THE INFLUENCE OF SYNTHESIS PARAMETERS ON SIZE AND MORPHOLOGY OF POLY(STYRENE-HYDROXYETHYL METHACRYLATE) COLLOIDS

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Poly(styrene-hydroxyethyl methacrylate) [P(ST-HEMA)] latex particles were prepared by surfactant-free emulsion copolymerization. As water-soluble initiator was used potassium persulfate (KPS). The influence of different reactions parameters, such as the reaction temperature, the both monomers (ST and HEMA) concentrations and the KPS concentration on the particles average diameter and particles size dispersion was investigated. Generally monodisperse spherical particles are synthesized, but we also obtained stable large three-dimensional colloidal aggregates. These are formed by the agglomeration of monodispersed spheres in certain polymerization conditions. The P(ST-HEMA) monodispersed spheres with 350 nm average diameter were assembled into colloidal crystals using dip-coating technique. Colloidal crystals with different thickness were obtained by modifying two experimental factors, the colloidal concentration and the substrate lifting speed. The morphologies of copolymer latex particles and colloidal crystals were observed using scanning electron microscopy (SEM). The optical properties of colloidal crystals films were also investigated by transmission spectroscopy.

1. Introduction

Colloidal materials have attracted recently much interest in various research fields including chemistry, materials science, condensed matter physics, applied optics and biology [1]. Usually, colloidal dispersions exhibit a continuous liquid phase (aqueous or organic) in which small particles having at least one dimension in the range of 1 nm and 1 μm are dispersed. If the solid phase contains highly monodisperse spheres these can serve, under proper conditions, as the basic elements for the bottom-up construction of colloidal crystals (CC) [2-4]. A wide variety of methods based on the self-assembling of colloidal particles such as sedimentation, centrifugation, filtration, electrophoresis or dip-coating have been reported for the preparation of CC [5]. Compared with other techniques, the assembling through dip-coating [6] is a simple and rapid method to obtain high quality CC with controllable thickness over large areas. Different growth parameters of CC such as concentration of the colloidal solution, the transfer speed of the particles towards the substrate, solvent evaporation temperature, the hydrophilic character of the substrate can induce modifications in CC thickness [7]. However, independent of the preparation technique, the polydispersity character of colloidal particles must be lower than 5% in order to allow the generation of CC with low defects density. If the monodispersity in size of spheres is not precisely controlled the optical properties of these organized colloidal structures can be affected.

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From colloidal particles, monodispersed polymer spheres are frequently used as building blocks in constructing CC, due to the following advantages: i) multiple choices of chemical composition; ii) relatively simple technique and iii) the ability to change their dimensions by controlling the polymerization reaction parameters. In addition, they can be easily removed by solvent dissolution or thermal calcinations, when they act as templates (substrates or masks) in the synthesis of different nanostructures, such as nano-films, nanowires, or macroporous structures with uniform pore size and highly ordered pore arrangement. Currently the most commonly used templates for the synthesis of different nanostructures are anodized alumina membrane and radiation track-etched polycarbonate membranes [8-11].

The polymer colloidal particles are synthesized usually by heterogeneous polymerization techniques: emulsion polymerization, precipitation polymerization, dispersion polymerization, seeded polymerization or surfactant-free emulsion polymerization (SFEP). The main advantage of the SFEP technique is the fact that it leads to monodisperse polymeric spheres with diameters ranging up to 1 micrometer in macroscopic amounts. Also, these polymeric latexes are particularly clean because they do not contain surfactant on the surface particles. Therefore they are useful in a wide field of applications ranging from life science and chemistry to optoelectronics and photonics. For example, colloidal dispersion obtaining by SFEP was used as a suitable reaction media for the growth of the semiconductor crystals with different morphology [12, 13]. In the SFEP, the synthesis conditions, including monomer concentration, initiator concentration and reaction temperature, are key factors influencing the size, the morphology and the size distribution of polymer spheres [14, 15]. In order to synthesize monodisperse spheres with narrow size distribution and good reproducibility, precise control of all of these conditions is necessary. For example, a good temperature control system is necessary to reduce the variation in temperature during the reaction. Since oxygen can stop polymerization, a degas procedure and inert gas protection are also necessary during polymerization.

The aim of this paper is to supply further information about the surfactant-free emulsion copolymerization of the styrene-hydroxyethyl methacrylate system emphasizing the influence of polymerization reaction parameters (reaction temperature, monomers concentration, initiator concentration) on the size of the colloids formed. Moreover, using dip-coating technique poly (styrene-hydroxyethyl methacrylate) spheres were assembled into colloidal crystals. We control the thickness of the colloidal crystals by modifying the experimental factors (the colloidal concentration and the lift-up rate of the substrate). The colloidal crystal thickness is a very important parameter that is related to their optical properties.

2. Experimental

The reagents used in this work, namely styrene (ST), hydroxyethyl methacrylate (HEMA) and potassium persulfate (KPS) were purchased from Alfa Aesar. The monomers, ST and HEMA were distilled under reduced pressure. The water-soluble initiator, KPS was recrystallized from the water and dried in vacuum. The copolymer latex was synthesized by surfactant-free emulsion copolymerization method. Since no surfactant is used, the main problem of the surfactant-free emulsion polymerization system is how to obtain a stable colloidal dispersion. The most convenient approach is to choose an ionic initiator as KPS and/or hydrophilic co-monomer as HEMA. The sulfate groups originating from the anionic initiator radicals contribute to polymerization and also to the electrostatic stabilization of polymer particles being presented on their surface. The addition of the functional co-monomer containing ionized carboxyl groups improves the electrostatic stability of latex during the particle growth period. In our case, the ionized carboxyl groups of HEMA units add supplemental charges for the electrostatic stabilization of latex particles without resorting to surfactant.

