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Functionalized polystyrene latex particles as substrates for ATRP: Surface and colloidal characterization

V. Mittal [b], N.B. Matsko [a], A. Butté [b], M. Morbidelli [b,*]

[a] Electron Microscopy Center ETH Zurich (EMEZ), ETH Zurich, 8093 Zurich, Switzerland
[b] Department of Chemistry and Applied Biosciences, Institute of Chemical and Bioengineering, ETH Zurich, 8093 Zurich, Switzerland

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Abstract

In this work, the process for producing polystyrene particles surface functionalized with a thin shell of ATRP initiator polymerized alone or along with styrene and a crosslinker, is presented. Copolymerization of styrene and acrylic end-capped ATRP initiator to generate a thin shell on the fully polymerized core particles suffered from secondary nucleation owing to their possible incompatibility with the core particles and their own colloidal stability. One step functionalization processes, where the shell forming monomers are added directly to the 70% polymerized core particles, lead to significant changes in the resulting particle morphologies. The shot addition of these monomers led to a very uniform surface morphology without any secondary nucleation owing to quick coalescence of the secondary particles on the soft surface of the seed particles. Addition of crosslinker to the system helped in effectively eliminating the smaller particles generated due to secondary nucleation along with the chemical networking.

Keywords: Polystyrene; Emulsion polymerization; Electron microscopy

1. Introduction

Surface properties of solid materials are often crucial in determining their final application characteristics. Accordingly, the development of materials with controllable surface properties has seen a growing interest in the recent years [1,2]. Many techniques to functionalize the surfaces have been reported in the literature, like physical adsorption [3–5], grafting ‘to’ surface [6,7] and grafting ‘from’ surface [8,9]. Physical adsorption of long polymer chains to the surface can help in attaching polymer chains of well defined length, molecular weight distribution and composition. However, this approach suffers from the limitations of steric hindrance posed by the long polymer chains, thus seriously limiting the final surface density of the grafts. Moreover, chains are only physically adsorbed onto the surface and have the tendency to be cleaved off easily as compared to the covalently bound chains. Grafting ‘to’ surface approach in which end-functionalized polymer chains are chemically attached to the surface also suffers from steric hindrance, especially when longer polymer chains are used. On the other hand, the grafting ‘from’ surface approach has enjoyed more success because of its ability to generate densely packed polymer functionalities in the absence of any kinetic hindrance along with the advantage of covalently bound polymer chains on the surface [8–11]. Such structures are referred to as polymer brushes, when the distance between the grafted chains is less than twice the radius of gyration of the unperturbed polymer chain [12].

Out of all the polymerization techniques used to graft polymer brushes, controlled polymerization techniques such as ionic [13,14], atom transfer radical polymerization (ATRP) [11,15–17] and reversible addition fragmentation transfer (RAFT) [18,19] have received widespread attention. Lamb et al. have also reported topology controlled systems for

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* Corresponding author. Tel.: +41 44 632 3034; fax: +41 44 632 1082.
E-mail address: massimo.morbidelli@chem.ethz.ch (M. Morbidelli).

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such surface initiated growth [20,21]. The growth of living polymer chains from the surfaces ensures better control over the molecular weight distribution and the amount of grafted polymer as compared to the conventional radical polymerization, which suffers from the unwanted bimolecular terminations. In particular, ATRP has been the most widely applied technique among those mentioned above because of its ease of process and excellent control on the resulting polymer. Aqueous ATRP has been studied during the recent years in order to generate water soluble polymers at room temperature [22–26]. When used to generate polymer brushes from flat surfaces and particles, ATRP is also quite efficient although not as much as in solution applications [27–30]. To this regard, Kizhakkedathu et al. have recently reported the extensive studies on the aqueous ATRP for the growth of substituted acrylamide layers from polystyrene latex particles [31–34]. Matyajaszewski et al. have reported the synthesis of versatile ATRP agents end capped with acrylic and methacrylic groups for easy polymerization on the substrate surfaces [35].

Most of the reported studies on grafting from surface, however, employ the use of flat substrates, whereas spherical substrates e.g. latex polymer particles have received little attention. As the polymer latex particle surfaces in water have been reported to be very different from the silica surfaces commonly used, because of surface charges, charge concentration, wetting properties, etc. [33], their behavior in the above mentioned functionalization processes has to be investigated in detail.

Surface functionalized spherical polymer particles are generally synthesized by emulsion polymerization, where the functionalizing monomer (e.g. ATRP initiator carrying the terminal acrylic or methacrylic groups) is polymerized onto seed polymer latex particles. The process is formally achieved in two different steps, where the polymer seed is formed first with the desired characteristics and the functionalizing monomer is polymerized afterwards on the surface. On the other hand, a single step process can be achieved by adding the functionalizing monomer to the seed particles before complete polymerization is achieved. In both cases, various surface morphologies can be achieved depending on various thermodynamic and the kinetic factors [36–41]. Control of surface morphology has always been a challenge as the homogenous surface distribution of the functionalizing entities is of utmost importance in order to achieve homogenous polymer brushes. Reaction conditions such as the weight ratio of the functionalizing monomer to the seed polymer, pre-swelling of the seed particles with the functionalizing monomer, mode of addition of the monomer to the seed, etc. dramatically influence the resulting particles' size, shape and morphology. However, very little has been reported for the functionalization of polymer latex particles with monomers carrying an ATRP initiator moiety [31,32,42–44].

The goal of the present work is to synthesize polystyrene latex particles carrying ATRP functional initiator on the surface. Surfactant-free emulsion polymerization of styrene is utilized to synthesize narrowly dispersed polystyrene latex particles which will serve as seed for the following functionalization. The functionalization is carried out by using an acrylic monomer carrying the ATRP initiator moiety, which is copolymerized in the presence of other monomers. In particular, the effect of the composition of such monomer mixture, its modality of addition, the influence of pre-swelling as well as the presence of crosslinking agents will be investigated. The resulting particles are extensively studied in terms of size and surface morphology by using electron microscopy. NMR studies are carried out with the solutions of dried latex particles in deuterated $CDCl_3$ in order to quantify the relative amounts of styrene and ATRP initiator units in the resulting particles. The growth of thermally responsive polymer brushes is intended to be studied from these functionalized particle surfaces as a future study.

