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Polyelectrolyte-Modified Microemulsions: Formation of Nanoparticles in the Presence of Anionic and Cationic Polyelectrolyte

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ABSTRACT

The paper is focused on the formation of calcium phosphate nanoparticles (CP) in polyelectrolyte-modified microemulsions, in a microemulsion template phase consisting of cyclohexane, water, anionic surfactantant and cosurfactant, in the presence of anionic and cationic polyelectrolyte. It is shown that polyelectrolyte, can be incorporated into the individual inverse microemulsion droplets. The microemulsion droplets and polyelectrolyte-filled microemulsion droplets can be successfully used as a template phase for the nanoparticles formation. Prepared CP in the presence of anionic polyelectrolyte has a different morphology from samples which are synthesized in the presence of cationic polyelectrolyte. Cationic polyelectrolyte(poly diallyl dimethyl ammonium chloride PDADMAC) leads to formation of needle-like CP (10-20 nm in diameter and 100-150 nm in length). Formation of CPat room temperature was confirmed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). Size and morphology of the CP samples were characterized using transmission electron microscopy (TEM).

Keyword: Microemulsion; Polyelectrolyte-modified microemulsion; Calcium Phosphate; Surfactant; Cosurfactant.

1. INTRODUCTION

Calcium phosphate has been used as artificial bone and tooth substitute. Besides its significance in biology, calcium phosphate is also a good candidate for applications incatalysts and ion exchangers due to its unique surface structure and substitutions. The preparation of calcium phosphate powders with given characteristics of morphology, stoichiometry, crystallinity, and crystal size distribution is important in biomedicine and material science [1-4].

Various synthesis methods, including co-precipitation, hydrothermal reactions, sol-gel synthesis, pyrolysis of aerosols, and recently microemulsion, have been used for preparation of CP. Among these methods, the microemulsion method is one of the most flexible and convenient methods, being able to deliver a particle size and morphology in nanometer scale with minimum agglomeration [5-8].

Microemulsion, i.e. thermodynamically stable, optically clear isotropic dispersions of two immiscible liquids consisting of nano-sized droplets of one liquid in

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another, In such a way the system is stabilized by added surfactant. Different types of microemulsion were known, such as water-in-oil (w/o), oil-in-water (o/w). In the case of a water-in-oil microemulsion, reverse micelles are formed when the aqueous phase is dispersed as micro droplets surrounded by a monolayer of surfactant in the continuous organic phase.

However, one problem is that the bending elasticity and stability of the surfactant film is often not strong enough to confine the growth of the particles to the interior of the microemulsion droplet. To overcome this problem, a component should be added which improve the surfactant film stability; control the particle growth processes and stabilize the particles against flocculation during the re-dispersion process. Recently different authors have shown that water-soluble polymers (polyelectrolytes) can be incorporated into inverse microemulsion droplets [9-12]. On the other hand, the polyelectrolytes can control the size and shape of the nanoparticles during the formation process, polyelectrolyte-modified microemulsion can be successfully used as a new type of template for synthesis of nanoparticles with controlled size, shape, and morphology.

The aim of the present study is to use the microemulsion in the presence of anionic and cationic polyelectrolyte as a template phase for the formation of CP.

2. EXPERIMENTAL DETAIL

The starting materials used in this work included $Ca(NO_3)_2.4H_2O$，$NH_4H_2PO_4$, NH_4OH, cyclohexane, n-butanol, sodium dodecyl sulfate，SDS with 98% purity, Na-Polyacrylate (PAA), polydiallyldimethyl ammonium chloride (PDADMAC), and deionized water. All chemicals were prepared with analytical grade and were used without further purification. Aqueous solutions were made by dissolving sufficient amounts of reagents in deionized water.

2.1. Synthesisroute A
After preparing of 0.1 M solution of SDS in 30 mL cyclohexane and 3 mL n-butanol, 0.5 mL aqueous solution of $Ca(NO_3)_2.4H_2O$ was injected slowly into the SDS solution. A transparent solution was obtained upon stirring of the system for about 15 min. For formation of CP precursors, under stirring, 0.5 mL aqueous solution of $NH_4H_2PO_4$ was directly added to the above-mentioned SDS reverse microemulsion. Then, a small amount of ammonia was added to the system to adjust pH in the range of 9-10. Transparent solution was gained with stirring the system for about 30 min, then age with continuous stirring at room temperature for one day. Finally, a small amount of ethanol was added into the transparent solution to afford the production of white slurry, which was centrifuged to collect the white colloidal CP. The precipitates were rinsed with ethanol for three times and dried at 50°C for 24 h. Dried products were characterized by XRD (Philips expert pro. with Cu Ka radiation ($λ= 0.154$ nm)), Transmission electron microscope (TEM; Philips) and Fourier-transform infrared spectroscopy (FT-IR; Thermo Nicolet Nexus 870).