This dual protective mechanism (giving by KPS and HEMA) provides the latex stability higher than the electrostatic repulsion alone. The reaction conditions in which we synthesized the P(ST-HEMA) colloids by surfactant-free emulsion copolymerization of ST with HEMA using KPS as radical initiator are summarized in Table 1.

Tabel 1 Preparation conditions of P(ST-HEMA) colloids

No.	Water, ml	ST, ml	HEMA, ml	KPS, g	T, ^{0}C
1	21	3.44	0.44	0.012	75
2	21	3.44	0.44	0.012	95
3	21	1.72	0.22	0.012	75
4	21	6.88	0.88	0.012	75
5	21	1.72	0.22	0.006	75
6	21	6.88	0.88	0.024	75
7	21	3.44	0.44	0.006	75
8	21	3.44	0.44	0.024	75

Polymerizations were carried out in flasks conditioned through nitrogen bubbling and then placed in a temperature-controlled water bath under constant magnetic stirring (300 rpm). Inert gas protection is needed during the entire polymerization procedure because the molecular oxygen can capture the free radicals during polymerization, which stops free-radical chain propagation. Therefore, oxygen should be completely removed from the reaction system. Another important reaction parameter in the surfactant-free emulsion copolymerization synthesis is the temperature. Uniform distribution and very small variation in the temperature are necessary to ensure spheres with narrow size distribution and good reproducibility. For this reason, thermostatic bath with precise temperature controller is generally necessary for this kind of polymerization reaction. In addition, the solution should be stirred vigorously to make the temperature distribution homogeneous, because the polymerization is an exothermic reaction, which can locally raise the water temperature. After the polymerization ending, the polymer latexes were purified by dialysis in distilled water for at least 1 weak, using cellulose membranes (molecular weight cutoff: 12000-14000).

Further colloidal crystal films were obtained by dip-coating using P(ST-HEMA) latexes. In brief, a glass substrate was settled vertically into the polymer latex for several minutes and then drew out from the latex at room temperature by a home made device. In our studies we used the P(ST-HEMA) latex synthesized by the recipe no. 1 in Table 1. The films deposited from this latex were too thick, leading to the peeling of copolymer colloidal multilayers. From this reason we prepared diluted dispersions starting from the initial P(ST-HEMA) colloidal dispersion containing the maximal concentration of polymer spheres. Thus, we prepared three P(ST-HEMA) latexes from dilution by 3, 6 and 30 times to a part of the initial colloidal dispersion containing the maximal concentration of polymer spheres, maintaining constant the lifting speed at 6 µm/min. Also, we deposited colloidal crystal films from the P(ST-HEMA) latex obtained from the dilution by 3 times of the initial polymer latex varying the lift-up rate of the substrate at 3, 20 and 80 µm/min. In this way we can investigate the influence of the colloidal concentration and the substrate lifting speed on the colloidal crystal thickness. The P(ST-HEMA) colloidal crystals appeared opalescent, as expected, prismatic colors like rainbow, depending on the angle of observation. It has to be mentioned that in all deposition cases, prior to immersion, the glass substrates were washed with water and liquid soap, rinsed with distilled water, dried with hot air and treated with oxygen plasma to make their surfaces hydrophilic. The plasma treatment of a glass substrate has as an effect the cleaning of the surface but also its activation by increasing the number of reactive SiOH groups, though leading to a considerable improvement of the hydrophilic character of the substrate.

The surface morphology of as prepared P(ST-HEMA) latex and colloidal crystal films were observed using a Zeiss Evo 50 XVP scanning electron microscope (SEM). The optical properties of P(ST-HEMA) colloidal crystals films were investigated by transmission spectroscopy, the spectra being recorded at normal incidence using UV-Vis-NIR Carry 5000 spectrophotometer. The AFM analysis (non-contact mode) was performed using a MultiView 4000 Nanonics System.

3. Results and discussion

As we mentioned above, one of the advantage of using polymer colloids to obtain colloidal crystals is the tunable particle size. In the following we present how the reaction parameters influence the particles size and the latex dispersion in the case of P(ST-HEMA) colloids.

