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Synthesis of polystyrene microspheres to be used as template in the preparation of hollow spherical materials: study of the operative variables

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Abstract

Mono-disperse polystyrene (PS) spheres were synthesized. The styrene polymerization was carried out using 4,4'-azobis 4-cyanovaleric acid (ACVA) or potassium persulfate (KPS) as initiators in the presence of polyvinyl pyrrolidone (PVP) as surfactant or stabilizing agent. Size measurement and its distribution were followed by scanning electron microscopy. A very narrow size distribution was obtained by controlling the synthesis temperature. For both initiators, it was observed that smaller PS particles are obtained when PVP amount increases. Besides, the sphere size decreased when KPS amount increased at a fixed PVP concentration. Similar results were obtained for the polystyrene spheres synthesized using ACVA as initiator. On the other hand, the influence of a co-monomer addition in the sphere size was also analyzed. The suitable selection of the initiator type and its concentration, as well as the surfactant agent amount, led to a controlled obtainment of the polystyrene microspheres, appropriate to be used as template in the synthesis of hollow spherical materials.

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Keywords: Polystyrene; operative variables; template; hollow spheres

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1. Introduction

A variety of hollow spherical materials have been prepared by using polystyrene (PS) spheres as hard templates (Zhang et al., 2009). These materials present interesting characteristics such as low density, high surface area, excellent charge capacity, high permeability and, in addition, they have potential application in different fields such as storage and delivery of drugs, catalysis, separations, chromatography, and immobilization systems (Yoon et al., 2006).

Various synthetic methods have been proposed for the fabrication of hollow materials, particularly for silica hollow spheres. Few studies have employed PS spheres as a polymeric template, though it has been reported as the most suitable method for the synthesis of mono-disperse hollow silica spheres (Suárez et al., 2007).

To obtain the polystyrene (latex) template, styrene polymerization by means of the radicalary polymerization mechanism has been used. The macromolecule formation by free radicals comprises the following steps: initiation, propagation and termination of chain growth by either termination or chain transfer. These radicals are generated employing polymerization initiators, organic or inorganic, which give different characteristics to the synthesized polymeric materials.

The water-soluble initiators (inorganic) produce almost all of the free radicals in the aqueous phase, while the initiators soluble in organic solvents distribute their radicals among four phases, monomer-micelle, monomer-polymer particles, monomer droplets and aqueous phase. Thus, water-soluble and oil-soluble initiators bring about differences in the mechanism of polymerization (Nomura et al., 2005). However, theoretical and/or experimental studies conducted in polymerizations using these initiators have concluded that the kinetics of polymerization is basically similar for both types of initiators (Nomura et al., 1993).

Also, a surfactant agent is added, whose role is to produce stable particles, preventing coagulation during the polymerization (Hong et al., 2010). Both the surfactant agent and the polymerization initiator and their concentrations play an important role in the obtained particle size and yield to final product (Paine, 1990).

The addition of a co-monomer in the synthesis of the PS spheres is an alternative strategy for modifying the surface of the spheres, and a factor to be considered during the preparation of materials as templates for the synthesis of hollow spheres.

We found that the most commonly polymerization initiator reported in the literature is 2,2'-azobisisobutyronitrile (AIBN). However, this compound is classified as highly inflammable and its exportation and importation is restricted in several countries. Taking this into account, we decided to replace AIBN by 4,4'-azobis 4-cyanovaleric acid (ACVA), which according to the literature has not been previously reported as polymerization initiator.

Since many of the results reported in the literature were not reproducible in the laboratory and, in some cases, were not suitable for the desired purpose, in this work polystyrene templates were synthesized using different polymerization initiators (ACVA or KPS) and a surfactant agent (PVP). Their influence on the size and distribution of the spheres was studied. Also 3-amino-1-propene as co-monomer was added, and its effect on the characteristics of the latex spheres was observed.

2. Experimental

2.1. Synthesis of polystyrene spheres

The polystyrene spheres were prepared from styrene (Aldrich, > 99%) using potassium persulfate (KPS) (Mallinckrodt, > 99%) or 4,4'-azobis 4-cyanovaleric acid (ACVA) (Aldrich, > 98%) as polymerization initiators, in the presence of polyvinyl pyrrolidone (PVP) (Aldrich, PM = 29000) as surfactant agent. Different

PVP to styrene ratios were employed: 1, 2, 3, 6, 8 and 10% (w/w). A fixed KPS or ACVA to styrene ratio (1% (w/w)) was used, and ethanol-water as solvent for the inorganic initiator (10:4 (v/v)) or ethanol for the organic initiator.