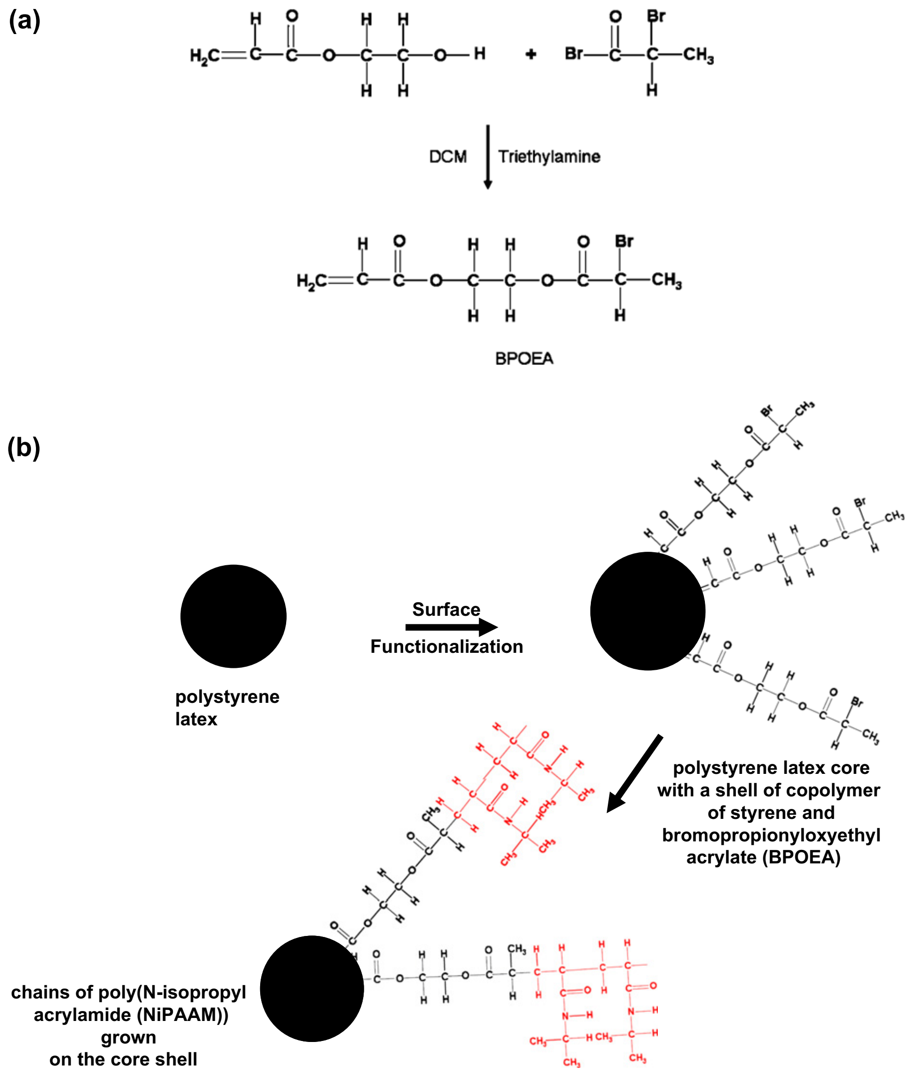
2. Experimental

2.1. Materials

Styrene (S, $\geq$99.5%), divinylbenzene (DVB, $\geq$80%), radical initiator (potassium peroxodisulphate, KPS, >99.0%) and dichloromethane (CH_2Cl_2, $\geq$99.8%) were purchased from Fluka (Buchs, Switzerland). 2-Bromopropionyl bromide (97%), triethylamine ($\geq$99.5%) and 2-hydroxyethyl acrylate (96%) were purchased from Aldrich (Buchs, Switzerland). Deuterated chloroform ($CDCl_3$, 99.8% D) was received from Dr. Glaser AG, Basel, Switzerland. All the monomers and solvents were used as supplied without further purifications. Ultra pure Millipore water was employed in all experiments. ATRP initiator end capped with acrylic monomer unit, i.e., 2-(2-bromopropionyloxy) ethyl acrylate (BPOEA) was synthesized as reported in literature [35] and Scheme 1 also shows the reaction scheme for its synthesis.

2.2. Synthesis of polystyrene seed latex

The seed latex was prepared in a Mettler Toledo Automatic Reactor (LabMax) equipped with a 600 mL jacketed glass vessel, mechanical stirrer, condenser and thermocouple. Temperature was controlled by a PI controller and kept within ±0.1 °C. The narrowly dispersed latex was prepared by surfactant-free emulsion polymerization of styrene. Millipore water (468 g) and styrene (22 g, 0.21 mol) were charged in the reactor. The reactor was purged with alternate cycles of nitrogen and vacuum and was finally left under nitrogen atmosphere. After the reaction mixture was heated to 70 °C under stirring of 400 rpm, the initiator solution (0.42 g, 1.5 mmol of KPS in 10 mL of water) was injected in the reactor by syringe. The reactor was allowed to run at these conditions for 24 h. Meanwhile, samples were withdrawn by syringe to measure the conversion gravimetrically as well as the hydrodynamic diameter of the particles by static light scattering (Malvern 2000). The latex was cleaned by repeated centrifugation and serum replacement cycles. The final polymer weight percent of the latex is 4.4 and the hydrodynamic diameter of the particles is 880 ± 40 nm.



Scheme 1. (a) The reaction scheme for synthesis of BPOEA and (b) representation of BPOEA functionalization of particles and subsequent growth of brushes by ATRP.