In the first step of this experimental study we investigated the influence of the reaction temperature (samples no. 1 and 2 in Table 1) on the average diameter (d_m) latex particles and their size dispersion. From Fig. 1 it can be observed that the spheres sizes increase, higher temperature almost doubles the sizes of the particles. The latex synthesized at 75 ^{0}C is monodispersed with d_m = 350 nm (Fig. 1A) and the particles obtained at 95 ^{0}C are d_m = 680 nm, maintaining the monodisperity (Fig. 1B). This effect can be explained by the enhanced reactivity of the initiator at higher temperature. In the beginning, the primary free sulfate anion-radicals resulted from thermally decomposition of KPS are generated inducing the copolymerization of ST with HEMA in the aqueous phase. In the propagation stage, the copolymer radicals grow and after reaching their limit of solubility coil up and precipitate from the aqueous solution to form primary particles. Further, macroradicals can be adsorbed or polymer molecules can be precipitated on surfaces of these nuclei particles. The accumulation rates of macroradicals and polymer molecules, which are continuously generated in the aqueous phase, increases with reaction temperature, in this way modifying the size of colloids.
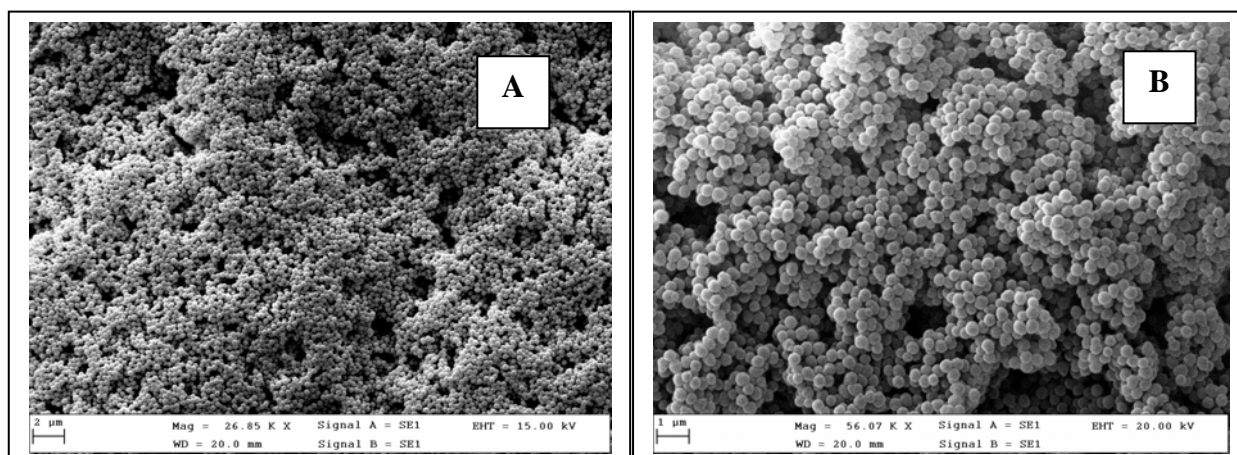

Fig. 1 SEM images of colloidal particles at two temperatures:
75 ^{0}C, monodisperse latex - d_m = 350 nm (A) and
95 ^{0}C, monodisperse latex - d_m = 680 nm (B)

In the following experimental studies we maintain constant the reaction temperature at 75 ^{0}C and we varied the other synthesis parameters. Such reaction parameter anticipated as being important for the final latex particles morphology was the monomers concentrations. Thus we halved (sample no. 3 in Table 1) and doubled (sample no. 4 in Table 1) the initial ST and HEMA monomers weights. While at lower concentration (Fig. 2A) the particles tend to keep a quasi-spherical shape, at higher concentration (Fig. 2B) colloidal particles lose the spherical shape. In the last case the colloids seem to result from the coalescence of sticky particles with lower dimension. These experimental results can be explained by the following mechanism: primary particles formed in the nucleation stage are grown consuming the monomers from the organic phase, the final size of the colloids being decided by its volume. In this context, comparing colloidal particles from Fig. 1A with those from Fig. 2A and Fig 2B it can be seen clearly that when the organic phase volume decreases mostly nanometric size particles are obtained. A different behavior is observed when the organic phase volume increases. In this case non-spherical micrometric size particles are synthesized.
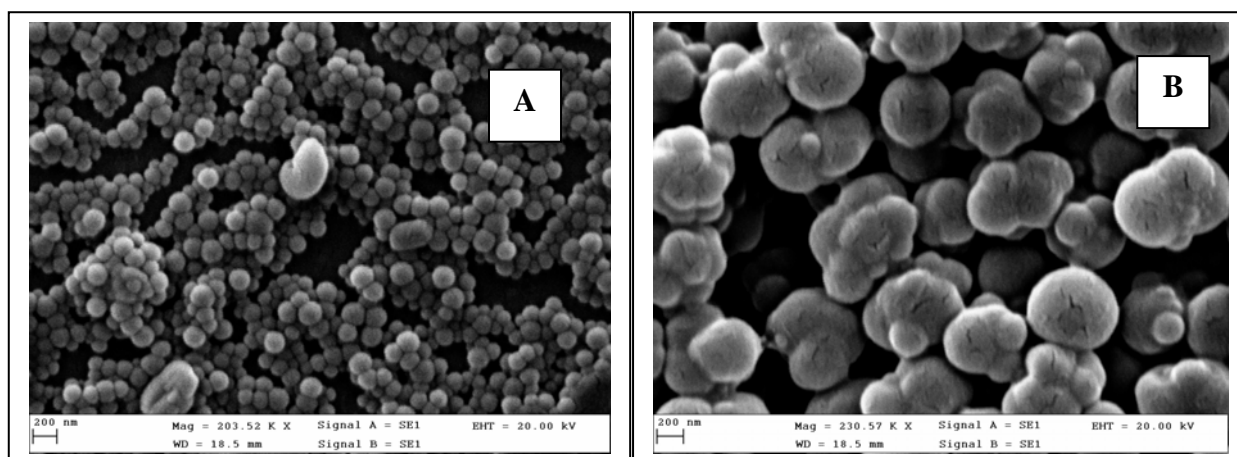
Fig. 2 SEM images of colloidal particles prepared at half (A) and double (B) monomers initial concentrations; polydisperse lattice