2.2. Synthesis route B
Route B was carried out similar to route A, but instead of using 0.5 mL of 0.5 M $Ca(NO_3)_2.4H_2O$ aqueous solution, 0.5 mL of 0.5 M $Ca(NO_3)_2.4H_2O$ in 4% (w/v) of polymeric aqueous solution was used to prepare CP nanoparticles.

3. RESULTS AND DISCUSSION

In this study, the influence of presence of anionic (polyacrylate sodium PAA) and cationic polymer on morphology and particle size of the CP was investigated. Polyelectrolyte-modified microemulsions seem to be very interesting template phases for the nanoparticles formation due to the special features of the incorporated polyelectrolyte, including polyelectrolyte-surfactant interactions, polyelectrolyte-nanoparticle interactions [19]. In this study, presence of polyelectrolyte changes the morphology and particle size of CP. In the presence of PAA and anionic surfactant, particle size is larger, because polyelectrolyte-surfactant interactions decrease the film stability of the microemulsion droplets, but in the presence of polyelectrolyte with opposite charge with surfactant the particle size is smaller because polyelectrolyte-surfactant interac-
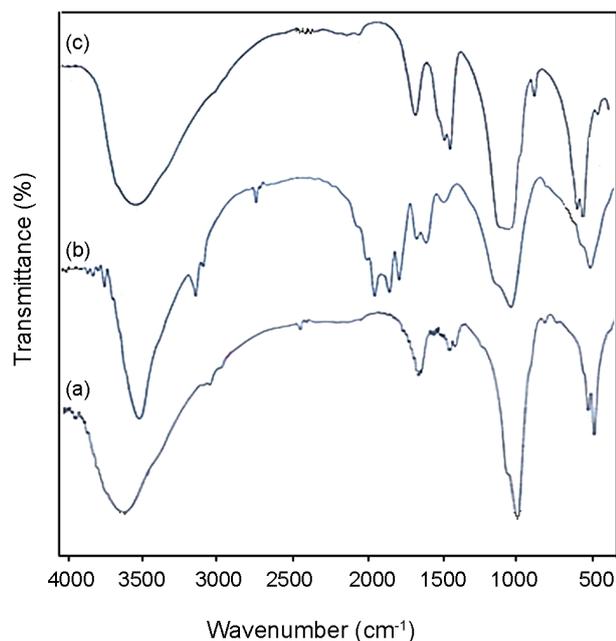
Figure 1: *FT-IR spectra of synthesized CP (a) in the microemulsion system, (b) in the polyanionic-modified microemulsion system, (c) in the polycationic-modified microemulsion system.*

tions increase the film stability of the microemulsion droplets [13, 14].

3.1. FTIR spectrum

Figure 1 shows the FT-IR of synthesized CP in the absence and presence of polyelectrolyte. The IR characteristic peaks of phosphate groups appeared between 1090-1030 and 600-560 cm^{-1}. The absorption bands at 3420 and 1640 cm^{-1} were assigned to the bending mode of the adsorbed water, while the sharp peak at 3570 cm^{-1} is assigned to the stretching vibration of the lattice OH$^-$ ions and a medium sharp peak at 630 cm^{-1} is assigned to the OH$^-$ group of hydroxyapatite [15]. For comparing, the FT-IR of synthesized CP in the absence of polyelectrolyte is displayed in Figure 1a, the weak bands of the CO$_3^{2-}$ group (870, 1415, 1450, and 1540 cm^{-1}) in this Figure, indicated that the CO$_3^{2-}$ substituting came from a reaction between atmospheric carbon dioxide and high-solution pH (>9) [16]. There is an increase in the intensity of the absorption bands of OH$^-$ and CO$_3^{2-}$ in the presence of polyelectrolyte [17-19].