2.3. Surface functionalization of polystyrene latex particles

All surface functionalization reactions were carried out in 50 mL round bottom flasks at a temperature of 70 °C and 400 rpm. Two different methodologies have been used. The first method (in the following referred to as "two step" method) was used in runs 1–3 in Table 1 and included the formation of polystyrene seed latex until complete conversion of the monomer, followed by functionalization of the particles with BPOEA. For the second step, the polystyrene seed latex (15 g) was heated to 70 °C at 400 rpm and purged with alternate vacuum/nitrogen cycles. BPOEA (0.85 mmol, 0.21 g) was either added alone (run 1) or along with styrene (2.5 mmol, 0.26 g) such as in runs 2 and 3. In particular, styrene was added together with BPOEA in run 3 and alone followed by BPOEA after 30 min in run 2. KPS solution (0.01 g in 2 mL of water when both styrene and BPOEA were added and 0.0025 g when only BPOEA was added) was added after 15 min. The reaction was allowed to run for 7 h and the resulting latex was cleaned by repeated centrifugation cycles. The experimental runs summarized in Table 2 are carried out in

Table 1
Details of the functionalization trials for the particles without crosslinker

Run	Seed	Second batch of monomers	Populations	d_{TEM}, nm
1	100% PS	100% BPOEA	1	920
2	100% PS	BPOEA:S = 1:3 (S added first)	2	1030, 190
3	100% PS	BPOEA:S = 1:3 (S and BPOEA together)	2	990, 170
4	70% PS	100% BPOEA (shot addition)	1	745
5	70% PS	BPOEA:S = 1:3 (shot addition)	1	780
6	70% PS	100% BPOEA (delayed addition)	2	590, 150
7	70% PS	BPOEA:S = 1:3 (delayed addition)	2	490, 50
8	100% PS	100% S	1	1040

d_{TEM} = average diameter calculated from TEM micrographs; populations = number of families of particles in the latex. PS = polystyrene; BPOEA = 2-(2-bromopropionyloxy) ethyl acrylate; S = styrene.

Table 2
Details of the functionalization trials with acetone swelling without crosslinker

Run	Seed	Second batch of monomers	Populations	d_{TEM}, nm
9	100% PS	100% S	1	1020
10	100% PS	100% BPOEA	1	950
11	100% PS	BPOEA:S = 1:3	2	1070, 110

d_{TEM} = average diameter calculated from TEM micrographs; populations = number of families of particles in the latex. PS = polystyrene; S = styrene; BPOEA = 2-(2-bromopropionyloxy) ethyl acrylate.

the presence of acetone. In this case, before starting the second polymerization step, the polystyrene seed particles were left to swell overnight in the presence of BPOEA and styrene, together with a small amount of acetone (2–3 mL).

The second methodology investigated in this work combines the two steps described above, i.e., particle functionalization was initiated without letting the polystyrene seed latex to achieve full conversion (see Table 1, runs 4–7). The general procedure, with reference as an example to run 5 was as follows. Styrene (0.721 g, 6.93 mmol) and water (15 g) were heated to 70 °C at 400 rpm, followed by degassing and nitrogen atmosphere. KPS solution (0.015 g, 0.056 mmol in 2 mL of water) was then injected in the reaction mixture. After 70% conversion of styrene was reached, the second charge of monomers including BPOEA, i.e., pure BPOEA in runs 4 and 6 and 1:3 molar mixture of BPOEA with styrene in runs 5 and 7 (in the following generally referred to as shell forming monomers) was injected in the reaction mixture without any additional initiator. The reaction was allowed to run for further 7 h followed by cleaning. The effect of shot (runs 4 and 5) or delayed (runs 6 and 7, when the monomer mixture was added over 40–60 min through a funnel maintaining a constant flow rate of 5 μL/min) addition of these shell forming monomers on the resulting morphology was also investigated. Run 8 in Table 1 does not include any BPOEA and has been included in the study in order to provide a measure of comparison as will be discussed shortly.

Finally, the effect of the presence of a crosslinking agent both in the seed and in the shell forming monomer mixture was investigated. In the runs 12–16 described in Table 3, divinylbenzene was added to the system, while keeping the same reaction conditions as in the experiments described above without the crosslinker. The molar ratio of styrene to divinylbenzene in the seed latex was ∼50, while a ratio of ∼40 was used for the shell forming monomers.

Table 3
Details of the functionalization trials for the particles with crosslinker

Run	Seed	Second batch of monomers	Remarks	Populations	d_{TEM}, nm
12	70% P(S + DVB)	BPOEA + DVB	Shot addition	1	440
13	70% P(S + DVB)	S + BPOEA + DVB	Shot addition	1	520
14	70% P(S + DVB)	BPOEA + DVB	Delayed addition	1	500
15	70% P(S + DVB)	S + BPOEA + DVB	Delayed addition	1	560
16	100% P(S + DVB)	S + BPOEA + DVB	Delayed addition	1	530

d_{TEM} = average diameter calculated from TEM micrographs; populations = number of families of particles in the latex. S = styrene; DVB = divinylbenzene; BPOEA = 2-(2-bromopropionyloxy) ethyl acrylate.