The mixture was poured into a 250 cm³ reactor, fitted with a reflux condenser, a temperature controller and a magnetic stirrer. N₂ was bubbled for 15 min in order to remove oxygen from the reactor.

The temperature was increased up to 70 ° C, and then the initiator dissolved in an aliquot of ethanol (or ethanol-water) was added to the reactor. The polymerization was carried out at 300 rpm for 24 h. After completion of this time, the latex was repeatedly washed with ethanol and stored in the form of dispersion in ethanol.

To study the influence of the initiator concentration on the size of the spheres and its distribution, the same test was carried out, but this time the amount of initiator was varied between 0.5% and 1% w/w respect to styrene, and the PVP to styrene ratio was fixed in 3% (w/w), for both KPS and ACVA initiators.

Similarly as described above, polystyrene spheres were synthesized by adding 3-amino-1-propene (allylamine) as co-monomer to 10 g of styrene, in a ratio of 10 and 20% respect to styrene, using in this case fixed amounts of ACVA as initiator and surfactant agent (PVP) of 1% and 3% (w/w), respectively.

2.2. Characterization

The morphological study of polystyrene spheres was performed by scanning electron microscopy (SEM), using Philips model 505 equipment. The determination of the sphere diameter, its distribution and the average diameter was carried out from the SEM images of the samples, measuring 150 spheres in each image.

3. Results and discussion

The polymerization starts in homogeneous phase by action of the initiator, generating nuclei from which colloidal particles are produced, which grow and end up separating of the reaction medium. PVP could be considered as a stabilizing agent in the polymerization reaction, which acts as a surfactant. PVP also plays an important role in obtaining stable particles with spherical shape, and prevents the aggregation of colloidal particles during the polymerization (Zou et al., 2008).

For both initiators, it was observed that the addition of PVP allows to obtain spheres in suspension without them are grouped in clusters. It was also found that the particle size decreased when the amount of PVP is increased. At higher concentrations smaller particles are produced, so the PVP can stabilize a large surface area (Kim et al., 2006).

Figure 1 shows the morphology of the polystyrene microspheres prepared with 1, 3 and 10% of PVP to styrene ratio, using ACVA as polymerization initiator. The average diameter of the spheres according to the different PVP proportions used is presented in Figure 2; as example it can be mentioned that the average diameter of the spheres obtained with 3% of PVP respect to styrene was 2.5 µm.

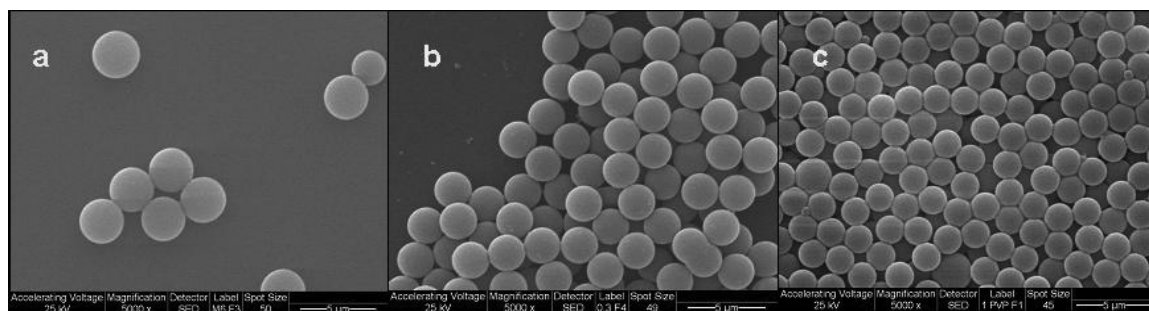


Figure 1. SEM micrographs (5000X) of polystyrene spheres prepared using ACVA as polymerization initiator and different PVP to styrene ratios: a) 1, b) 3, c) 10% (w/w). Bar: 5 μ m.

