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# Development of a system by atomization for the formation of polymeric particles in micro and sub-micro scales

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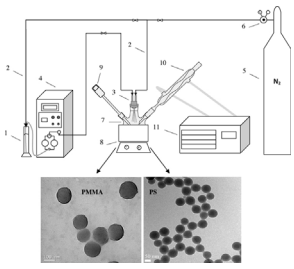
## HIGHLIGHTS

- A process by atomization is applied to miniemulsion and suspension polymerization.
- A simple atomizer is used as an alternative method to break the monomer droplets.
- The droplets formed with the atomizer are directed to the liquid reaction medium.
- We produce submicron particles of poly(methyl methacrylate) and polystyrene.
- Polymeric particles were obtained with size between 40 and 300 nm.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Several studies in nanotechnology have demonstrated significant advantages of nanoparticles compared with microparticles. The main reason for this is the higher ratio of surface area per volume, which results in specific characteristics. Such considerations have driven researchers to develop techniques to obtain polymeric nanoparticles with properties that allow application in different areas. The objective of this work is to present a polymerization process by atomization applied to miniemulsion and suspension systems for formation of submicron particles of poly(methyl methacrylate) (PMMA) and polystyrene (PS). Reactions were carried out using the proposed technique and polymeric particles were obtained with size between 40 and 300 nm, according to dynamic light scattering (DLS) analysis, and with spherical morphological characteristics, according to the results of scanning electron microscopy (SEM) and transmission electron microscopy (TEM).



*Abbreviations:* PMMA, Poly(methyl methacrylate); PS, Polystyrene; SEM, Scanning electron microscopy; TEM, Transmission electron microscopy; PSD, Particle size distribution; KPS, potassium persulfate; SLS, Sodium lauryl sulfate; BPO, Benzoyl peroxide; PVA, Polyvinyl alcohol; $N_2$, Nitrogen or Azote; AscAc, Ascorbic acid; $H_2O_2$, Hydrogen peroxide; MMA, Methyl methacrylate; St, Styrene.

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## 1. Introduction

Nanoparticles are of great scientific interest due to a wide variety of potential applications in biomedical [1–3], optical [4], and electronic fields [5]. Many studies have been carried out in order to produce polymeric particles in nanometric scale [6,7]. Two groups of manufacturing techniques have been reported for producing polymeric nanoparticles: in the first group, the particles are obtained from preformed polymers (natural or synthetic), which may be accomplished by emulsification/solvent evaporation [8–15] solvent displacement [16–19], interfacial deposition [16], salting out [20], emulsion/solvent diffusion [21–23] or by supercritical fluid technology [24]; in the second one, polymerization reactions can be produced or by interfacial polymerization [25,26] or by methods based on emulsion [27], such as surfactant-free emulsion [28], miniemulsion [29–33] and microemulsion [34].

In particular case of minemulsion, conventional methods are used to reduce the size of the monomer droplets with the aim of forming polymeric nanoparticles. Usually, such methods use either mechanical stirring at high rotation or ultrasonic waves or both [35,36]. On stirring, the dispersion of the droplets is performed by applying a high shear stress mechanism maintaining equilibrium in effects of droplet breakup and coalescence [27,37–40]. In sonification, the droplets are broken by cavitation and this approach is generally used in laboratory scale due to the limited field of action of the ultrasonic waves [41–47]. Such conventional methods, although are widely applied in the study of miniemulsions have limitations for use on a large scale due the high energy cost required to generate droplets in production scale on the order of cubic meters.

Another method of obtaining polymeric nanoparticles during microemulsion polymerization was proposed by Chen et al. [34], which consists in feeding the monomer as gas phase at the reaction medium instead of traditional method of feeding in liquid phase.

In the present work, a simple atomizer device is used as an alternative method to break the monomer droplets before feeding and dispersing them in the reaction medium. The monomer droplets formed with the atomizer are directed to the liquid reaction medium and suspension or miniemulsion polymerizations are performed. The proposed method here has the advantage in relation to conventional techniques (mechanical stirring at high rotation or ultrasonic waves) of creating droplets by using only a pump to feed the monomer and a nitrogen line to promote the atomization. In addition, this device is low maintenance cost and relatively straightforward to scale-up. As this technique can be performed in different conditions of feeding (semi continuous or intermittent), it seem to be a promissory technique of producing polymerizations with moderate-to-high solid content, as well as an alternatively way to produce carrier particles.