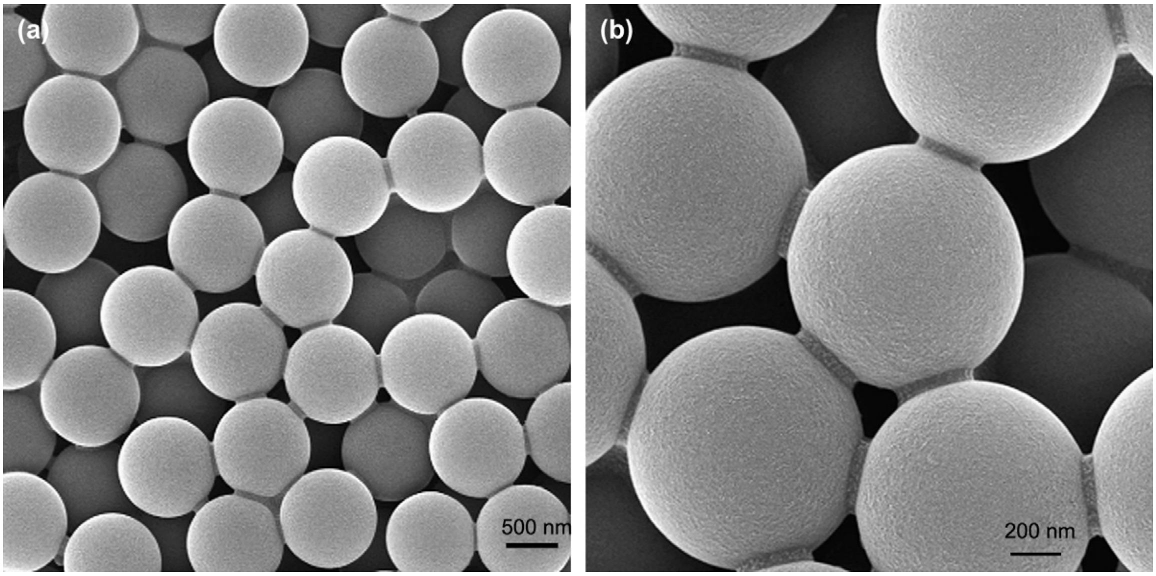


Fig. 1. SEM micrographs of polystyrene seed latex particles before functionalization at two different magnifications.

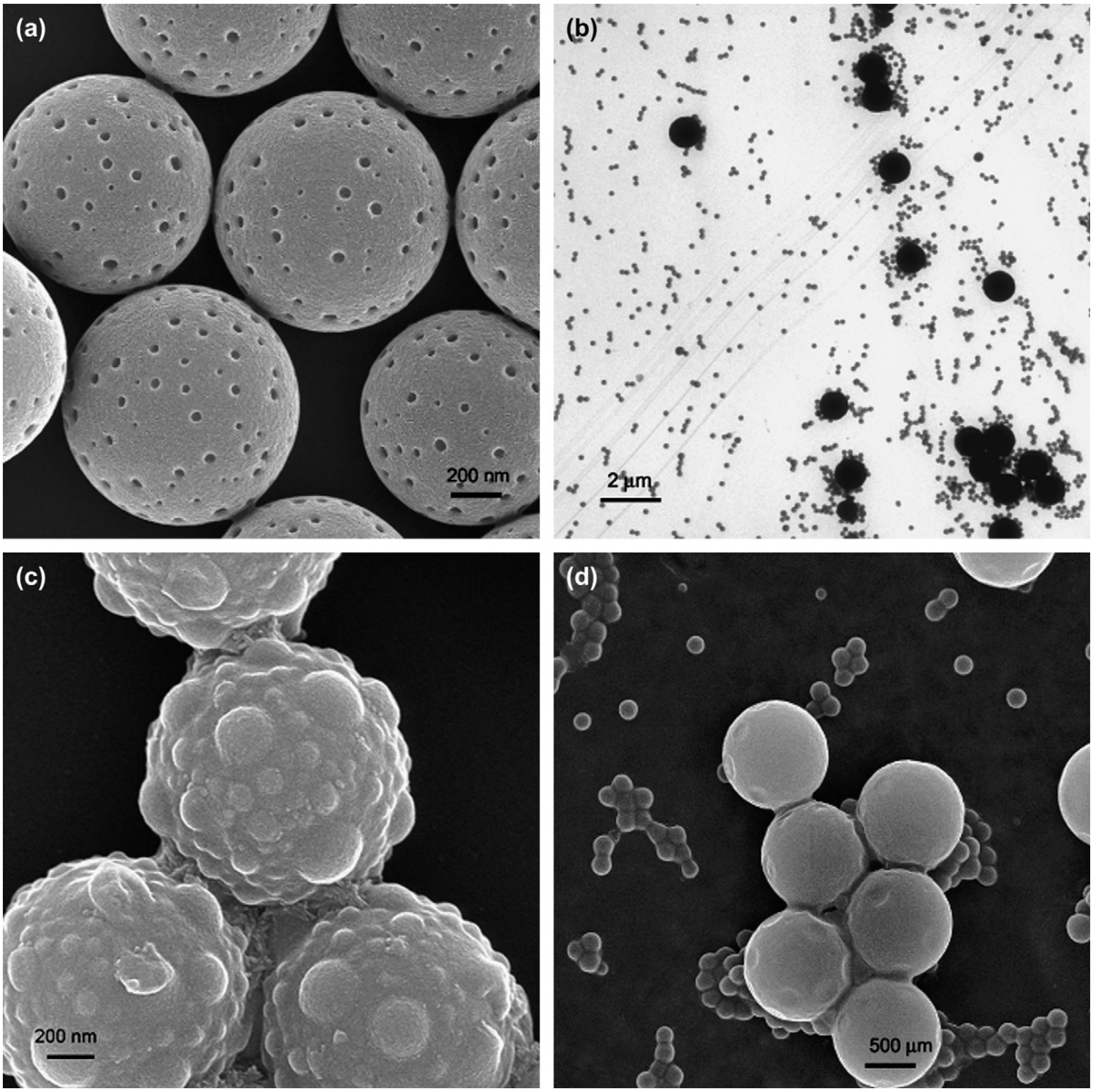


Fig. 2. (a) Scanning electron micrograph of the 100% polymerized PS seed particles functionalized with homopolymer of BPOEA on the surface (run 1); (b) transmission electron micrograph of the 100% polymerized PS seed particles functionalized with 1:3 molar ratio of BPOEA to styrene polymerized on the surface with styrene added first (run 2); (c) scanning electron micrograph of the particles shown in (b) and (d) scanning electron micrograph of the 100% polymerized PS seed particles functionalized with 1:3 molar ratio of BPOEA to styrene polymerized on the surface when monomers were added together (run 3).

