

Synthesis of hybrid microspheres from zirconium butoxide and an ionic–non-ionic copolymer

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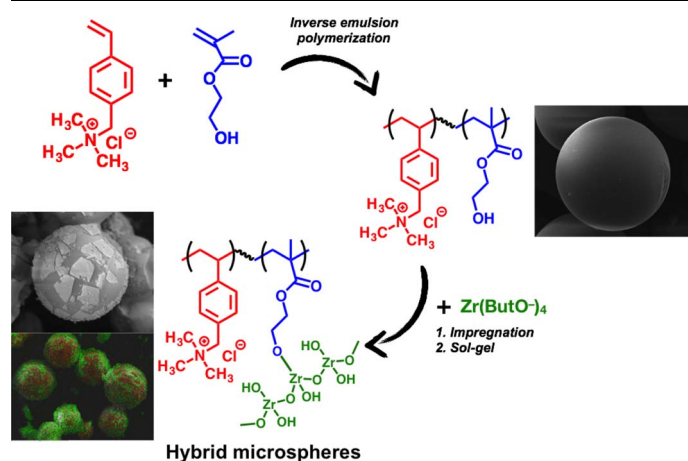
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GRAPHICAL ABSTRACT



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ABSTRACT

This work presents the synthesis and characterization of hybrid microspheres made of hydrated zirconium oxide and an organic copolymer. The synthesis was carried out in a two-stage procedure. First, the polymer microspheres were synthesized via the inverse emulsion polymerization of 4-vinyl benzyl trimethyl ammonium chloride (CIVBTA) and 2-hydroxy ethyl methacrylate (HEMA), and second, the copolymeric beads were impregnated with an inorganic precursor ($\text{Zr}(\text{ButO})_4$) to form the hybrid through a sol-gel reaction. Several experimental variables were controlled in both stages of the synthesis, such as the formulation of the emulsion, concentration of the surfactant, molar ratio of the monomers, concentration of the inorganic precursor, and soak time. Well-defined microspheres with low polydispersity were obtained with a volume ratio of 0.2 and a low Span 80 surfactant concentration. While an increase in the CIVBTA/HEMA molar ratio enhanced the hydrophilicity of the particles, it did not necessarily increase the incorporation of oxide. Additionally, an increase in CIVBTA/HEMA decreased the resistance of the composite microspheres to the osmotic shock, resulting in rupturing of the beads. This polymer hybrid microspheres can be used in applications where surface processes are involved.

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1. Introduction

Organic-inorganic polymeric hybrid materials have developed significantly in recent decades, and their synthesis, properties, and applications have been reported in several reviews [1–3]. A hybrid material is a composite material where the constituents are mixed at a molecular level. The concept of hybrid materials should be differentiated from nanocomposites since the former ideally corresponds to a homogeneous system, while the nanocomposite displays discrete domains at a nano scale (1–100 nm), leading to a heterogeneous system [4]. The interactions between the two moieties play a key role in achieving a hybrid with desirable properties. Hence, hybrid materials can be classified into two categories: i) Class I corresponds to those systems where the inorganic and organic phases interact through weak intermolecular forces, such as Van der Waals, hydrogen bonding and electrostatic interactions, and ii) Class II corresponds to hybrids with a strong chemical interaction between the components, such as covalent bonds [5].

In general, the objective of hybrid material synthesis is to combine the properties of each phase into one material and, ideally, obtain a synergy that produces a material with new properties. The possibilities of combining organic and inorganic materials are tremendous, and the applications of these materials are extensive, ranging from devices for energy generation [6,7], catalysis [8,9], dental applications [10], sensors [11,12], and actuators [13,14] to adsorbent materials [15–17], among others. Polymeric–metal oxide hybrid materials are obtained through several synthetic routes. For instance, the main synthesis strategies can be broadly categorized as i) *in situ* metal oxide formation into the polymer network [18], ii) impregnation of polymerizable monomers (or oligomers) into an oxide gel and polymerization, and iii) simultaneous formation of the polymeric and inorganic phase through polymerization and sol-gel reactions [19–21].

This work presents the synthesis of a hybrid polymer-metal oxide with a spherical shape. In the first stage, the polymer microspheres were prepared from a cationic monomer and a non-ionic monomer polymerized in an emulsion (w/o). Subsequently, the polymer microspheres were impregnated with an inorganic precursor, and then, the sol-gel reaction was used to obtain the oxide network. Usually, polymer microspheres are synthesized through a polymerization of oil-in-water emulsion (or dispersion polymerization) with nonpolar monomers, resulting in hydrophobic microspheres, which disfavours access of the molecules of the precursor during the impregnation of the microspheres and decreases the content of the inorganic phase. In this way, we believe that the use of hydrophilic monomers and polymerization through an inverse emulsion will favour the impregnation of the precursor, resulting in a polymer with a high oxide content. Moreover, the use of a monomer that can react with the inorganic phase (i.e., covalently) strengthens the interaction between the organic and inorganic phases.