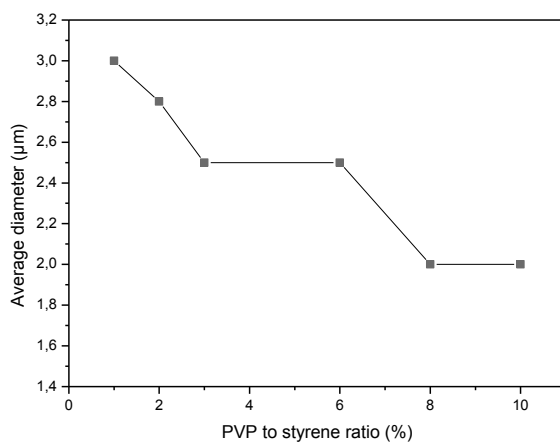


Figure 2. Mean diameter of polystyrene spheres obtained using ACVA as polymerization initiator and different PVP:styrene ratios.

Regardless the PVP amount used in the synthesis of the latex spheres, the diameter distribution was very narrow, which was achieved by carefully controlling of temperature during the synthesis. For example, Figure 3 shows the distribution obtained for spheres synthesized with 3% PVP (w/w), and ACVA as polymerization initiator.

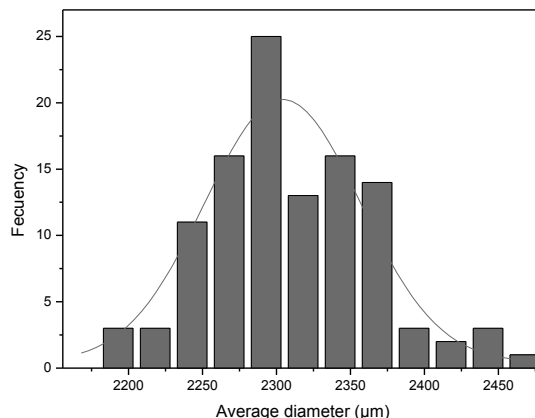


Figure 3. Size distribution of PS spheres synthesized using ACVA as polymerization initiator and 3% (w/w) PVP: styrene ratio.

The same dependence on the amount of surfactant agent was observed for polystyrene spheres synthesized with 1, 3 and 10% (w/w) of PVP, using KPS as polymerization initiator. In this case, the average diameter of the spheres was 2 µm for the minimum proportion of PVP, 1 µm for the intermediate quantity and an average diameter of 0.5 µm when 10% (w/w) is used (Figure 4).

The difference in the size of the PS particles obtained with different initiators has been studied in detail by Nomura et al., 2005, who attributed this size difference to different diffusion rates of the initiators. The KPS, soluble in aqueous phase, diffuses at a fast rate to the monomer drop where polymerization takes place, resulting in particles of smaller diameter. In contrast, the diffusion rate is lower in aqueous phase for the organic initiator (ACVA), slowing down the polymerization process and, therefore, obtaining larger size particles. Similar results were obtained by Capek, 2001, who considers that the diffusion rate of the initiator molecules is the controlling step of the polymerization rate.

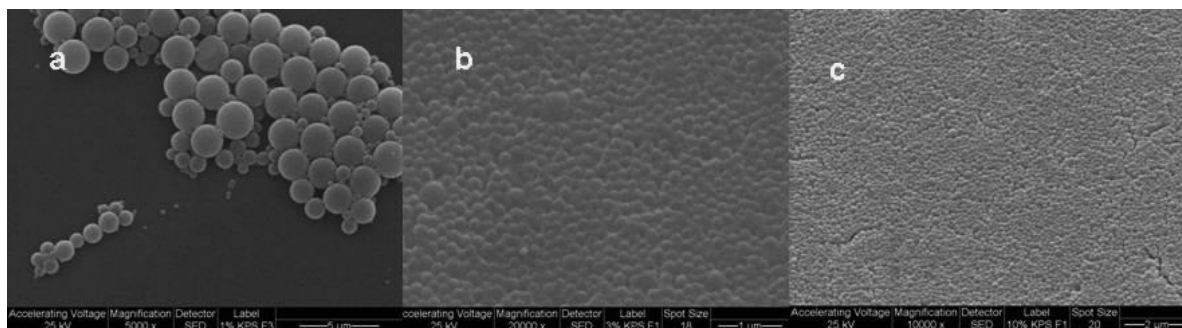


Figure 4. SEM micrographs of polystyrene spheres prepared with KPS as polymerization initiator and different PVP:styrene ratios: a) 1% (w/w) (5000X); b) 3% (w/w)(20000X), c) 10% (w/w). (10000X).

