowering the pH, in parallel with the reversal of flocculation.

Forbes [7] and Sakohara *et al.* [2] indicate that transition temperature of PNIPAM is weakly dependent on the pH of solution. On the other hand, the LCST of cationic and anionic copolymers strongly depends on the pH value. In the first case transition temperature decreased with the increase in the pH while in the second case it increased. The transition temperatures of these polymers were considerably high in the neutral pH region. Similar results were reported by Sakohara and Nishikawa [28].

Temperature

Burdukova *et al.* [12] investigated the impact of temperature on the particle size distribution of alumina powder destabilized with PNIPAM. They divided the dependence between aggregate size and temperature into three distinct regions. In the first region, below the LCST, the polymer is inactive and the size of aggregates is constant. In the second region a rapid increase in diameter appears due to the hydrophilic/hydrophobic transition. Finally, in the third region the aggregates continue to grow but at a significantly slower rate with respect to temperature. These authors concluded that the growth of

aggregates cannot be attributed to the decrease of suspension viscosity but to the increase in the force of adhesion with rising temperature.

Franks [14] proved that cooling of sediment leads to enhanced consolidation. He used zircon suspension and methylcellulose as thermosensitive agent. Identical conclusions were made by authors of other papers [6, 9, 19, 21–23]. The reversibility of the state of aggregation and dispersion can be used both to produce rapid sedimentation and enhance sediment consolidation. This approach appears to be more effective than filtration of sediment above LCST [9]. The mechanism of this process is obvious. Above the LCST particles create stiff structure of flocs which form sediment bed. This structure is porous in nature which results in high amount of water trapped in aggregates as well as between them. On the other hand, when suspension is cooled below LCST, flocs break up due to repulsive forces resulting from steric stabilization. This allows particles to create dense sediment with less content of water. In the same paper [9] authors proved that PNIPAM assisted flotation may be more effective than flotation using dodecylamine hydrochloride. On the other hand, O'Shea *et al.* [21] noticed that after cooling the solids content in the supernatant can increase, indicating that re-dispersion occurred due to polymer re-solubilisation and desorption and associated reduction in aggregate mechanical strength.

Kuźnik *et al.* [16] performed an experimental research on reversibility of calcium carbonate suspension thermosensitive flocculation. They proved that there exists a critical polymer dosage above which aggregation process is fully reversible (Fig. 1). On the other hand, the dosages below critical value result in partial breakage of flocs which are bonded via polymer bridging. O'Shea *et al.* [22] stated that in case of PNIPAM homopolymer the effects of temperature are more important than for the charged copolymers. Incorporation of charge into PNIPAM reduces the temperature sensitivity of the interactions between particles in suspension. On the other hand, the incorporation of charge into the polymer architecture results in selective flocculation.

O'Shea and Tallon [24] investigated zeta potential value below and above LCST for silica suspension treated with PNIPAM of different molecular weights. They proved that due to the collapse of the adsorbed layer above LCST the plane of shear is closer to the surface which results in slightly higher zeta potential. This conclusion is in conflict with research reported by Burdukova *et al.* [10]. It is worth to emphasize that in the contrast to the standard coagulation or flocculation high zeta potentials do not have to characterize stable suspensions. In case of thermosensitive flocculation the attractive forces may appear. Lemanowicz *et al.* [17] investigated the impact of heating method on the floc formation. They used two methods of heating: gentle via thermostated coat and rapid via hot water injection. In the second case authors present a mechanism of superfloc creation

(Fig. 1) and using this mechanism they explained the formation of extra large aggregates of insoluble polymer and attached particles. Such findings are in accordance with research of Li *et al.* [18]. These authors measured long range interactions and adhesion between kaolin clay particles covered with PNIPAM using atomic force microscopy.

Addition method

Li *et al.* [19] emphasize that both methods of mixing the polymer solution into suspension and the shear conditions during the temperature increase are important in determining the aggregate properties. It is with agreement with findings of other authors [16, 17]. O'Shea *et al.* [23] indicate that above LCST the coil to globule transition, site nucleation and polymer aggregate deposition are the mechanism of adsorption. In the case of high molecular weight counterionic random copolymer an additional and temperature independent electrostatically driven adsorption results. When counterionic bloc copolymers are used their adsorption is facilitated by the formation of polymer micelles. O'Shea and Tallón [25] investigated the effect of salt addition during the solid-liquid separation of silica suspension with PNIPAM. They proved that suspension instability increased with increasing NaCl concentration up to a maximum and then decreased. The electrical double layer compression accompanying the increase in salt concentration means that the weak and reversible flocculation becomes less reversible.

Sakohara *et al.* [2, 30] proposed the application of dual ionic thermosensitive polymer system. The compaction of TiO₂ suspension occurred through formation of polymer complex of the cationic and anionic polymers at relatively low temperature. Similar experiments were performed by Sakohara *et al.* [3] where kaolin clay suspension was flocculated. Authors emphasize that ionic thermosensitive polymers have high LCST. This problem may be overcome by using oppositely charged polymers or by incorporation of hydrophobic copolymer (*e.g.* *N-tert-butylacrylamide*) into the flocculants chain. Sakohara *et al.* [29] also suggest that thermosensitive ionic polymers could be used for dewatering of activated sludge. The high LCST values of such polymers would be decreased by the creation of complexes with extracellular polymeric substances. Moreover authors proved that moisture content may be decreased markedly in comparison to that obtained using conventional polymeric flocculant. Finally, Sun *et al.* [44] proved that porosity of substrate influenced the hydrophobicity of adsorbed PNIPAM. They raised contact angle of investigated surface from 93.2° (flat surface) to 149.3° for rough surface (6 μm microgroove).

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