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From miniemulsion to nanoemulsion polymerization of superhydrophobic monomers through low energy phase inversion temperature

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ABSTRACT

Miniemulsion preparation by low-energy phase inversion temperature (PIT) was performed for lauryl methacrylate (LMA) using polyethoxylated non-ionic emulsifiers. The minimum emulsifier content (4.5 wt%) and maximum amount of monomer (33 wt%) that led to stable miniemulsions was optimized and the corresponding miniemulsions polymerized. Depending on the polymerization temperature, a conventional miniemulsion polymerization or a nanoemulsion polymerization (NEP) mechanism were followed. The possible explanation for the change of the reaction mechanism has been presented. Moreover, the robustness of the PIT technique for industrial applications was confirmed by polymerizing a LMA/isobornyl acrylate superhydrophobic monomer mixture.

Introduction

Emulsion polymerization is the most widely used process for the production of waterborne dispersed polymers, because it enables the production of high-quality materials in a consistent, safe and environmental friendly way. A crucial requirement in this process is the monomer transport through the aqueous phase from the monomer droplets into the growing polymer particles, which represents a severe limitation for the polymerization of superhydrophobic monomers. The diffusional limitations may be overcome if polymerization occurs in submicron droplets, which is the inherent advantage of miniemulsion polymerization. This technology has been used extensively in laboratory scale during the last 40 years. However, the special equipment required for miniemulsification, such as sonifiers, rotor–stators and high pressure homogenizers have met resistance at an industrial scale [1].

Temperature induced phase inversion (PIT) of water in oil (W/O) emulsions is a low-energy method that allows the formation of stable and finely dispersed miniemulsions by taking advantage of the physicochemical properties of the system. When using thermo-sensitive emulsifiers, the affinity of the emulsifier for the dispersed and continuous phases is exchanged by adjusting temperature, triggering an emulsion inversion [2,3]. At the inversion point, a sharp reduction of interfacial tension between oil and water phases is observed, which leads to the stabilization of three phases in equilibrium: a water dispersed in oil rich phase, and oil dispersed in water rich phase, together with the formation of an emulsifier-rich middle phase, also known as a bicontinuous microemulsion phase. By cooling under continuous mixing the middle phase is ruptured, yielding very small droplets, while the mechanical emulsification of the remaining phases produces larger droplets. The result is a stable bimodal miniemulsion that can be polymerized by droplet nucleation.

This method was originally introduced by Shinoda and Arai [4], and the underlying mechanisms have been a topic of discussion for the past 50 years [5–8]. A recent article of Solans et al. presented a concise overview of the topic [9]. However, just a few examples pertaining to PIT emulsification of monomers and the subsequent polymerization of the miniemulsions generated can be found in literature. Spernath and Magdassi [10] were the first to use the PIT method to polymerize lauryl acrylate, using polyethoxylated non-ionic emulsifiers, Brij 96V (polyoxyethylene 10 oleoyl ether) and combinations of Brij 96V and Brij 92V (polyoxyethylene 2 oleoyl ether). The emulsions contained 20 wt% oil phase and a minimum of 4 wt% emulsifier, yielding nanoparticles having an average diameter in the range of 50–120 nm with a narrow size distribution, depending on surfactant hydrophilic/lipophilic balance (HLB) and concentration. As the surfactant concentration decreased, they observed a greater reduction between the average

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miniemulsion droplet and final latex particle sizes, which they attributed to micellar nucleation triggered by trace amounts of styrene in their recipes. Alvarado et al. [11] polymerized miniemulsions of hexyl methacrylate stabilized with Brij 56 (polyoxyethylene 10 cetyl ether) as surfactant and squalene as costabilizer. Surfactant concentrations between 11–15 wt%, with solids content up to 20%, were selected in order to obtain single phase microemulsions at the inversion point that lead to droplet sizes as low as 32 nm. Polymerization of the miniemulsions was performed at 20 °C and the authors claimed that they were exceptionally fast and that droplet nucleation was the predominant mechanism. Suzuki et al. [12] reported the preparation by PIT and later polymerization of styrene miniemulsions in the presence of pyrene. A poly(ethylene oxide) nonyl phenyl ether with an average of 20 EO was used as surfactant at a 1:1 weight ratio with respect to the monomer, and with solids content below 10%. The polymerizations were carried out at the phase inversion temperature, achieving particle sizes as low as 22 nm. Recently, Sasaki et al. [13] reported the PIT emulsification of styrene, using amphiphilic comb-like block polymers synthesized by Atom-Transfer Radical-Polymerization (ATRP) of styrene and oligo(ethylene glycol) methyl ether methacrylate, and the subsequent synthesis of latexes with particle sizes between 30 and 120 nm by controlling the styrene chain length of the surfactant. Surfactant:Oil phase: Water weight ratios of 4:8:100 were used in those experiments. As it can be seen, a broad range of particle sizes have been reported by the polymerization of phase inverted emulsions, but their production lacks of an adequate explanation.