To study the influence of the initiator amount in the sphere size and its distribution, the same test was performed, but this time the initiator concentration was varied between 0.5 and 1% (w/w) respect to styrene,

and left the PVP: styrene ratio fixed in 3% (w/w), for both the initiator KPS and for the ACVA. It was observed that, when the concentration of the initiator increased, the sphere size decreased. The average diameter was 2 μm for a KPS concentration of 0.5% (w/w), 1.4 μm in diameter for 0.8% (w/w) of initiator, and 0.5 μm for the maximum used concentration (1% (w/w)). It can be concluded that, as the initiator concentration increases, the polymerization process rate is higher and, therefore, smaller PS particles are obtained. This is consistent with studies by Miller et al., 1995, who reported that the decrease in the particle size is a result of the formation of a high fraction of small monomer droplets for a short period of nucleation. Furthermore, they attributed the increase in the particle diameter, when the amount of initiator is decreased, to the presence of large droplets of monomer for a longer nucleation time, and to the entry of free radicals at an early stage of polymerization.

Two different volumes of 3-amino-1-propene were used for the synthesis carried out with the co-monomer, and fixed amounts of initiator (ACVA) and surfactant agent. It was observed that the sphere diameter varied according to the amount of co-monomer. For the addition of 1 ml of 3-amino-1-propene, spheres of 1 μm in diameter were obtained, whereas when 2 ml of co-monomer were added, the particle size decreased obtaining PS spheres of 0.5 μm in diameter. The results obtained by SEM are presented in the following micrographs (Figure 5).

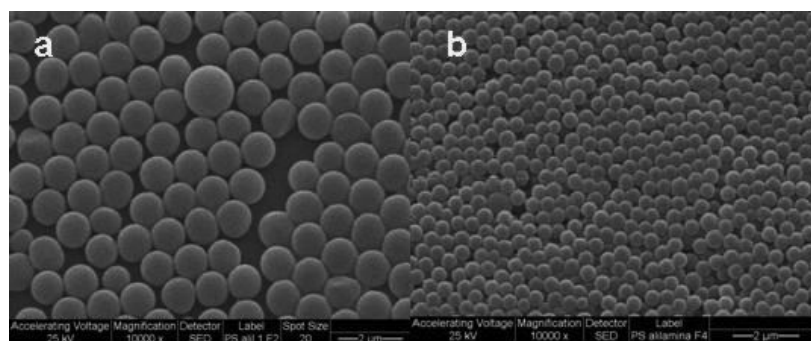


Figure 5. SEM micrographs (10000X) of polystyrene spheres prepared using ACVA as polymerization initiator and different allylamine amount as co-monomer: a) 1 ml; b) 2 ml. Bar: 2 μm .

It is clear that the addition of co-monomer influences the size of the synthesized latex spheres. Indeed, the main objective of this addition is to modify the surface of the spheres, since the amino groups of the co-monomer would cover the surface of the PS spheres with positive charge. It can be considered that this effect of the 3-amino-1-propene addition is an important factor in optimizing the coating of the spheres to obtain certain hollow spherical materials (Zou et al., 2008). In the particular case to which the templates studied in this work are aimed, corresponding to silica-based materials, an acid-base interaction with the hydroxyl groups of silica can be generated.

4. Conclusions

In this work we report for the first time the use of 4,4' azobis 4-cyanovaleric acid (ACVA) as organic polymerization initiator and its comparison with potassium persulfate (KPS) inorganic one in the synthesis of polystyrene microspheres. PS particles were obtained in a controlled manner with a very narrow size distribution for the different conditions employed during the synthesis, being changed the type of

polymerization initiator and its concentration, as well as the concentration of surfactant agent, under a careful control of the reaction temperature. Thus, polymeric materials suitable to be used as template in the synthesis of hollow spheres were achieved.

The results showed that the variation of the concentration of both the surfactant agent and the initiators can modify the average diameter of the obtained spheres. For a fixed concentration of initiator, a decrease in the size of the spheres was observed as the surfactant concentration increased. In the case that the PVP concentration is held fixed and the initiator concentration varied, a similar trend was obtained. In all cases, the PVP acts as an excellent stabilizer of the materials obtained.

The use of ACVA as polymerization initiator let us to synthesize latex spheres with controlled diameter and very narrow size distribution, so we can consider ACVA as a suitable replacement of the most employed but highly inflammable AIBN initiator.

The addition of 3-amino-1-propene as a co-monomer is an important factor of study and currently we are more deeply working on this synthesis parameter, which will allow obtaining results concerning the surface characteristics of the material and its future application in the synthesis of hollow spherical materials.

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