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Miniemulsion polymerization templates: A systematic comparison between low energy emulsification (Near-PIT) and ultrasound emulsification methods

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ABSTRACT

Poly(ethylene oxide)-covered polystyrene nanoparticles were prepared by free radical miniemulsion polymerization after using an original low energy emulsification procedure called Near-PIT method. This procedure consisted in heating the initial monomer emulsion up to a temperature close to the phase inversion temperature (PIT) but lower. The surfactants used were commercial Brij® 78 and Brij® 700 and mixtures of both. The Near-PIT method was showed to allow the preparation of nanoparticle suspensions with average diameters lower than 100 nm and solid contents higher than 20 wt% while avoiding heating the initial monomer emulsion above PIT like in usual low energy methods. The influences of various formulation and operating parameters were investigated. Finally, the Near-PIT method was compared to other well-known procedures for nanoparticle preparation, miniemulsion polymerization after ultrasound emulsification and macroemulsion polymerization under mechanical agitation. The performances of Near-PIT procedure were comparable to ultrasound emulsification.

1. Introduction

Miniemulsions are specially formulated heterophase systems where stable nanodroplets (with a diameter lower than 500 nm) of one monomer phase are dispersed in a second, continuous phase before polymerization takes place often following a radical mechanism. Since its introduction, this approach has extended the classical emulsion radical polymerization, as ideally each nanodroplet could be regarded as an individual batch reactor, a nanoreactor. Indeed, when (oligo)radicals are generated in the continuous phase, nanodroplets compete with micelles for their capture. In addition, the amount of surfactant added in the feed is usually adjusted so as to minimize (or avoid) the presence of micelles in the continuous phase. In those conditions, it could be a good approximation to consider that every droplet behaves as an independent reaction vessel, a hypothetical bulk state where the continuous phase may still transport initiators, side products and heat. Thus, miniemulsion polymerization allows preparing water-based formulated polymers with high solid contents and taking advantage of an additional mode of design of nanoparticles, since the chemical composition and colloidal characteristics of the initial nanodroplets directly conditions that of the final nanoparticles [1,2].

As a consequence of their droplet size, the kinetic stability of initial miniemulsions is often dominated by Ostwald ripening which is the relevant ageing process [3,4]. Indeed, because of their submicronic size, nanodroplets are not sensitive to creaming (within relevant timescales for radical polymerization) and, provided that the surfactant ensures sufficient steric repulsions between droplets, coalescence and flocculation do not occur either. Thus, for miniemulsion polymerization, it is necessary to considerably slow down mass transfer between nanodroplets by the addition of a ultra-hydrophobe compound in the monomer (for direct miniemulsions, hexadecane is a usual example). The aim is to provide enough stability to monomer nanodroplets during polymerization so that droplet nucleation occurs thus allowing the production of polymeric nanoparticles with a size distribution close to that of initial monomer droplets. In addition, polymer formed in nanodroplets contributes to reduce mass transfer (acting as hexadecane even less efficiently) at the beginning of polymerization and reduces coalescence probability at higher monomer conversions (increasing particle viscosity).

Emulsification processes for nanoemulsions generation may be classified in two fundamentally different types, on the one hand high-energy emulsification methods like high pressure homogenizers [5] or ultrasounds generators [6–11], and on the other hand low-energy methods like spontaneous emulsification [12], phase

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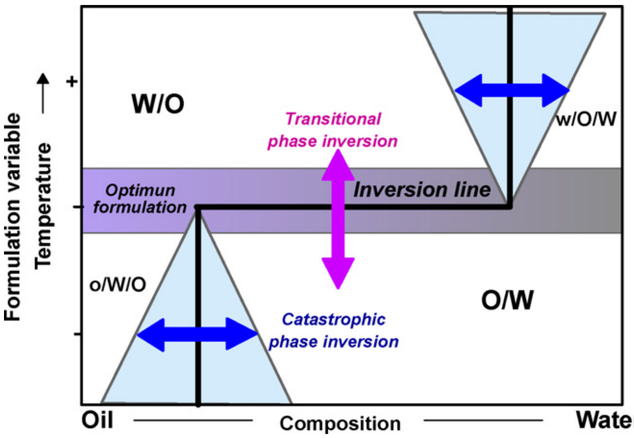

Fig. 1. Formulation–composition map. The bold line is the standard inversion frontier.

inversion temperature (PIT) [13–18], or emulsion inversion point (EIP) [19,20].