The atomizer utilized here is similar to those employed in drying systems. In “spray drying”, the liquid is sprayed through the nozzle into small droplets, and put in contact with the drying gas, which is hot enough to lead to the evaporation of moisture. Spray drying is a method used in pharmaceutical and food industries to produce particles from a liquid phase and to encapsulate several materials from a polymeric solution [48–50]. In the proposed system in this study, the monomer is sprayed through the atomizer nozzle into small droplets and dispersed by magnetic agitation into the reaction medium in order for polymerization to occur.

In this study, particles obtained by suspension or miniemulsion polymerizations using the aforementioned technique were analyzed in respect to the size and morphology. It was observed through dynamic light scattering and microscopy analyses that particles are in the nano to submicrometric size with spherical morphology. The technique of polymerization by atomization can be an alternative way to produce carrier particles.

## 2. Materials and methods

### 2.1. Materials

The monomers used in this work were methyl methacrylate (MMA) and styrene (St) obtained from Sigma–Aldrich. The initiator used in the miniemulsion polymerization was the redox pair composed of hydrogen peroxide ($H_2O_2$)—ascorbic acid (AscAc) obtained from Synth and for suspension polymerization benzoyl peroxide (BPO), purchased from Vetec Química. The surfactant sodium lauryl sulfate (SLS) produced by Vetec Química was used in miniemulsion polymerization. Polyvinyl alcohol (PVA) from Vetec Química was used in suspension polymerization. Hydroquinone from Synth was used as polymerization inhibitor. All materials were used as received. Distilled water and nitrogen gas ($N_2$) was used in all experiments.

### 2.2. Apparatus

The suspension and miniemulsion polymerizations were performed using the experimental system shown in Fig. 1. The monomer (1) under $N_2$ atmosphere (2) was conducted to the atomizer nozzle (3) by a pump (4) at a constant flow rate and at room temperature. The atomizer receives the monomer and pressured $N_2$. The $N_2$ gas comes from a cylinder (5) and its pressure is maintained constant by a regulator valve (6). The mixture of monomer and $N_2$ passes through the atomizer nozzle that forms small monomer droplets. The monomer jet is sprayed in the reaction medium prepared previously, depending on the type of polymerization. For miniemulsion polymerizations, distilled water, initiator and emulsifying agent are initially added to the glass reactor (7). For suspension polymerizations, the initiator is added directly to monomer while distilled water and suspending agent are added to the reactor. During the reaction, the medium is stirred and maintained at approximately 60 °C by a heating mantle with magnetic stirrer (8). The operating temperature is monitored by a digital thermometer (9). The system is kept in an inert medium with continuous flow of $N_2$ and the reaction is conducted for about two hours. For avoiding loss of monomer by evaporation and drag, a condenser (10) is used and connected to a thermostatic bath (11) with water recirculation at a temperature of 15 °C. The product of the miniemulsion polymerizations is presented in latex form. On the other hand, the product obtained via suspension polymerization is dispersed in an aqueous medium.

### 2.3. Atomizer

The atomizer used in this work (Fig. 2) was designed by Oliveira [51] and built in stainless steel with internal parts in Teflon. It is an atomizer with external mixture, having an inlet for gas and another for liquid. The monomer passes by a needle of 0.45 mm and finds the gas at the outlet of the atomizer. The mixture forms a “spray” jet with long and narrow cone format. Thus, monomer droplets are formed in the jet.

### 2.4. Experimental procedures

The reactions of miniemulsion and suspension polymerization were based on formulations of Sandler et al. [52] Braun et al. [53] and Romio et al. [32,33].

#### 2.4.1. Miniemulsion polymerizations

The miniemulsion reactions were performed under experimental conditions with variation in monomer by using the monomers MMA and St. The reaction medium containing initiator and emulsifying agent was prepared before the polymerization. Then the