3.2. XRD pattern

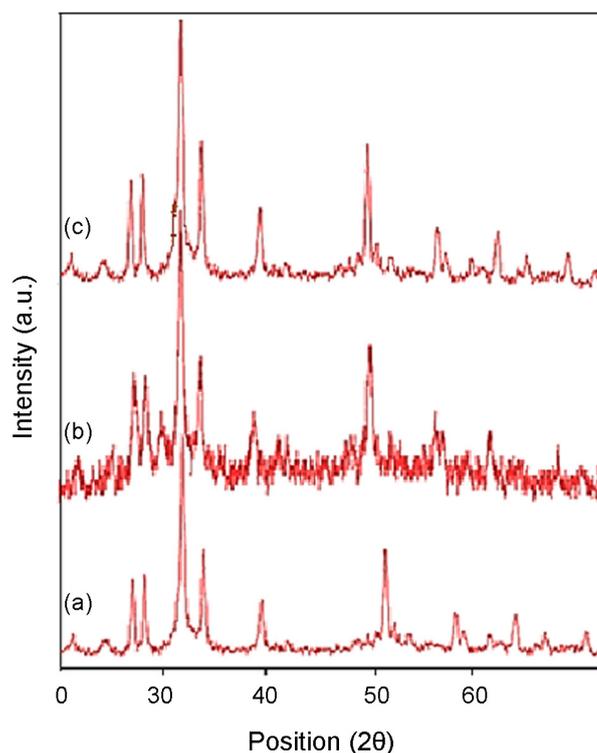Figure 2 shows the XRD patterns of the obtained

Figure 2: *XRD patterns of synthesized CP (a) in the microemulsion system, (b) in the polyanionic-modified microemulsion system, (c) in the polycationic-modified microemulsion system.*

particles in the microemulsion media at room temperature. As it can be seen from this Figure, the CP synthesized with reverse microemulsion and polyelectrolyte modified microemulsion systems have the similar XRD pattern. The average crystalline size using the more intense peak was calculated to be 20 nm for CP obtained in the presence of cationic polyelectrolyte, 40 nm for CP prepared in the absence of polyelectrolyte, and 100 nm for CP prepared in the presence of anionic polyelectrolyte using Debye-Scherrer formula.

$$D = K\lambda / B\cos\theta$$

Where D is the mean grain size, K is a geometric factor, λ is the X-ray wavelength, B is the FWHM of the diffraction peak and θ is the diffraction angle.

3.3. SEM study

Figure 3 shows the SEM micrograph of CP obtained in absence and presence of polyelectrolyte. As can be seen from this Figure, the overall morphology of the obtained powders in absence and presence of poly-
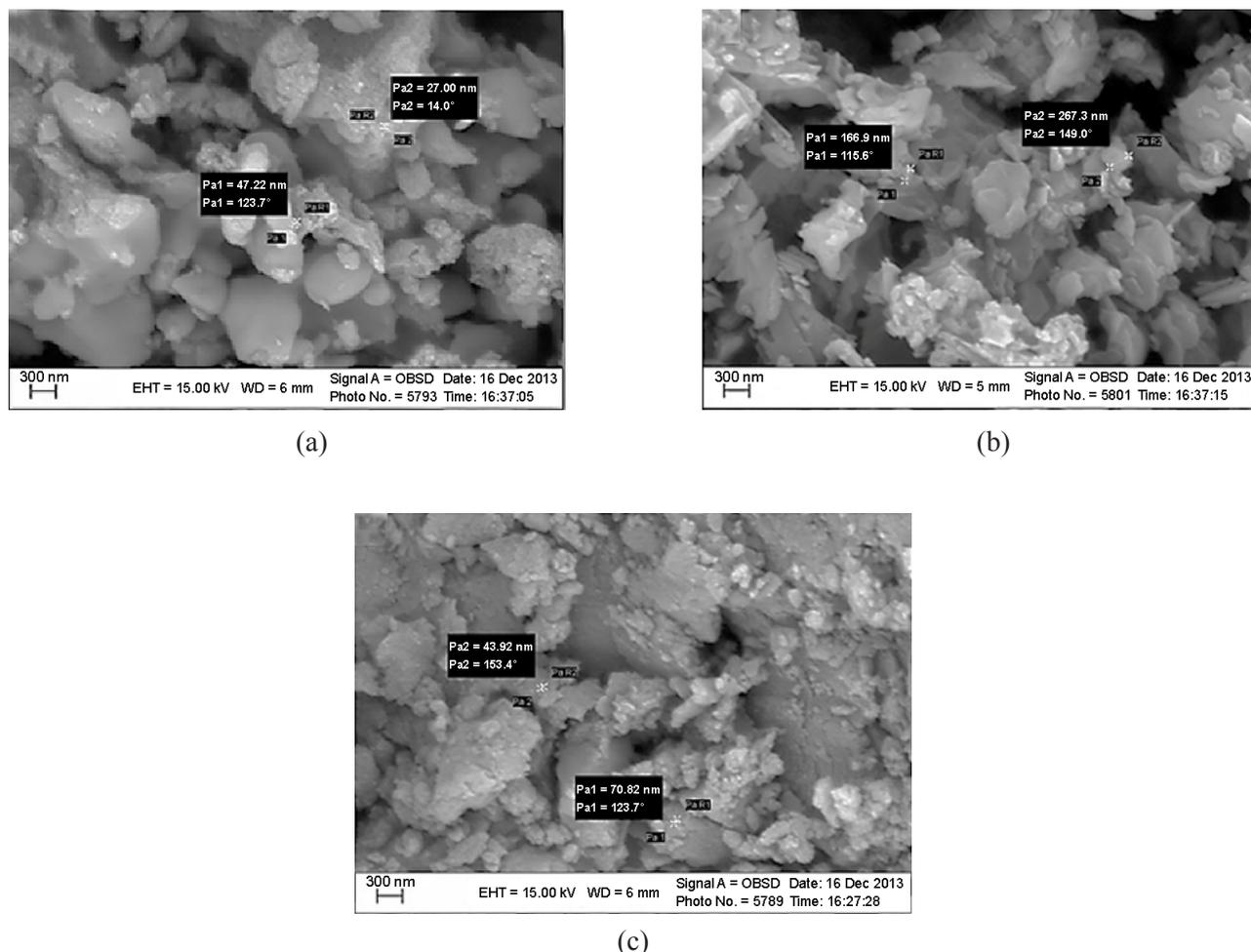
(a)

