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Suspension polymerisation in the presence of an inhibitor; prolonged transition stage and suppressed emulsion particle formation

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ABSTRACT

A typical suspension polymerisation accommodates a simultaneous emulsion polymerisation that produces emulsion particles. A consecutive emulsion and suspension polymerisation was carried out, which clearly indicates that these emulsion particles destabilise the suspension by adsorbing the stabiliser and thus enlarge the size of final beads. These emulsion particles can coagulate and reach a size that is similar to those of satellite particles formed by drop rupture mechanisms in the stirred reactors. Methyl methacrylate was considered as a model monomer. Inclusion of a water-soluble inhibitor in the formulation recipe was found to decrease the average bead particle size and sharpen their size distribution. An inhibition effect contributes to drop stability in two ways. First, it does not allow polymerisation to occur in the drops during induction time and thus prolongs the transition period during which the size of drops is reduced. Second, it hinders particle nucleation in the water phase so that the stabiliser remains available for protecting the bead particles against coalescence. The main conclusion is that the inhibitor should not always be removed from monomers prior to suspension polymerisation.
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1. Introduction

Polymer beads are usually produced by suspension polymerisations. This process, however, is associated with the formation of particles with a rather broad size range [1–3]. The control over the average size of particles is usually maintained by combination of the stirring system including baffling, impeller type and speed, and the stabiliser system including type and concentration of the stabiliser used. However, a rather uniform size distribution is always difficult to achieve.

The reason for formation of particles with a broad size distribution is because different mechanisms of particle formation coexist in suspension polymerisations. Three size classes of particles can be obtained from a suspension polymerisation reactor. They are bead particles, satellite particles, and emulsion particles.

The bead particles are the main products from suspension polymerisations. Their diameters are usually within 50–500 μm depending on application. Satellite and emulsion particles are usually considered as off-grade products which are screened from the main beads and disposed or used as resin ingredients in polymer solutions. They are different from the bead particles, not only in terms of size, but also because of having different properties including molecular weight, morphology and cross-linking density.

Diameters of satellite particles are usually about a few microns. They are formed because of the chaotic nature of drop rupture by turbulent eddies, and nonhomogeneities of mixing in the reactors [1–3].

Emulsion particles are the result of radicals formed in the water phase, by decomposition of initiator, reacting with monomer dissolved in the water phase. When the growing radicals reach a critical size they become insoluble in the water phase and then precipitate to form polymeric nuclei (i.e., homogeneous nucleation). These primary particles are continuously formed in the course of polymerisation [4] and they can adsorb stabiliser from the aqueous phase. However, they are usually very unstable and coagulate with other primary particles to reach a stable colloidal size. These particles are usually smaller than the satellite particles, but it can be difficult to distinguish them from satellite particles. They are usually assumed to be smaller than 1 μm in diameter. Sometimes these off-grade particles can constitute more than 30 wt% of the desired product [5]. The prerequisite for formation of these particles is that both monomer and initiator have to be at least slightly soluble in the water phase. For example, AIBN was found to produce the maximum amount of emulsion particles

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while lauroyl peroxide (LPO) produced the least [1,5,6]. In many suspension polymerisations, initiators with low water solubility, such as benzoyl peroxide and lauroyl peroxide are used in order to avoid excessive secondary nucleation.

The formation of secondary particles via micellar nucleation is important in conventional suspension polymerisation only if the reaction is carried out in the presence of micelles which enhance formation of secondary particles [7]. The monomer concentration in emulsion particles is usually different from that in suspension beads. The monomer concentration in emulsion polymer particles is usually constant during intervals I and II as the result of system minimising its free energy (contrasting free energy of mixing and surface free energy). The surface free energy is negligible for droplets of the size encountered in suspension polymerisation leading to a higher monomer concentration in suspension particles than in emulsion ones. Reaction rate is higher in emulsion particles because of reduced rate of radical termination (radical compartmentalisation), and polymers with higher molecular weights are usually produced.

Droplet nucleation can also contribute to the formation of emulsion particles [8]. Submicron droplets can be formed by Ostwald ripening of satellite droplets formed via the chaotic nature of drop rupture mechanisms. Ostwald ripening promotes diffusion of monomer from the small drops through the water phase to large drops. Polymerisation in such small droplets can then occur in a similar way to that found in miniemulsions by capturing radicals from the water phase or from their interiors, depending on the water solubility of initiator. The reduction of Ostwald ripening, that occurs when polymer is formed in the drops, can also be enhanced if an ultrahydrophobe is included in the reaction ingredients. That can boost stability of the drops so that they survive complete dissolution in water and can be transformed into polymer particles. Conclaves et al. claimed that secondary particle formation was enhanced with LPO, in comparison with benzoyl peroxide (BPO), despite being less soluble in water because of its effect on stability of droplets and promotion of droplet nucleation [9].