The synthesis of materials with well-defined shapes is important in practical applications. For example, in surface phenomena (e.g., catalysis, adsorption, ion exchange, etc.), the use of spherical particles maximizes the exposed surface (the area of contact between two spheres is a point), increasing the efficiency of the processes, which is contrary to the results obtained with irregular particles. Additionally, from the point of view of catalysis and adsorption, zirconium oxide is an interesting compound to study [22–25].

2. Experimental part

2.1. Reagents

All of the reagents were used as received unless otherwise indicated. For the synthesis of polymeric microspheres, 4-vinylbenzyltrimethylammonium chloride (CIVBTA, 99%, Sigma-Aldrich) and 2-hydroxyethylmethacrylate (HEMA, 97%, Aldrich) were used as monomers, *N,N*-methylene-bis-acrylamide (MBAAm, 99%, Sigma-Aldrich) was

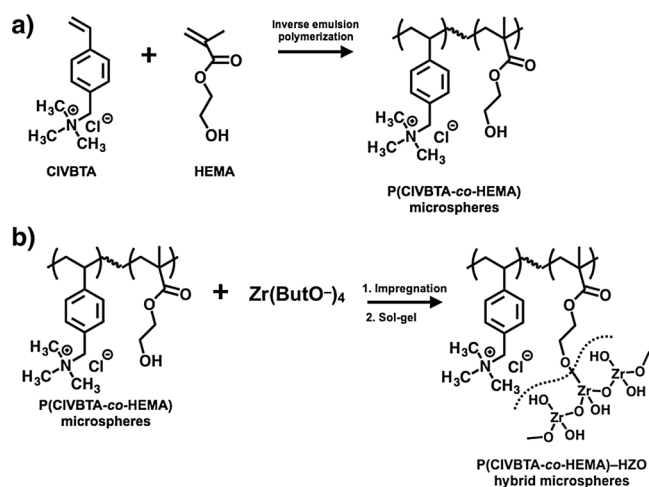


Fig. 1. Scheme of synthesis route of the P(CIVBTA-co-HEMA)-HZO hybrid microspheres.

used as the crosslinker, and the co-initiators were ammonium persulfate (APS, 98%, Sigma-Aldrich) and *N,N,N',N'*-tetramethylethylenediamine (TEMED, 99%, Merck). The organic phase of the emulsion was composed of *n*-heptane (99%, Merck) or *n*-decane (94%, Merck) and sorbitan monoleate (Span 80, HLB = 4.3, Merck) as the emulsifier. To synthesize the hybrid microspheres, zirconium tetrabutoxide Zr(ButO)₄ (80% in 1-butanol, Aldrich), was used as precursor for the oxide formation. For the impregnation step, the following solvents were used: methanol (99.9%, dielectric constant, $\epsilon = 32.7$, Merck), ethanol (99.5%, $\epsilon = 24.6$, Merck), 2-propanol (99.5%, $\epsilon = 17.9$, Merck), 2-butanol (99.5%, $\epsilon = 17.3$, Merck) acetone (99.5%, $\epsilon = 21.0$, Merck) and 1,4-dioxane (99.5%, $\epsilon = 2.2$, Merck).

2.2. Synthesis of P(CIVBTA-co-HEMA) microspheres

The synthesis of the poly(4-vinyl benzyl trimethyl ammonium chloride-co-2-hydroxy ethyl methacrylate), P(CIVBTA-co-HEMA), and microspheres was carried out by emulsion polymerization in a water-in-oil (w/o) system (see Fig. 1a). The formulation parameters included the following: H₂O/organic solvent volume ratio (ϕ) of the emulsion (0.2–0.5 v/v), surfactant concentration (0.025–0.200 mol/L), organic solvent (*n*-heptane, *n*-decane), and stirring rate (300–800 rpm) were studied. Additionally, the monomer mole ratios of the CIVBTA/HEMA were studied in the range of 1.0–5.0.

The aqueous phase consisted of the following reagents: CIVBTA and HEMA, MBAAm (20 mol%), and the co-initiators APS and TEMED at 1.0 mol% and 2.0 mol%, respectively. The organic phase was composed of *n*-heptane or *n*-decane, and Span 80 was used as the emulsifier. First, the solution of monomers, crosslinker and ammonium persulfate was prepared and then slowly added into the organic solution. After 10 min of emulsification, the co-initiator (TEMED) was added, and the polymerization was carried out for 30 min at 70 °C with constant stirring. Later, the temperature of the system was reduced, and the polymers were isolated and washed by Soxhlet extraction (Soxtherm SE-412, Gerhardt), first with *n*-heptane (or *n*-decane) and then with ethanol for 8 h each. Finally, the sample was dried at 40 °C for 24 h and sieved to obtain a particle size in the range 75–180 μ m.

2.3. Synthesis of hybrid microspheres

The synthesis of hybrid microspheres was carried out by impregnation of polymer microspheres with an inorganic precursor (IP) of Zr(ButO)₄, followed by a sol-gel reaction, leading to the oxide formation (see Fig. 1b). The impregnation step included the study of the chemical precursor concentration (30–80 wt%), the solvent for impregnation (ethanol, 1,4-dioxane, 2-propanol, 1-butanol) and time (2–5 days). The

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