(b)

(c)

Figure 3: *SEM micrographs of synthesized CP (a) in the microemulsion system, (b) in the polyanionic-modified microemulsion system, (c) in the polycationic-modified microemulsion system.*

electrolyte is quite different. These images suggest that the presence of polyelectrolyte has great influence on the regularly nanoparticls distribution and morphology of the product due to polyelectrolyte-surfactant and polyelectrolyte-nanoparticle interactions in the polyelectrolyte-modified microemulsion droplets.

3.4. TEM study

Figure 4 shows the TEM micrograph of CP products in presence of cationic polyelectrolyte, in the form of a needle-likes hape. The particle size is about (10-20 nm in diameter and 100-150 nm in length) Crystal grew along a single crystal direction under the restriction of the water conduit of the micro-emulsion.
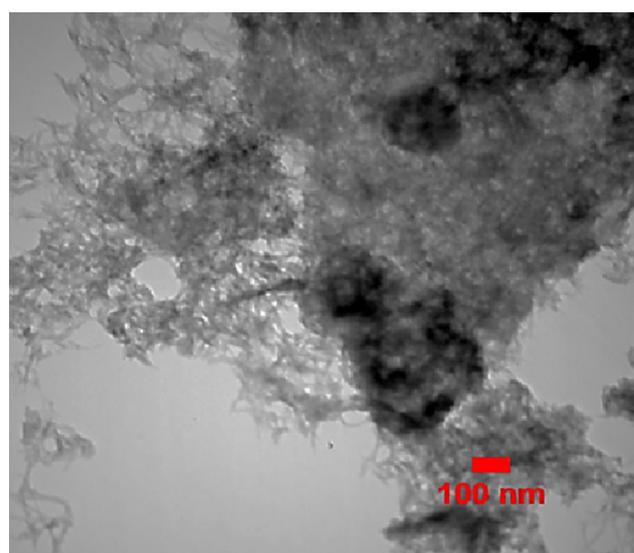

Figure 4: *TEM micrographs of synthesized CP in the polycationic-modified microemulsion system.*

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4. CONCLUSIONS

The aim of the research was to produce well-stabilized nanoparticles by using polyelectrolyte-modified microemulsions containing butanol, water, anionic surfactant and polyelectrolyte. First of all, our experiments show that the particle formation process in polyelectrolyte-modified microemulsions strongly depends on the type of polyelectrolyte. When PDAD-MAC is used nanoparticles with particle dimensions of 10-20 nm are predominantly formed, which are well stabilized during the process of solvent evaporation and redispersion. This means that the PDAD-MAC solubilized into individual microemulsion droplets can increase the templating effect of the microemulsion and stabilize the formed nanoparticles during the solvent evaporation and the redispersion process. Therefore, the polymer fulfills indeed the requirements of a size-regulating and stabilizing component in the process of nanoparticle formation and redispersion [14]. In general, PAA do not seem to be interesting in the formation of significantly smaller, ultrafine nanoparticles. When PAA is used the particle diameter of the resulting dispersion increases drastically. This means the addition of apolyanion increases the tendency to form larger particle aggregates in the presence of anionic surfactant.

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