2.4. Electron microscopy

The surface morphology of the particles was observed in Hitachi field emission in-lens S-900 high resolution scanning electron microscope at accelerating voltages of 10–20 kV. Carbon/collodium coated 400-mesh copper grids, freshly etched by charged oxygen plasma (10 s, 100 mV, 5 mbar of O_2) in Balzers GEA-003-S glow-discharge apparatus (Balzers), were placed on the droplets of particle suspensions for 2 min, dried on filter paper followed by sputter-coating with 3 nm platinum. Bright-field TEM (Zeiss EM 912 Omega, Leo, BRD) equipped with a ProScan slow scan CCD camera was also used to study the surface periphery of the particles to accurately calculate the particle size as a complement to SEM. Carbon coated 400-mesh copper grids, freshly glow discharged, were placed on the droplets of particle suspensions for 20 s, washed with distilled water and negatively stained with 2% aqueous uranyl acetate for 20 s.

2.5. Nuclear magnetic resonance

The latex samples were dried under vacuum and then dissolved in deuterated $CDCl_3$. Proton NMR spectra of these solutions were collected on a Bruker 300 spectrometer with observing frequencies of 300 MHz. Comparison of the intensities of the peaks corresponding to $-O-CH_2-CH_2-O-$ and $-CHCl-$ (4.1–4.3 ppm) with peaks of aromatic protons of polystyrene (6.7–7.2 ppm) led to the determination of the mole percent of the ATRP initiator present in the functionalized particles [31].

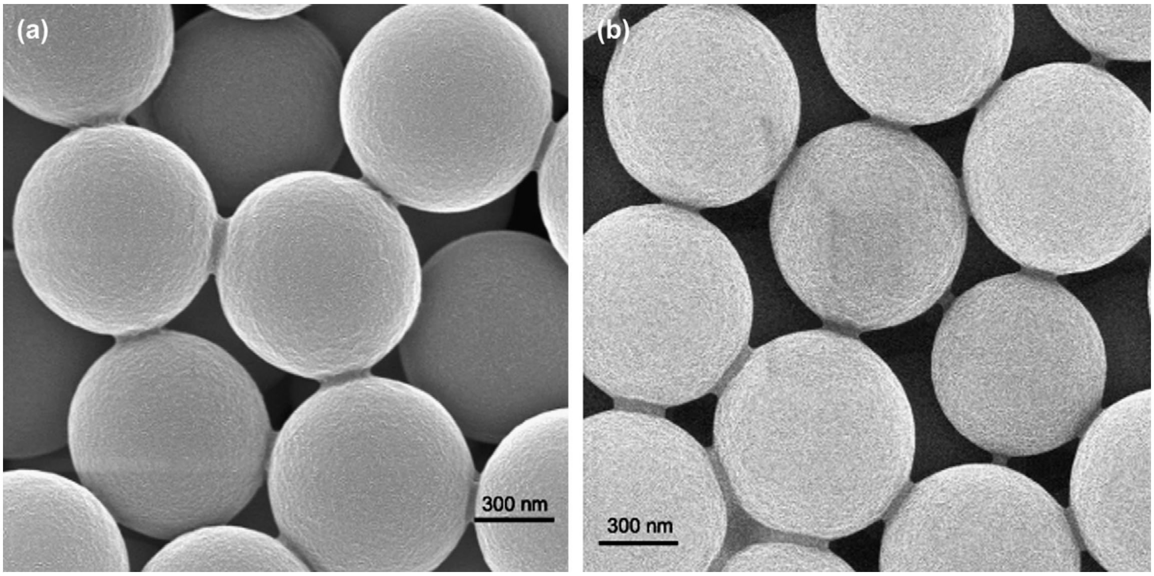


Fig. 3. SEM micrographs of 70% polymerized PS seed particles containing a shell of (a) homopolymer of BPOEA (run 4) and (b) copolymer of styrene and BPOEA (BPOEA to styrene mole ratio of 1:3, run 5). The shell forming monomers were added in a shot.

3. Description of the obtained results

Scheme 1 shows the process of synthesis of seed latex and its subsequent functionalization with the ATRP initiator to grow e.g. poly(*N*-isopropylacrylamide) brushes from the surface. In order to have a successful functionalization of a given support with the ATRP initiator, we have to avoid the formation of secondary particles through the precipitation of polymer chains made in the aqueous phase with BPOEA. Such secondary particles have, in fact, different properties than those of the seed, which presumably has been designed for some specific applications. In addition, the distribution of polymerized BPOEA and hence the ATRP initiator on the support surfaces must be uniform. This is crucial to subsequently obtain a homogenous distribution of the polymer brushes. Some other characteristics which would be convenient for an efficient functionalization process are as follows. First, the surface density of the initiator must be adjustable. This means that the possibility of copolymerization of BPOEA with styrene must be considered. Second, for some applications, it is important to crosslink both the support and the initiator carrying shell. This is needed to avoid excessive swelling of the support and the removal of initiator from the surface by solvation. The realization of these requirements is discussed in the following.

Let us first describe the production of the seed particles. Narrowly dispersed polystyrene latex particles were synthesized by surfactant-free emulsion polymerization, thus producing particles with average diameter of 880 nm. Fig. 1 represents SEM micrographs of the polystyrene latex particles at two different magnifications. It can be noticed that the particle surface is perfectly smooth and the particles are very uniform in size. These micrographs correspond to the fully polymerized seed particles, which are then used to carry out the two step functionalization process, as described in run 1 in Table 1. The aim of this experiment was to generate a thin shell of solely polymerized BPOEA on the particles. As it can be observed in Fig. 2a, this led to a very distinctive 'orange-peel' morphology and no secondary nucleation. On the other hand, similar trials to functionalize the same seed in the presence of styrene led to a secondary nucleation of the monomers, as indicated by the presence of large number of small particles (Fig. 2b–d, runs 2 and 3 in Table 1). In particular, in run 2, styrene was added first alone to swell the polystyrene particles, followed by BPOEA after 30 min and the free radical initiator after 15 min (Fig. 2b and c); in run 3, styrene was instead added together with BPOEA followed by the free radical initiator solution after 15 min (Fig. 2d). In both cases, a significant amount of secondary nucleated smaller particles is observed, while in the latter case the bigger particles exhibited a much smoother surface, which has instead a typical 'strawberry' morphology in the first case. The average particle size of both fractions is reported in Table 1. It can be observed that, in both cases, some polymerization occurred on the seed particles, as indicated by the increase of size with respect to the seed particles. Moreover, it can be observed that the secondary particles have similar size, indicating a similar partitioning of the monomers (which is responsible for secondary nucleation) in the two cases, in spite of the very different final morphology.

