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Synthesis of functionalized nanoparticles via copolymerization in microemulsions and surface reactions

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Abstract

Oil-in-water microemulsions of mixtures of styrene and comonomer are easily prepared using titration methods in the presence of nonionic (NPn) or anionic (SDS) surfactants. Functionalized nanoparticles in the 20–30-nm diameter range bearing chloromethyl, active-ester, acid or pyridyl surface end-groups are prepared by polymerization of microemulsions containing mixture of styrene (St) and, respectively, vinylbenzylchloride (VBC), *N*-acryloyloxysuccinimide (NHA), methacrylic acid (MA) or vinylpyridine (VP). Reactions of nucleophiles on particles bearing either chloromethyl or active-ester surface end-groups, performed directly in the aqueous suspensions, give rise to a wide range of nanoparticles with various functionalities. The main role of the surfactant on such surface reactions is demonstrated and used to improve the reaction yields.

Keywords: Polymerization in microemulsion; Functionalized nanoparticles; Surface reactions; Chloromethyl; Active-ester surface end-group

1. Introduction

Aqueous suspensions of nanoparticles may find very specific applications in drug delivery, microencapsulation, biomedical diagnosis [1–3] provided that suitable ligands or binding groups are linked to the surface to ensure recognition. Moreover, the very large specific area of particles in the 20–30-nm diameter range offer new opportunities in other domains like catalysis and chromatography. Therefore, there is a great demand for highly functionalized nanoparticles bearing 'at will' various kinds of chemical functions. Aqueous suspensions of nanoparticles can be obtained by polymerization of hydrophobic monomers in oil-in-water microemulsions and numerous studies have been devoted to polymerization in microemulsion during the last decade [4,5]. Nevertheless, the preparation of highly functionalized nanoparticles via copolymerization in microemulsion has been scarcely studied [1,6–10] and no general procedure for their synthesis has been proposed.

In this paper, we describe a versatile method leading, in one or two steps, to highly function-

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alized nanoparticles with various functionalities. Actually, one of the most important limitations for performing copolymerization in microemulsion is the preparation of the starting microemulsion: the addition of a new component most often modifies the phase diagram and therefore the composition of the microemulsion domain. We show that microemulsions of mixture of monomers are easily prepared using titration processes. The polymerization of these microemulsions leads to nanoparticles bearing various kinds of chemical functions.

The synthesis of well-defined highly functionalized nanoparticles can also be achieved by performing surface modifications of previously prepared nanoparticles: this route is more versatile than copolymerization, provided that suitable reactive groups are linked to the surface. To the best of our knowledge, such chemical modifications have never been performed on nanosized particles prepared by polymerization in microemulsion although one can obviously take advantage of the high specific area resulting from the reduced size. Nevertheless, nucleophilic substitutions on polychloromethylstyrene microspheres or crosslinked resins have been successfully used to introduce various chemical functions via reaction of nucleophilic anions or amines [11–13]. Reactions of primary amines on polymer-bearing *N*-hydroxysuccinimide ester groups have been used to perform chemical modifications [14,15]. We show that such chemical reactions can be performed on nanoparticles bearing chloromethyl or active-ester surface end-groups leading to a wide range of functionalized nanoparticles. Moreover, we demonstrate that one can take advantage of the 'microemulsion process' to control the level of functionality.

2. Results and discussion

2.1. Copolymerization in microemulsions

Two simple and versatile methods, based on titration, have been used to prepare oil-in-water microemulsions of mixture of two monomers. The first method, developed by Tadros et al., [16], uses a mixture of two nonionic surfactants: this consists in forming a water-in-oil emulsion using a low-HLB surfactant (NP5) and then titrating with an aqueous solution of a high-HLB surfactant (NP15). The second one, widely described, uses a mixture of an ionic surfactant and a cosurfactant [17–20] and consists in titrating an o/w emulsion, stabilized using an anionic surfactant (sodium dodecylsulfate: SDS), with an alcohol (pentanol) until a clear microemulsion is obtained. These titration processes readily permit the adjustment of the microemulsion composition. In the present work, both of these methods have been found successful for preparing o/w microemulsions of various mixtures of styrene (St) and functionalized comonomers like vinylbenzylchloride (VBC), *N*-acryloyloxysuccinimide (NHA), vinylpyridine (VP) and methacrylic acid (MA) with molar ratio styrene/comonomer ranging from 90/10 to 70/30 (Table 1 and Scheme 1).

Polymerizations of these microemulsions have been performed under mild conditions below 35°C in order to ensure the microemulsions remain stable during the reaction and to avoid side reactions on functional groups. Water-soluble redox systems like hydrogen peroxide/ascorbic acid at 30°C [16] and ammonium persulfate/tetramethyldiaminomethane at room temperature [21] have been mainly used to initiate the polymerizations. An oil-soluble radical initiator, DMPA (2,2-dimethoxy-2-phenylacetophenone), decomposed under UV irradiation has also been successfully used [22]. Whatever the experimental conditions, polymerization of both monomers, monitored by gas chromatography, readily takes place, reaching 100% conversion within 2 h (Table 1). It can be seen that stable translucent bluish suspensions of nanoparticles with diameter in the region of 20–30 nm are obtained with both types of microemulsion provided that the radical initiator is properly chosen. These suspensions are remarkably stable since neither flocculation nor aggregation of the particles have been observed after more than one year.