In low-energy emulsification methods, the production of submicron size droplets relies on the physico-chemical properties of the system. All the data regarding the type of disperse system obtained are usually represented on a formulation–composition two-dimension map, a graphical representation of the so-called generalized formulation (Fig. 1). The middle shaded zone corresponds to the three phase behavior at or near the optimum formulation, the formulation variable scale is such that the hydrophilicity increases from top to bottom and the stair like bold line is the standard inversion frontier that separates the regions in which O/W and W/O emulsions are formed as the result of the stirring of an equilibrate surfactant–oil–water system [21,22]. The crossing over through the inversion frontier represents a dynamic phase inversion, since the curvature of the liquid–liquid interface swaps its bending from one way to the other, as a consequence of a change in one of formulation variables (*i.e.*, surfactant affinity) or composition variables (*i.e.*, oil/water ratio) during the stirring process. If the change is rendered in the map as a vertical shift (crossing through the horizontal branch of inversion line), as for instance in the continuous change in temperature, the inversion will always take place under the same conditions (at so-called optimum formulation). Such a dynamic inversion, which is found to be reversible has been called transitional because it is linked to a phase behavior transition [23]. On the other hand, when the inversion takes place by crossing through a vertical branch of the inversion line, it is called catastrophic because it may be modeled by using catastrophe theory [22,24]. This inversion occurs as a result of the complete coalescence of unstable emulsion morphology as the closest packing arrangement condition is approached.

The transitional phase inversion is based on the particular ability of emulsions stabilized by poly(ethylene oxide) (PEO)-based nonionic surfactants to undergo a phase inversion upon temperature variation [13]. A change of formulation (*i.e.* induced by temperature increase) along a vertical line, results in a minimum of both the interfacial tension and the emulsion stability at the optimum formulation (Fig. 1). The minimum of stability at optimum formulation has been attributed either to the percolation through liquid crystals located across the thin film, or to the trapping of all surfactant in the microemulsion [25]. Thus as optimum formulation is approached (either from above or from below the standard inversion line) both the interfacial tension and the emulsion stability decrease. As far as the emulsion droplet size is concerned, the two resulting effects are opposite, since decrease in interfacial tension tends to enhance the efficiency of stirring-mixing process and thus produces smaller droplets, while a decrease in emulsion stability favors the occurrence of coalescence events, and thus results in larger droplets [26] (see Fig. 2).

The use of the low-energy PIT method has been reported for miniemulsion polymerization by heating above PIT temperature to inverse the emulsion and then cooling to induce a re-inversion followed sometimes by a rapid cooling in an ice bath to set droplet size within a submicronic range [27–29], demonstrating the potential of these low energy methods.

The present paper focuses on miniemulsion polymerization in which the submicronic emulsion template is formed by Near-PIT method. This low energy emulsification procedure makes use of very strong decrease in interfacial tension near to optimum formu-

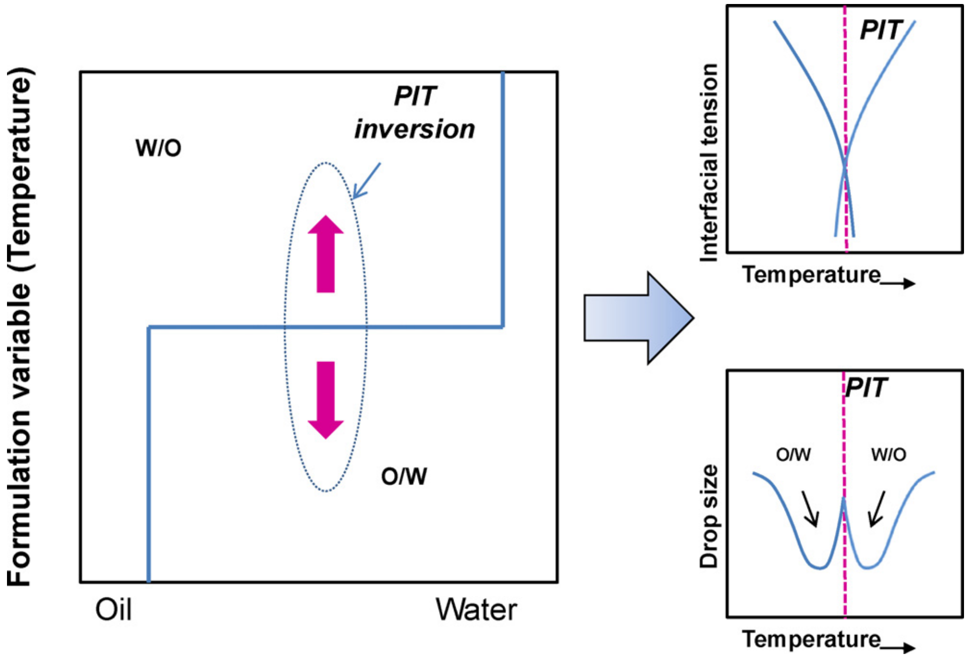

Fig. 2. Evolution of interfacial tension and droplet size during transitional phase inversion.