Furthermore all the reported works show that an elevated quantity of surfactant is necessary to stabilize low amount of monomer, which is an important limitation of the technique from an industrial point of view, because of the adverse effects of surfactant on the final properties of the latex films. In this work, this technique wanted to be further explored aiming at polymerizing very hydrophobic waterborne dispersions with high solids content and low surfactant concentration. For this purpose, lauryl methacrylate was the investigated monomer. The determination of phase inversion temperature of the selected surfactant and optimization of total monomer and surfactant contents is described. The droplet size and stability of the miniemulsions obtained by PIT were evaluated, and the relevant characteristics of the obtained polymer latexes analyzed. Moreover, the mechanisms of polymerization of those miniemulsions are discussed, by polymerizing the miniemulsions at temperatures far from and close to the PIT, where different polymerization behaviors were observed. The work is extended by the copolymerization of lauryl methacrylate with isobornyl acrylate at a 50:50 weight ratio, performed by polymerization of a miniemulsion previously prepared by PIT.

Experimental

Materials

The monomers lauryl methacrylate (LMA, 96% rest on isomers, Sigma–Aldrich) and isobornyl acrylate (IBA, technical grade, Sigma–Aldrich) were used without any additional purification steps. Brij O10 (Oleyl ether Ethoxylate 10 EO, HLB = 12.4, provided kindly by Uniqema) was the non-ionic emulsifier used. Polymerizations were initiated by a redox system consisting of several pairings of *t*-butyl hydroperoxide (TBH, 70% solution in water from Sigma–Aldrich) oxidant and ascorbic acid (ASA, 99% ACROS) and sodium formaldehyde sulfoxylate (SFS, 99% Fluka) reductants. Sodium chloride (NaCl, >99.5% Sigma–Aldrich) was added to the aqueous phase during the miniemulsification process. Hydroquinone (99%, Panreac) was used for stopping the polymerization in the samples withdrawn from the reactor, and double deionized water (MilliQ standards) was used in all the experiments.

Miniemulsion preparation by PIT

Monomer miniemulsions were prepared in a small 200 mL jacketed glass reactor fitted with a low-energy magnetic stirrer, as well as with a temperature and electrical conductivity probe (Crison micro CM2201). An external water bath with a heating power of 2.6 kW (Lauda ECO Gold) was connected to the reactor's jacket and was used to adjust the emulsion temperature.

A typical phase inversion temperature procedure was followed. Initially, a coarse oil in water (O/W) emulsion consisting of water, monomers and emulsifier was prepared under continuous low-energy agitation applied with a magnetic stirrer. Taking into account that the conductivity measured of a normal emulsion under agitation is that of the continuous phase, this variable is commonly used to detect the moment at which phase inversion takes place. To that end, a small amount of NaCl was also added to the aqueous phase to provide enough electrical conductivity to facilitate the identification of phase inversion temperature without affecting the phase distribution behavior of the emulsion. The emulsion was heated until a sharp decrease down to zero conductivity was observed (characteristic of the oil phase), and the inversion temperature was registered. The now water in oil (W/O) emulsion was then cooled, returning to an O/W morphology.

Polymerization

Batch polymerization of the miniemulsions prepared by PIT was carried out in a Mutiplant M100 system (Chemspeed). The miniemulsions were transferred to 80 mL small metallic reactors and purged with nitrogen during 10 min, before they were heated to the polymerization temperature. Reaction temperatures ranging from 30 °C to 60 °C were tried. Aqueous solutions of TBH, and ASA or SFS were fed in parallel over a period of 60 min after which the reactor was kept at the reaction temperature for additional 30 min, before cooling down the reactor to room temperature and filtering the resulting latex with a filter with a pore size of 80 μm. The total TBH content fed was equivalent to 1 wt% based on monomers, while the total amount of reductant corresponded to a 2 TBH/ASA or 1 TBH/SFS mole ratio. Samples were regularly withdrawn from the reactor in order to analyze conversion and particle size evolution.

Characterization

The stability of the miniemulsions was determined using static multiple light scattering in a Turbiscan Lab Expert apparatus (Formulaction). A 25 mL vial was filled with approximately 20 mL of the miniemulsions shortly after they were prepared, and scanned every 10 min for a period of 1 to 12 h, at either 30 °C or 60 °C. A comparative analysis of these profiles over time allows the discernment of colloidal instability events that could be taking place in the samples, such as droplet migration or droplet coalescence.

The average droplet/particle diameter was measured using dynamic light scattering (DLS) (ZetaSizer Nano S, Malvern) at 25 °C. Before the analysis, the obtained dispersions were diluted with deionized water to avoid multiple scattering. In this work, z-average is reported for monomodal distributions, whereas for bimodal distributions, the volume average of each population is given instead. PDI index (Đ), which is representative of the broadness of the distributions, is also reported.

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