Noticing that the variation of monomers (ST and HEMA) concentrations leads to highly polydispersed latexes we halved (sample no. 5 in Table 1) and doubled (sample no. 6 in Table 1) both the initial monomers (ST and HEMA) and initiator (KPS) weights. Fig. 3A presents the image of the quasi-monodispersed P(ST-HEMA) spheres obtained at halved monomers and KPS concentrations, the particles being similar in size and shape, with those observed in Fig. 1A. In the case of doubled monomers and KPS concentrations, Fig. 3B reveals large three-dimensional aggregates formed from quasi-monodispersed P(ST-HEMA) spheres with d_m = 470 nm. This aggregation may be linked to the high content of HEMA units in the copolymer colloids and to the likelihood that most of these would preferably locate on the particles surfaces.
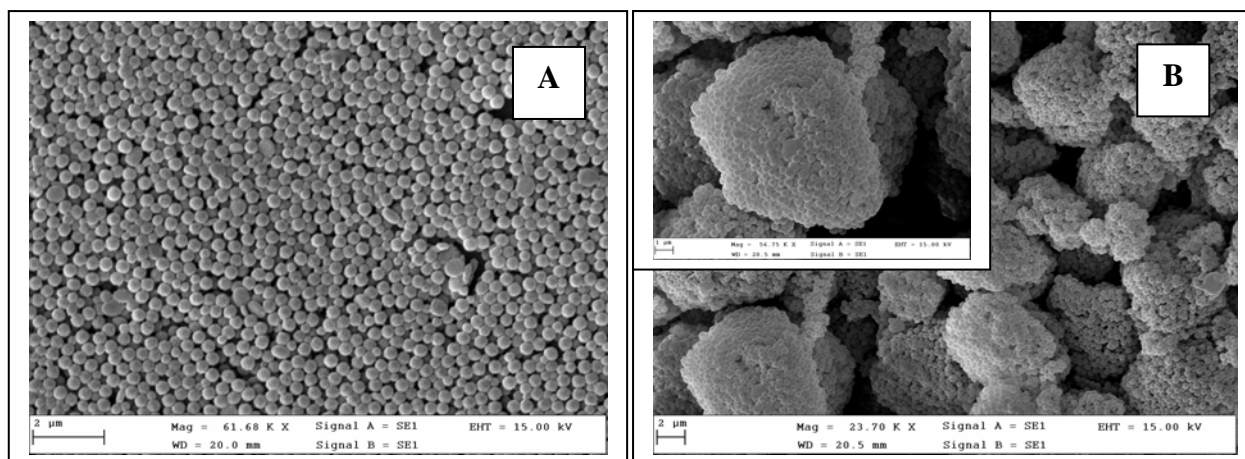

Fig. 3 SEM images of colloidal particles prepared at half (A) and double (B) both monomers and initiator initial concentrations; quasi-monodisperse latex - d_m = 340 nm (A) and quasi-monodisperse latex - d_m = 470 nm (B).
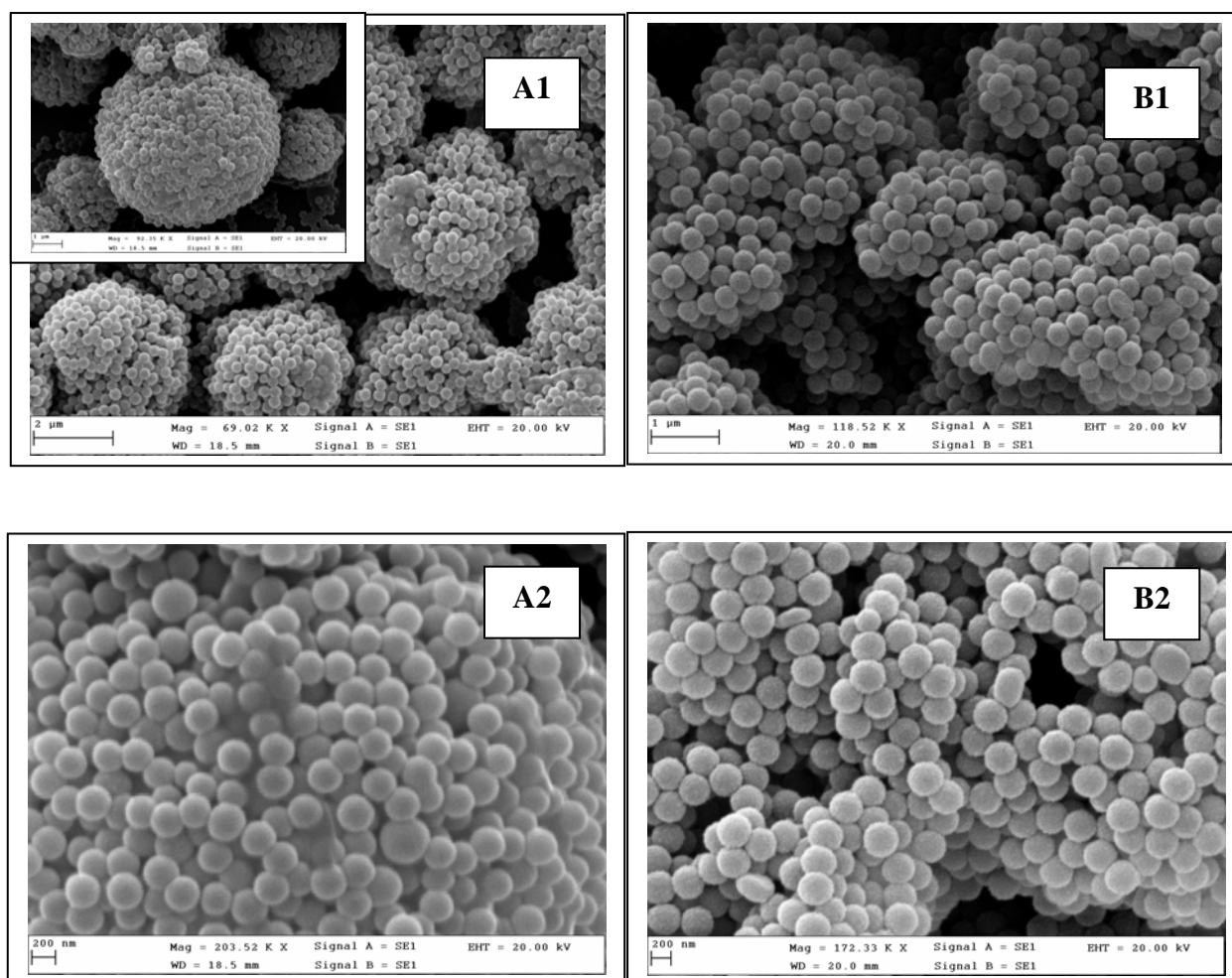
Fig. 4 SEM images of colloidal particles prepared at half (A1, A2) and double (B1, B2) initiator concentrations; quasi-monodisperse latex - d_m = 280 nm (A1, A2) and quasi-monodisperse latex - d_m = 330 nm (B1, B2).