In order to further characterize the nature of the system, a second set of experiments were performed, where functionalization was achieved in a single step (runs 4–7 in Table 1). In these runs, once the seed polymerization reached 70% conversion, a mixture of shell forming monomers containing BPOEA was added, either in a shot by a syringe, or over a period of 40–60 min (delayed addition) through a funnel at a constant flow rate (5 μL/min). The shot addition of either BPOEA alone or in the presence of styrene (runs 4 and 5 in Table 1, respectively) caused no secondary nucleation during

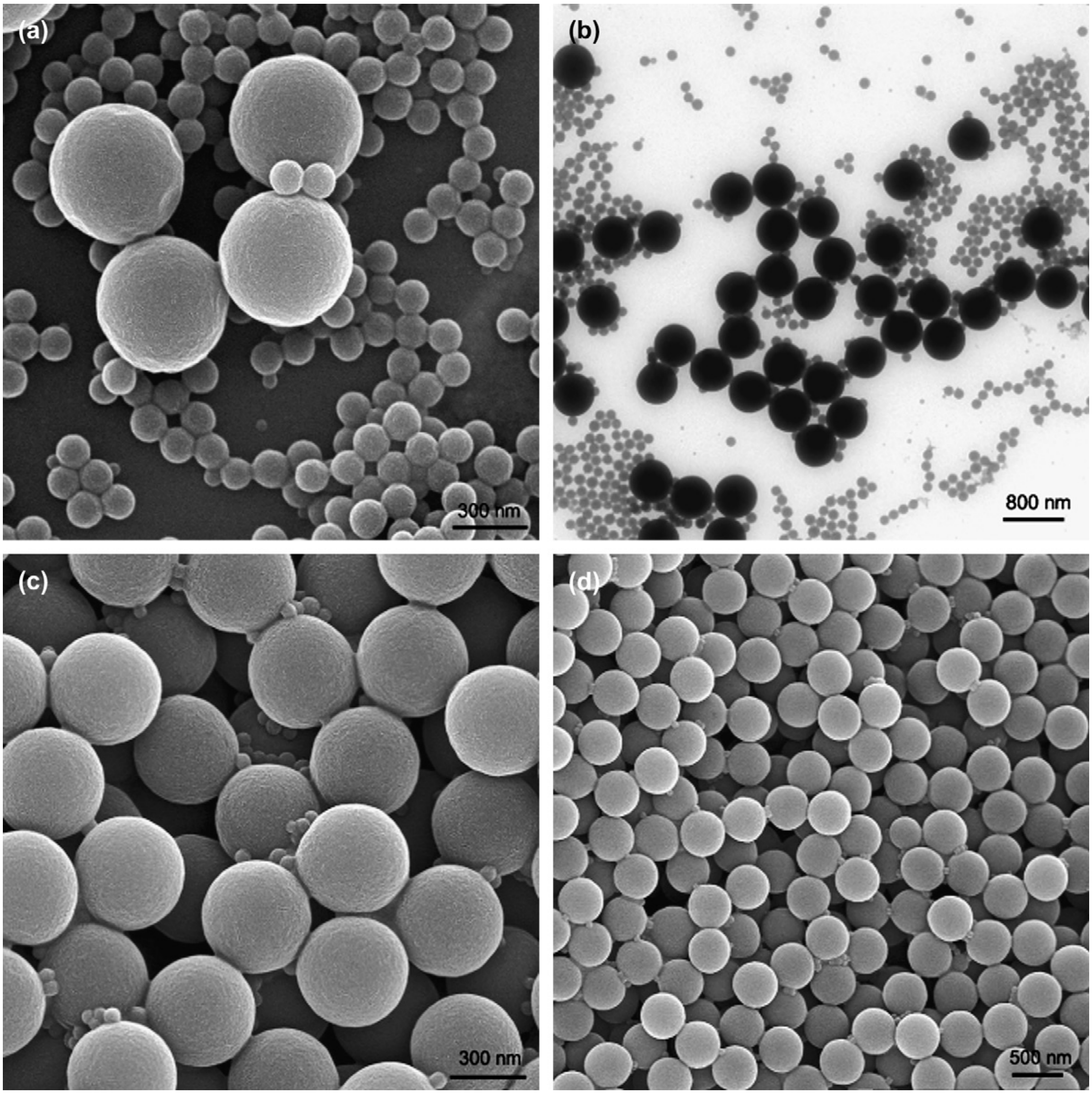


Fig. 4. SEM characterization of 70% polymerized PS seed particles functionalized with a shell of (a) and (b) homopolymer of BPOEA (run 6) and (c) and (d) copolymer of styrene and BPOEA (BPOEA to styrene mole ratio of 1:3, run 7). The shell forming monomers were added in the delayed mode.

any stage of the polymerization, as shown by the fairly monodisperse sizes of the particles in Fig. 3a and b. Moreover, it can be observed that the particle surface is very smooth, possibly indicating a homogenous distribution of polymerized BPOEA. It is worth noting that the final diameter of the particles is smaller than that of the seed particles in Fig. 1, possibly due to non-complete conversion of the seed particles. On the other hand, it should be observed that slight changes in the surfactant-free polymerization conditions can cause important changes in the final number of seed particles, thus, on their final diameter. Starved (delayed) addition of the shell forming monomers to 70% polymerized seed particles (runs 6 and 7, in Table 1) caused the generation of various amounts of secondary particles, as shown in Fig. 4a and b for run 6 (BPOEA polymerized alone) and Fig. 4c and d for run 7 (BPOEA:styrene = 1:3). It can be noticed that different from run 1, where pure BPOEA was used and no secondary nucleation was observed, the use of pure BPOEA in run 6 led to a significant production of secondary particles. As a test, the experimental run 8 described in Table 1 was performed, where only styrene was added after the seed reached full conversion. As it can be seen in Fig. 5, a smooth particle surface and no secondary nucleation was observed. The same result has been obtained in the case, where the seed formation is stopped at 70% conversion (not reported). These two experiments indicate that the peculiar behavior (secondary nucleation) of the system is observed in the presence of the functionalizing monomer, BPOEA, except in the case of a shot addition.

