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Facile synthesis of cauliflower-like hydrophobically modified polyacrylamide nanospheres by aerosol-photopolymerization

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ABSTRACT

Amphiphilic copolymers consist of hydrophilic and hydrophobic monomer units have attracted great technological attention recently, owing to their unique properties and their ability to stabilize various interfaces in aqueous systems. This paper presents a novel and facile approach to produce spherical polyacrylamide, polystyrene and hydrophobically modified polyacrylamide (HM-PAM), as one of the most important type of amphiphilic copolymers, using a continuous aerosol-photopolymerization for the first time. To this end, the monomer droplets were generated by an atomizer, then photopolymerization was initiated “in flight” by ultraviolet (UV) irradiation of the aerosol monomer droplets containing photoinitiator within the average aerosol residence time of 30 s in the photoreactor. To control the aqueous solubility, size and morphology of the resulting HM-PAM copolymers, different styrene/acrylamide monomer concentrations were introduced to the system. The textural properties of the obtained materials were characterized by TEM, SEM and N₂ adsorption-desorption isotherms. The results revealed that the copolymers and polyacrylamide have cauliflower-like morphologies, while polystyrene has a nearly smooth morphology. Moreover, chemical compositions of the obtained materials were investigated by several characterization techniques such as ¹H NMR, FT-IR, TGA and elemental analysis. ¹H NMR and elemental analysis of resulting copolymers microstructures displayed successful incorporation of styrene in copolymer with a good agreement compared to initial ratios. The production of amphiphilic copolymer of acrylamide and styrene using the facile aerosol-photopolymerization method might open new avenues to produce various amphiphilic copolymers with a variety of hydrophobic and hydrophilic monomers with desirable properties.

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1. Introduction

Water-soluble polymers (WSPs) are a significant class of materials from both scientific and industrial aspect due to their specific properties in thickeners, flocculants, dispersants or emulsifiers in aqueous based media [1–3]. It is well known that WSPs are gaining more and more importance in specific fields like enhanced oil recovery (EOR) applications, pharmaceutical products and food additives [4–7], moreover, due to environmental hazardous issues; water-based formulations are

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replacing organic ones in important areas such as drilling fluids, cosmetics and paints [8]. In spite of their importance, conventional WSPs suffer from drawbacks in that their aqueous solution properties are adversely affected by external working conditions such as temperature, pH, shear and the presence of salt.

To address the mentioned problems, associating polymers (APs) or also known as hydrophobically modified polymers (HMPs) have been widely studied over the past two decades [9–16]. Fundamentally, HMPs are hydrophilic water-soluble polymers that contain a small amount of hydrophobic groups [17]. In aqueous solutions, above a certain polymer concentration, the hydrophobic groups have a strong tendency to self-associate into micelles-like structures to minimize their exposure to water. The polymer backbone forms an intermolecular physical network structure which lead to an increase in viscosity as compared to the unmodified polymer [18,19]. Furthermore, these kind of polymers exhibit reversible dissociation of the physical links under increasing shear that attracted great technological attention especially in EOR application [20,21].

Generally, HMPs are synthesized via conventional liquid phase methods such as micellar polymerization technique [22], and inverse emulsions or microemulsions methods [23–25]. However, one major difficulty of these methods originates from the insolubility of the hydrophobic comonomer in water [17]. To overcome this problem, an adequate amount of surfactant is essential, especially in microemulsions methods. Consequently, the potential applications of these methods were limited because surfactants might be incorporated into the polymers chains and reduce the purity of resulting polymers [26]. It should be noted here that in some application such as drug delivery [27,28], cancer therapy [29] and food additives purity of polymers is a crucial matter. Moreover, these methods most often use thermal initiator and after polymerization, the produced polymers should be washed in a large excess of an anti-solvent such as methanol to remove unreacted monomers and surfactant and then dried under vacuum which consume time and cost.

As a promising alternative to the conventional liquid methods, the polymer particles or nanoparticles coated with a polymer shell can be prepared in a aerosol-polymerization [30–33]. Aerosol-based methods possess many advantages in comparison to the other solution-based techniques, such as simple fabrication steps, fast particle production, low fabrication cost and green processes. These methods can also avoid the requirement of surfactants and solvents, and produce directly solvent-free dry powders with a high purity and spherical morphology in a continuous process which is desirable in pharmaceutical applications [34]. Moreover, in contrast to the traditional thermally induced polymerization, photopolymerization has many merits, such as low energy consumption, fast initiation rate, low environmental pollution and curing out at room temperature. These properties make aerosol-photopolymerization a promising scalable method [35,36].

First report on the preparation of spherical polymer particles by continuous aerosol-photopolymerization was published in the early 1996, when Esen et al. produced spherical polymer particles with diameters of 5–50 μm by photopolymerization of aerosol droplets [37,38]. Thereafter, several additional studies were reported in this field, micrometer-sized polystyrene particles were produced by aerosol-polymerization via contact of monomer droplets with initiator vapor [39], similar results were obtained with the using a modified vibrating aerosol generator by Gao et al. [33] and finally smaller polymer particles were generated by Akgün et al. [30,32].

Nevertheless, to the best of our search, there is no report available on preparation of cauliflower-like amphiphilic copolymers by aerosol-photopolymerization so far. Furthermore, it should be noted that cauliflower-like organic and inorganic structures have attracted increasing attention in many fields such as size exclusion chromatography (SEC) [40], particles loading [41], light harvesting enhancement for dye-sensitized solar cells [42,43], battery with super high energy density [44] and preparation of superhydrophobic materials [45,46].

In this work, for the first time, we report an investigation on producing the cauliflower-like amphiphilic copolymers consisting of acrylamide and styrene, mainly hydrophobically modified polyacrylamide (HM-PAM), by the continuous aerosol-photopolymerization. In addition of HM-PAM, spherical particles of polyacrylamide and polystyrene are also reported by this method. Moreover, the method for controlling the size and morphology of the resulting polymer particles by adjusting the chemical composition of the starting solution and the polymerization kinetics in the droplet is discussed.

2. Experimental

2.1. Materials

Acrylamide (AM, Sigma-Aldrich, $\geq 99\%$) and styrene (Sty, Sigma-Aldrich, $\geq 99\%$) were employed as monomers. Irgacure 907 (Methyl-1[4-(methylthio)phenyl]-2-morpholinopropan-1-one, Sigma-Aldrich, 98% purity) and 1,6-hexanedioldiacrylate (HDDA, AlfaAesar, 99% purity) were used as the photoinitiator and crosslinker, respectively. All chemicals were used as received, without further purification.

2.2. Process

The continuous experimental setup for aerosol based photopolymerization is a combination of three main components, an atomizer, a flow-through photoreactor, and a collection filter, as illustrated in Fig. 1. The atomizer (Topas, Model ATM 220) was used to spray monomer solution in a nitrogen atmosphere to produce monodisperse droplets. In case of styrene,

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