HEMA is a soluble-water monomer and its polymer is insoluble but can absorb water. Thus the surface region of the primary particles can absorb a considerable amount of water, softly increasing the chance to entangle with other neighboring particles. As collisions between the particles occur, aggregation could take place until the surface charge density succeeds to stabilize the large aggregates.

The last reaction parameter that we modified in our study was the initiator concentration, halved (sample no. 7 in Table 1) and doubled (sample no. 8 in Table 1) the initial KPS weight. Large three-dimensional aggregates formed from quasi-monodispersed P(ST-HEMA) spheres with d_m = 280 nm can be noticed in the Fig. 4A1 and Fig. 4A2 at lower initiator concentration. These aggregates are very similarly with those observed in Fig. 3B. Because the initiator weight is lower, most probably, the ionic group resulted from KPS decomposition located on the particle surface are insufficient to provide an electrostatic repulsion and collisions between the particles takes place until they succeed in stabilizing the aggregates. Fig. 4B1 and Fig. 4B2 reveals that at higher initiator concentration, the colloidal particles are monodispersed with d_m = 330 nm like those observed in Fig. 1A.

It is noteworthy that all the colloids synthesized by us in different reaction parameters, meaning the colloidal spheres and consolidated aggregates, are very stable in time.

After we saw how the size and morphology of the P(ST-HEMA) colloids are dramatically influenced by the surfactant-free emulsion copolymerization reaction parameters, the next step is to assemble monodispersed spheres into three dimensional periodic latexes, knows as colloidal

crystals. We adopted as method to assembly CC from P(ST-HEMA) monodispersed particles (d_m = 350 nm) the dip-coating because this technique produces large area of crystals with uniform thickness and fewer defects within reasonable time. The SEM images of a P(ST-HEMA) film deposited from latex sample no. 1 (Table 1) can be observed in the Fig. 5A-D. Fig. 5A and Fig. 5B reveal the thickness of the deposited CC film. The low-magnification image (Fig. 5C) over a large area of highly ordered CC shows some "crystallographic" defects as point and line defects. The high-magnification SEM image (Fig. 5D) discloses the coexistence of two domains, hexagonal and square arrays, in which the each sphere have 6 or 4 nearest neighbors in the surface plane, respectively. From the SEM analysis of CC films investigated we concluded that the closely packed hexagonal structure appears more often than the square packed structure.
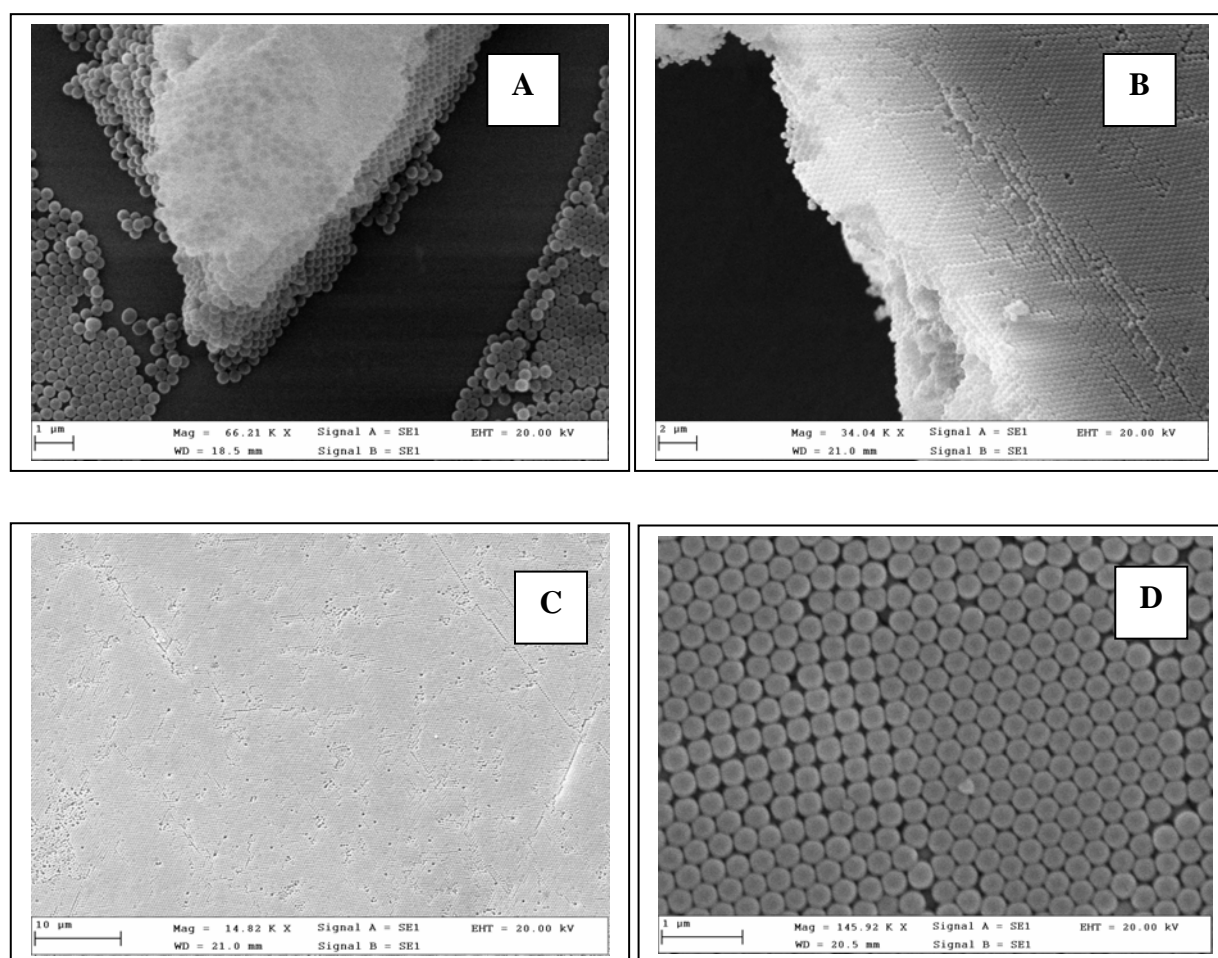

