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Challenges for industrialization of miniemulsion polymerization

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ABSTRACT

Miniemulsion polymerization facilitates the synthesis complex materials that cannot be produced otherwise. These materials have a broad range of potential applications including among others adhesives, coatings, anticounterfeiting, textile pigments, bio-based polymer dispersions, gene and drug delivery, anti-viral therapy, tissue engineering, catalyst supports, polymeric photoresists, energy storage and self-healing agents. However, 40 years after the pioneering work of Ugelstad, El-Aasser and Vanderhoff the promises have not been fulfilled and the presence of miniemulsion polymerization in commercial products is scarce. This article reviews the advances in the field, discusses the reasons for this delay and analyzes the challenges that have to be overcome in order to fully use this process in commercial practice.

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1. Introduction

Miniemulsion polymerization [1–9] seems to be the perfect technique to synthesize complex materials that cannot be produced otherwise. Claimed applications of materials synthesized by means of miniemulsion polymerization include adhesives [10–13]; anti-reflection [14], anticorrosive [15,16] and UV resistant [17] coatings; anticounterfeiting [18]; textile pigments [19]; bio-based polymer dispersions [20]; gene and drug delivery [22–27]; anti-viral therapy [28]; low viscosity high solids dispersions [29–31]; chemosensors [32–35]; polyolefin waterborne dispersions [36–39]; catalyst supports [40]; enzymatic polymerization [41]; controlled free radical polymerization [42–50]; responsive materials [51,52]; photoswitchable fluorescent particles [53]; encapsulation [54–58]; polymer fillers [59]; polymeric photoresists [60]; light emitting diodes [61]; night-vision displays [62]; multicolor optical coding [63]; ultrabright fluorescent polymer nanoparticles [64]; single photon emission quantum dots [65]; tissue engineering [56,66–68]; energy storage [69–73]; glass and ceramics coatings [57]; DNA separation [26,74]; surface-enhanced Raman scattering substrates [75]; self-healing agents [58] and dielectric elastomer actuators [76]. However, 40 years after the pioneering work of Ugelstad et al. [1] the presence of miniemulsion polymerization in commercial products is still scarce.

This article reviews advances in the field, discusses the reasons for this delay and analyzes the challenges that have to be overcome in order to fully use this process in commercial practice.

2. Industrial constraints for miniemulsion polymerization

The performance of the materials mentioned above is determined by the characteristics of the particles: particle size and size distribution; polymer functionality and architecture; molecular weight distribution (MWD); number, type and relative amount of the phases; particle composition distribution; and particle morphology (including the characteristics of the surface of the particles). In addition for biomedical applications, biocompatibility is a must. These materials are “products-by-process” and hence their characteristics are attained in the reactor, namely, they depend on the way in which the process is conducted. The controlled synthesis of these materials requires (i) to form the miniemulsion of composite droplets of controlled size and composition, making them colloidally stable and stable with respect Oswald ripening, (ii) to polymerize most of these droplets avoiding both other nucleation mechanisms and coagulation with particles and droplets, (iii) to achieve high conversion minimizing the residual monomer, (iv) to control polymer architecture (composition, MWD, branching, gel, ...), and (v) to achieve the adequate particle morphology.

In addition to obtaining a high performance material, to make the process industrially viable, it should be implemented in a cost effective, flexible and consistent way, and under safe and environmentally friendly conditions [77].

The impact of these constraints on the process strongly depends on the application. For high tonnage applications, cost effectiveness and flexibility involve the use of relatively large reactors (typically from 10 to 60 m^3) that can be used for the synthesis of different products. This leads to batch or semicontinuous operations. In addition, high solids content (>50 wt%) dispersions are desirable as the production of the valuable material per unit volume of the reactor is maximized and the shipping costs associated to the presence of water in the dispersion are lower. Moreover, the total process time (formation of the miniemulsion, reactor charge, polymerization, product removal and reactor cleaning) should be as short as possible. Last but not least, the investment should be kept at minimum, which in many cases means the use of existing reactors that are currently employed for conventional emulsion polymerization. Consistency in the production refers to avoiding run-to-run irreproducibility.

In large scale polymerization reactors, the occurrence of thermal runaways that cause pressure runaways is the main safety concern. Thermal runaways are associated to sudden and prolonged increases of the polymerization rate, which often resulted from monomer accumulation due to non-detected inhibitions and/or erroneous dosage of the initiator system, as well as to failures of the cooling system. The best way to reduce the occurrence of thermal runaways and their severity is to limit the amount of free monomer in the reactor [78]. In most cases, this precludes the use of batch processes in favor of semicontinuous operations. Semicontinuous processes have the additional advantage of giving better control of the polymer

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