Runs 1, 3 and 8 in Table 1 were repeated after having let the seed to swell overnight in the presence of a small amount of acetone (2–3 mL) (runs 9–11 in Table 2). Acetone is expected to improve and speed up the swelling of the seed

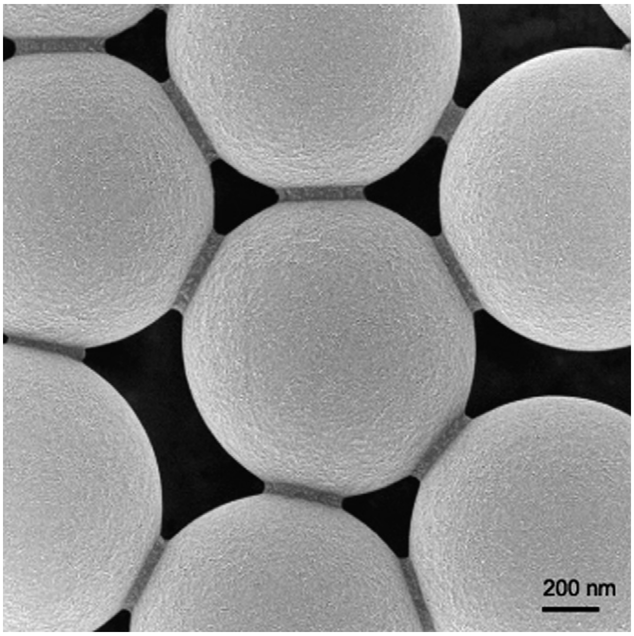


Fig. 5. SEM image of the latex particles after forming a shell of polystyrene on the preformed PS seed latex particles (run 8).

particles by the two monomers, as confirmed by the absence of any monomer droplets after the swelling. However, it can be seen in Fig. 6 that the same results as in the absence of acetone were obtained. This might indicate that the final result of the polymerization is independent of the time let to the system to swell.

In Table 3, an additional set of experiments (runs 12–16) carried out in the presence of a crosslinker (DVB) are detailed. The crosslinker was added to both the seed and the mixture of shell forming monomers. Similar to the runs 4–8 in Table 1, the shell forming monomers were added after the seed reached 70% conversion (runs 12–15 in Table 3) or after complete conversion of the seed (run 16 in Table 3). Moreover, the monomer feed with BPOEA was added either by shot addition (runs 12 and 13) or by delayed addition (runs 14–16). From the micrographs in Fig. 7, it can be seen that in all runs the addition of crosslinker was successful in eliminating secondary nucleation. In spite of this, it can be observed that the surface morphology of the particles is very different. In particular, the addition of BPOEA without styrene led to the formation of rather smooth surfaces (Fig. 7a and c). In the presence of styrene, the best results were obtained when the shell forming monomers were added under delayed conditions, as shown in Fig. 7d and e (runs 15 and 16, respectively). However, even in this case, particle surfaces seemed irregular.

In a selected number of experiments (i.e., those leading to monodisperse latexes), the dried latex particles dissolved in $CDCl_3$ were analyzed with NMR in order to estimate the ratio of BPOEA and styrene (and divinylbenzene) in the particles after polymerization and to compare it with the one when monomers are introduced in the system. As it is clear from Table 4, the final mole ratio of styrene (and divinylbenzene) to the ATRP initiator was always higher than the starting ones indicating that the whole of BPOEA may not have polymerized. This is also indicated by the decreased number of moles of BPOEA per gram of latex as compared to the starting values. This low yield of the process is, however, not a serious problem, since actually only a thin layer of the copolymer of styrene (and divinylbenzene) with BPOEA is enough for the functionalization, as long as a uniform functionalization of the surface can be obtained.

4. Discussion of the obtained results

In the following, we attempt a rationalization of the above results in spite of the complexity of the system, due to the many factors which simultaneously play a role. The most important among them are particle compatibility and colloidal stability, interphase monomer partitioning rates and nucleation rate. In order to emphasize the role of these phenomena, some additional test experiments were carried out. First of all, surfactant-free emulsion polymerization of BPOEA in the absence of polystyrene seed particles was performed (not shown). This led to the formation of large coagulum, indicating that polymerized BPOEA in water leads to polymer precipitation, therefore, hindering the formation of polymer particles by homogenous nucleation. Copolymerization of styrene and BPOEA in two different mole ratios in the absence of any preformed seed particles was also performed, and the corresponding SEM images are shown in Fig. 8. The polymerization with 1:1 mole ratio of the monomers proceeded very slowly and led to the formation of a limited amount of small particles and coagulum. On the other hand, fast formation of very big particles was observed when styrene to BPOEA mole ratio was 3:1. This result indicates that: (1) the polymerization rate is a strong function of the monomer composition and lower styrene ratios lead to lower polymerization rates, (2) the presence of large amounts of styrene seems to help the formation of particles by homogenous nucleation. In the following, all these evidences have been considered in an attempt to explain the results of Figs. 1–7.