Fig. 5 SEM images of colloidal crystals prepared from
monodispersed P(ST-HEMA) spherical particles (d_m = 350 nm)

The close-packed of P(ST-HEMA) spheres arrays assembling into CC film was also proved by AFM analysis (Fig. 6). Other defects such as cracks that appear due to the contraction of the CC when the water was completely evaporated were evidenced.
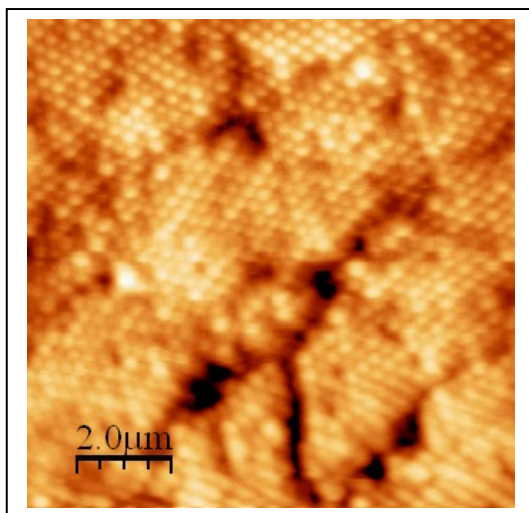
Fig. 6 AFM image of colloidal crystals prepared from
monodispersed P(ST-HEMA) spherical particles (d$_m$ = 350 nm)