In a typical suspension polymerisation all the three mechanisms; bead/drop formation (the main mechanism), satellite formation, and homogeneous nucleation (to form emulsion particles), are at work giving a wide particle size distribution to the product. However, in most studies, the effects of emulsion particles are usually ignored. This even applies to modelling attempts that have been made to describe the evolution of particle size distribution (PSD) in suspension polymerisations, which often considered only bead and satellite particles in association with turbulent rupture of mother drops into daughter and satellite drops [10–12].

The use of an inhibitor may affect kinetics of polymerisation as well as the rates of drop rupture and coalescence. Therefore a brief description of four intervals involved in a typical suspension polymerisation reaction is useful. In interval I, *transition stage*, the average drop size decreases exponentially and drop size distribution narrows dramatically due to a higher rate of drop break up in comparison with drop coalescence ($R_{break} >> R_{coal}$). The importance of this interval, which had been often ignored in the literature, was recently highlighted by Jahanzad et al. [12], and has subsequently received significant attention from others [13]. During this stage drops are reduced in size until they reach an almost constant average size. In interval II, *quasi-steady-state stage*, the rates of drop break up and drop coalescence are almost balanced leading to a semi steady-state drop size average and distribution ($R_{break} \approx R_{coal}$). At the quasi-steady-state, coalescence removes as many drops from the dispersion as are made via the break up mechanism. Therefore, this steady-state is often of a dynamic nature. At high stabiliser concentration, however, the steady-state is transformed to a static one as neither new drops are formed nor lost ($R_{break} = R_{coal} = 0$). This interval may not exist for all systems and depends on the polymerisation conditions. Interval III is characterised by *growth period* or so-called *sticky stage* during which the rate of drop break up falls considerably below the rate of drop coalescence ($R_{coal} >> R_{break}$) due to the viscosity build up in drops, leading to the drop enlargement and size distribution broadening. The last interval, *identity stage*, is marked by final transformation of soft drops into solid particles which cannot not undergo further coalesce ($R_{break} = R_{coal} = 0$).

The aim of this research is to investigate how the presence of emulsion particles in a suspension polymerisation system can affect the stability and size distribution of the desired beads and how the formation of emulsion particles can be avoided in order to improve the product quality. Application of water-soluble inhibitors as a means to reduce the formation of emulsion particles has been occasionally reported in the literature [6,13,14], but scarcely analysed. A model monomer, methyl methacrylate (MMA), which is sufficiently water soluble to induce secondary nucleation and has been widely studied in the literature [15–17] has been selected for this study. The formation of emulsion particles by more water-soluble initiators such as AIBN is well appreciated [18]. In this research, we use LPO to highlight such effects in the presence of a water-insoluble initiator.

2. Experimental

2.1. Materials and experimental set up

MMA (analytical grade from Aldrich) was distilled at reduced pressure to remove inhibitors. Poly vinylalcohol (PVA; M_w = 85–146 kDa, degree of hydrolysis = 87–89%) and lauroyl peroxide (LPO; 97%) and hydroquinone (HQ; 99%), all from Aldrich, were used as stabiliser, initiator, and inhibitor, respectively, without any further purification. Distilled water was used as the continuous phase. PVA solution was always filtered prior to use. The experiments were carried out using a 1-l jacketed glass reactor (internal diameter 10 cm) equipped with four 90° baffles. A four-bladed flat turbine impeller with a diameter of 5 cm was used for agitation. The temperature of the vessel content was controlled within ±0.5 °C of the desired reaction temperature. Nitrogen purging was carried out for 30 min before the monomer phase was added to the aqueous phase. Samples were withdrawn, at the desired time intervals, from the reaction vessel using a hypodermic syringe to measure the monomer conversion and drop/particle size distribution. In order to avoid irreproducibility, the sampling point was fixed at 2 cm away from the impeller shaft and 3 cm below the suspension level. Experiments were carried out at 70 °C, with two agitation speeds of (N=) 300 and 500 rpm. The monomer volume fraction was 20% and PVA and LPO concentrations were 1.0 g/l (based on water phase) and 1.0 wt% (based on monomer phase), respectively. The total volume of water was 560 ml. Similar experiments were always conduced in the absence of initiator in order to be able to compare reactive and non-reactive systems.

2.2. Measurements

Monomer conversion was measured gravimetrically. The surface tension was measured using Du Nouy ring method. A particle sizer (Coulter LS130), based on Fraunhofer diffraction, was used for drop/particle size distribution measurements. The particle sizer, Coulter LS130, has 84 channels (bins) which accommodate size ranges that change logarithmically. The average size of particles was calculated taking into account these variable bin sizes. However, the generated PSD curves, based on logarithmically increasing bin sizes, overestimate the average size of particles [12].

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