In order to see the influence of the parameters which can induce the modifications into the CC thickness we varied the colloidal concentrations and the substrate lifting speed. As it can be seeing from Fig. 7 and Fig. 8 we obtained CC with different number of layers: one layer (Fig. 7A and Fig. 8A), approximately 10 layers (Fig. 7B and Fig. 8B) and more than 10 layers (Fig. 7C and Fig. 8C).
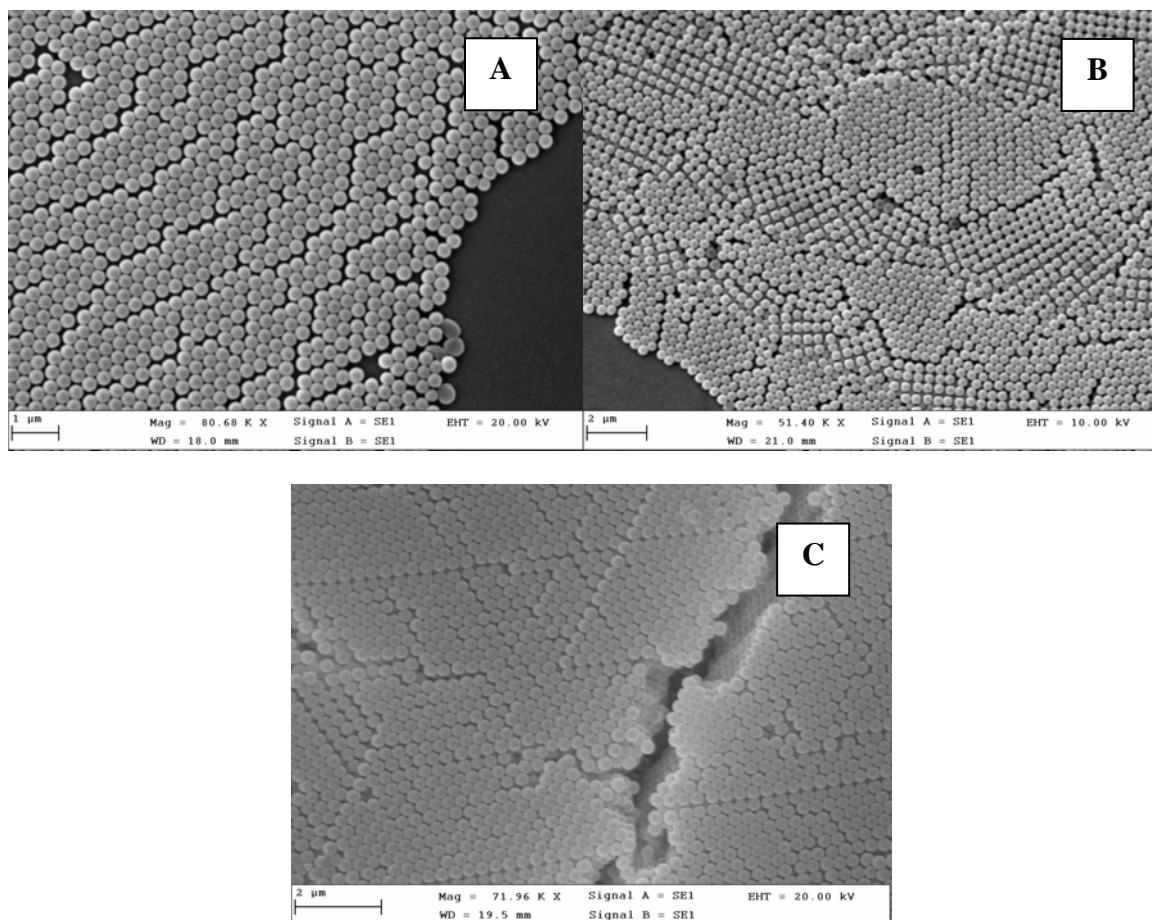

Fig. 7 SEM images of colloidal crystals prepared at different colloidal concentrations:
x30 (A), x6 (B) and x3 (C) times dilution to a part of the initial P(ST-HEMA) latex,
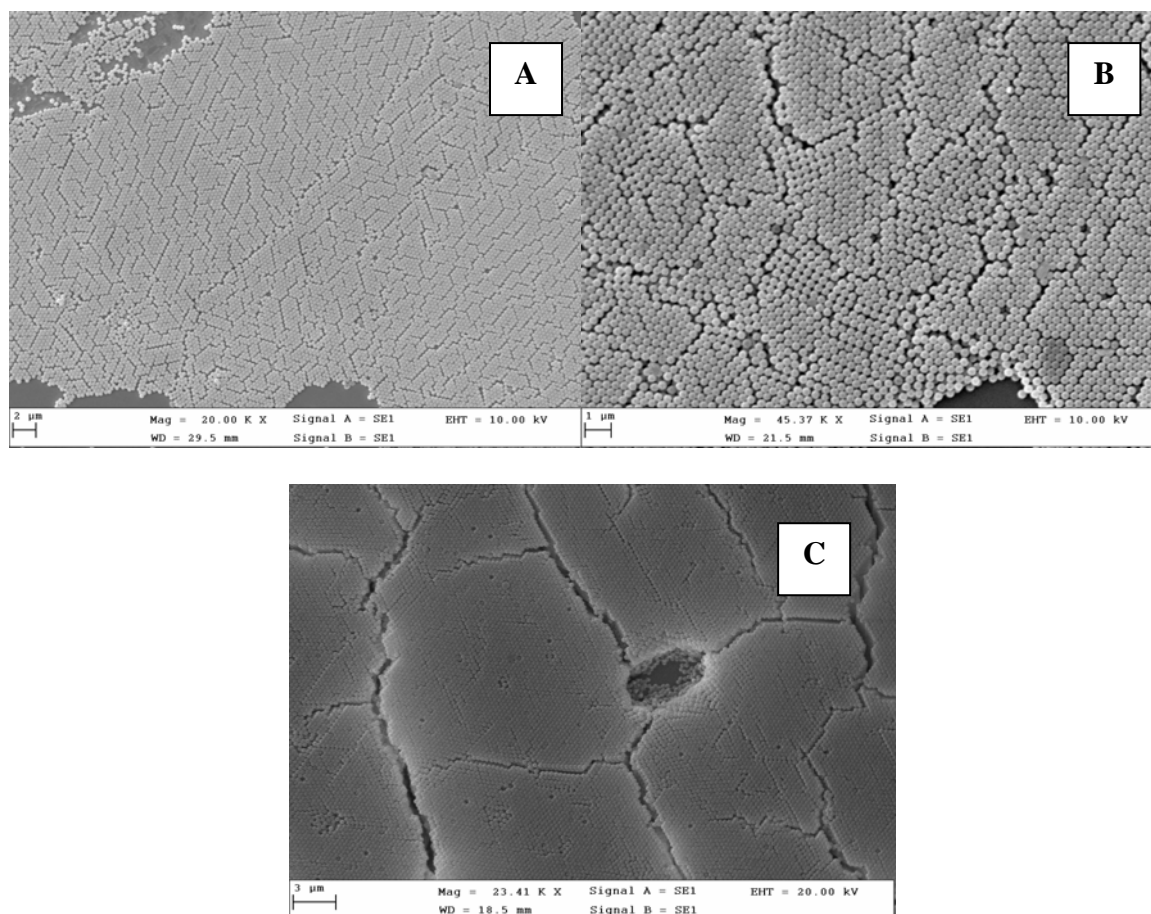*constant lifting speed of 6 μm/min*

Fig. 8 SEM images of colloidal crystals prepared at different lifting speed:
80 (A), 20 (B) and 3 (C) μm/min, constant colloidal concentration of 3 times dilution of the
initial P(ST-HEMA) latex

It was observed that the adhesion of the films to the substrate was significantly degraded when the concentration increase above an optimum. Below this optimum the film became very thin. In the case of the substrate lifting speed, a higher speed leads to assembly of spheres into sparse structures with low coverage. A lower speed leads to an increase of colloidal crystal layer thickness. At an optimum speed, the hydrophilic substrate entrains some amount of colloidal dispersion due to the surface tension and the colloidal crystals forms the meniscus sweeps over the substrate. Freshly cleaned glass surfaces have a high surface energy and are well wettable. Beside the glass cleaning, a treatment in oxygen gas plasma improves the glass surfaces wetting.

The influence of the CC thickness on the optical properties was evaluated using transmission spectroscopy. The transmission spectra of the six CC films obtained at different deposition parameters were recorded and displayed in the Fig. 9A (different colloidal concentrations) and Fig. 9B (different lifting speed of substrate). In all the opalescent P(ST-HEMA) films transmission spectra two bands with peaks located at about 390 nm and 680 nm are observed, the last representing the attenuation band. The asymmetric attenuations of stop bands increase as the number of layers in CC increases.
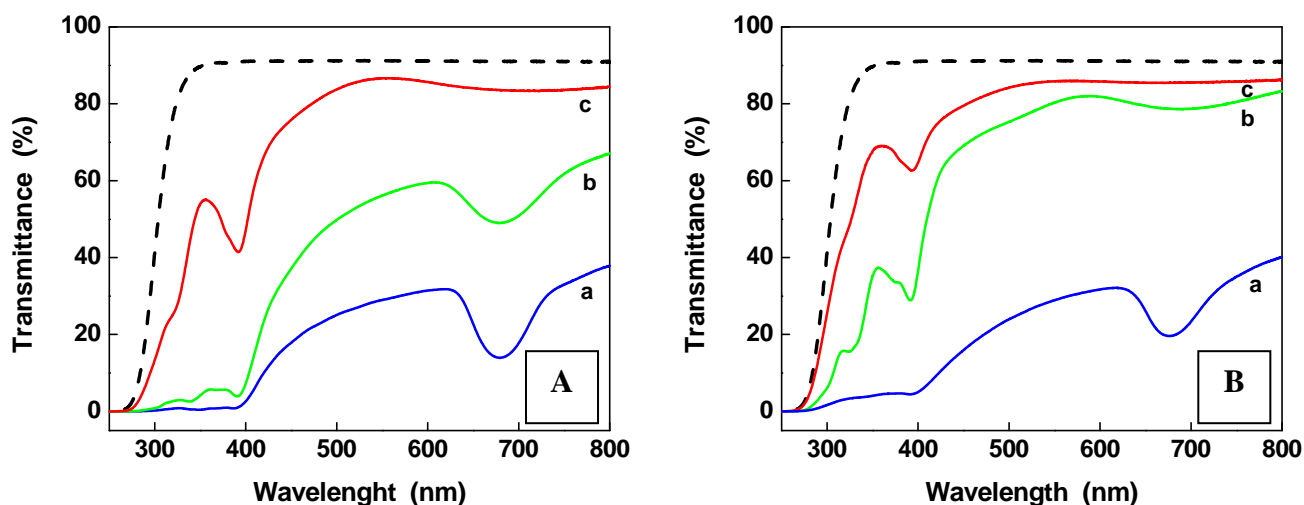
Fig. 9 Optical transmission spectra of colloidal crystals prepared at: (A) different colloidal concentrations: x30 (a), x6 (b) and x3 (c) times dilution to a part of the initial P(ST-HEMA) latex, constant lifting speed of 6 μm/min; (B) different lifting speed: 80 (a), 20 (b) and 3 (c) μm/min, constant colloidal concentration of 3 times dilution of the initial P(ST-HEMA) latex. The dash lines represent the transmission spectra of glass substrate.

Besides, the classical anodized alumina and radiation track-etched polycarbonate membranes such polymeric colloidal crystals with different thickness can be used as templates, substrates or masks, in the synthesis of different nanostructures, such as nano-films or nanowires.

4. Conclusions

In this paper we have studied the influence of different reaction parameters (reaction temperature, both monomers concentrations and initiator concentration) on the surfactant-free emulsion copolymerization of styrene with hydroxyethyl-methacrylate. The morphologies observed using SEM prove that in most of the cases monodisperse spherical particles were synthesized, but also stable large three-dimensional aggregates can be obtained. These are formed by the agglomeration of monodispersed spheres in certain polymerization conditions. The assembling of P(ST-HEMA) monodispersed spheres with 350 nm average diameter has as a result the generation of colloidal crystals. SEM analysis shows that the thickness of colloidal crystals depends strongly on the two experimental factors: the colloidal concentration and the substrate lifting speed. Such polymeric colloidal crystals with different thickness can be used as template in the synthesis of the nanostructured materials with controlled morphology.

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