Let us first consider the experimental runs in Table 1, where no crosslinker has been used. The characteristic morphology observed in Fig. 2a, when only BPOEA was polymerized in the presence of 100% polymerized PS seed particles, can be explained in terms of colloidal stability and compatibility between styrene and BPOEA. As discussed above, the formed polymer chains of BPOEA tend to precipitate and hence do not favor nucleation of new stable particles. On the other hand, it has been observed that BPOEA is not able to swell the fully polymerized polystyrene seed particles, thus indicating that the two polymers are not fully compatible. We can, therefore, conclude that this process proceeds as a precipitation polymerization where the precipitation of the BPOEA polymer nuclei occurs on the surface of the seed PS particles. Subsequently, they grow by polymerization but they are never integrated in the PS particles leading to the characteristic 'orange-peel' morphology shown in Fig. 2a. It is worth noting that the same reaction after overnight swelling in the presence of acetone (run 10 in Table 2) has produced identical

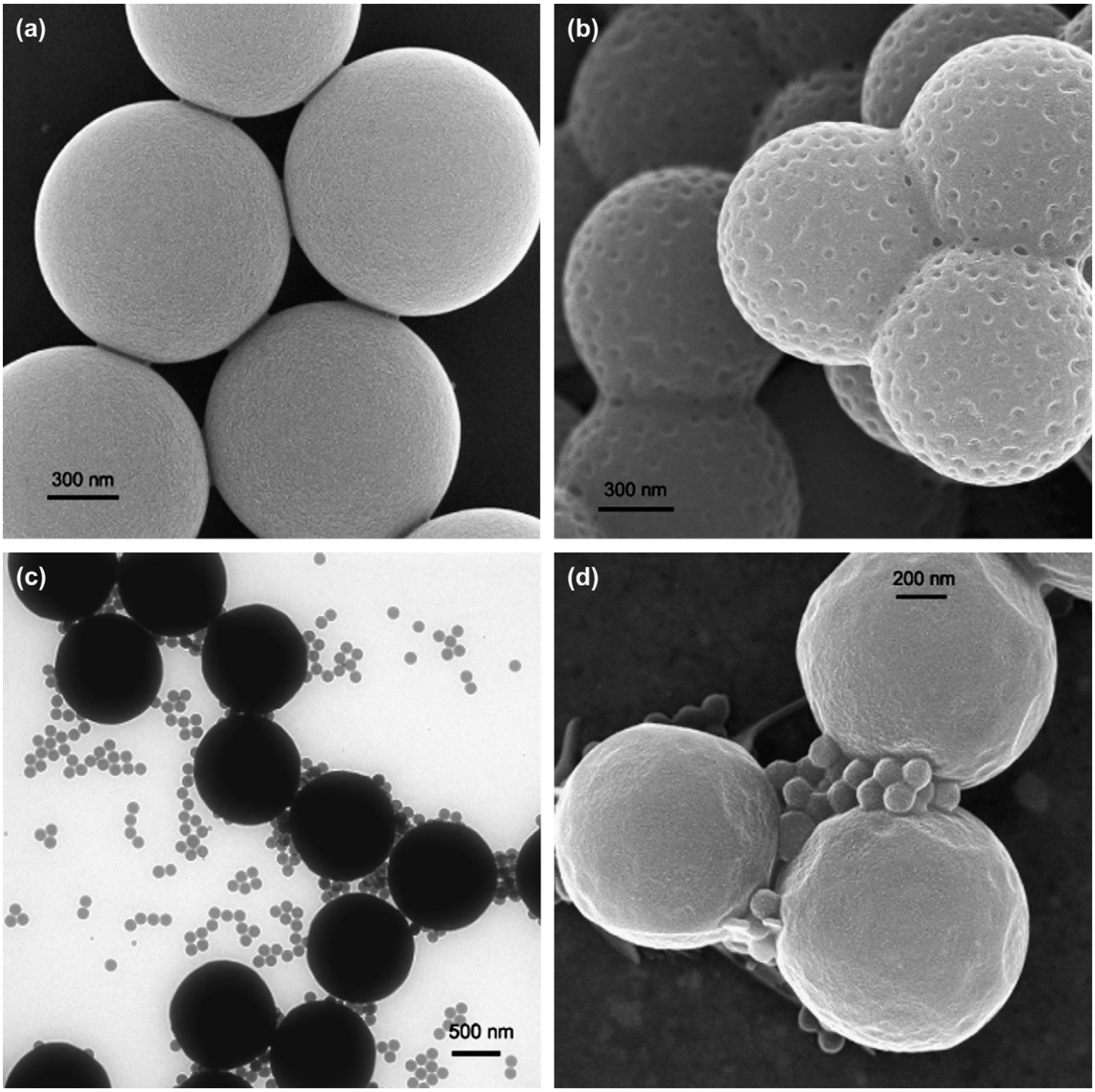


Fig. 6. (a) SEM image of the particles obtained after overnight swelling of the 100% polymerized PS seed particles with styrene (run 9); (b) SEM image of the particles obtained after overnight swelling of the 100% polymerized PS seed particles with BPOEA (run 10); (c) TEM image of the particles obtained after overnight swelling of the 100% polymerized PS seed particles with BPOEA and styrene in the mole ratio of 1:3 (run 11), followed by polymerization and (d) SEM image of the particles shown in (c).

results, thus confirming the strong incompatibility of BPOEA with PS.

The introduction of styrene in the previous process (runs 2 and 3 in Table 1) leads to secondary nucleation, as shown in Fig. 2b–d. This is consistent with the results relative to the surfactant-free copolymerization of styrene with BPOEA as shown in Fig. 8, which indicates that the presence of styrene promotes the formation of particles by homogenous nucleation. The result of runs 2 and 3 is very similar, especially with respect to the average size of the seed and secondary particles. This is probably due to the fact that, even if in run 2 the addition of BPOEA was delayed by 1/2 h, this time is much smaller than the total polymerization time. On the other hand, a macroscopic difference between the final morphology of the seeded particles in the two cases can be observed, the reason for which can only be found in the initial stages of the reaction. It should be considered that, when styrene is added to the system (run 2) before BPOEA, a good portion of it will serve to swell the polystyrene seed particles, thus, in this case the subsequent polymerization takes place with a mole ratio of styrene to BPOEA which is smaller than the value of 3:1 characteristic of run 3 when the two monomers are added simultaneously. Accordingly, we expect that the secondary particles formed in run 2 are less stable than those in run 3. This would justify their coagulation with the seed particles leading to the ‘strawberry’ morphology shown in the high magnification image of Fig. 2c. This particle morphology clearly indicates that part of the particles produced by homogenous nucleation coagulated with the surface of seed particles. In this regard, it can be assumed that the initial stages of the

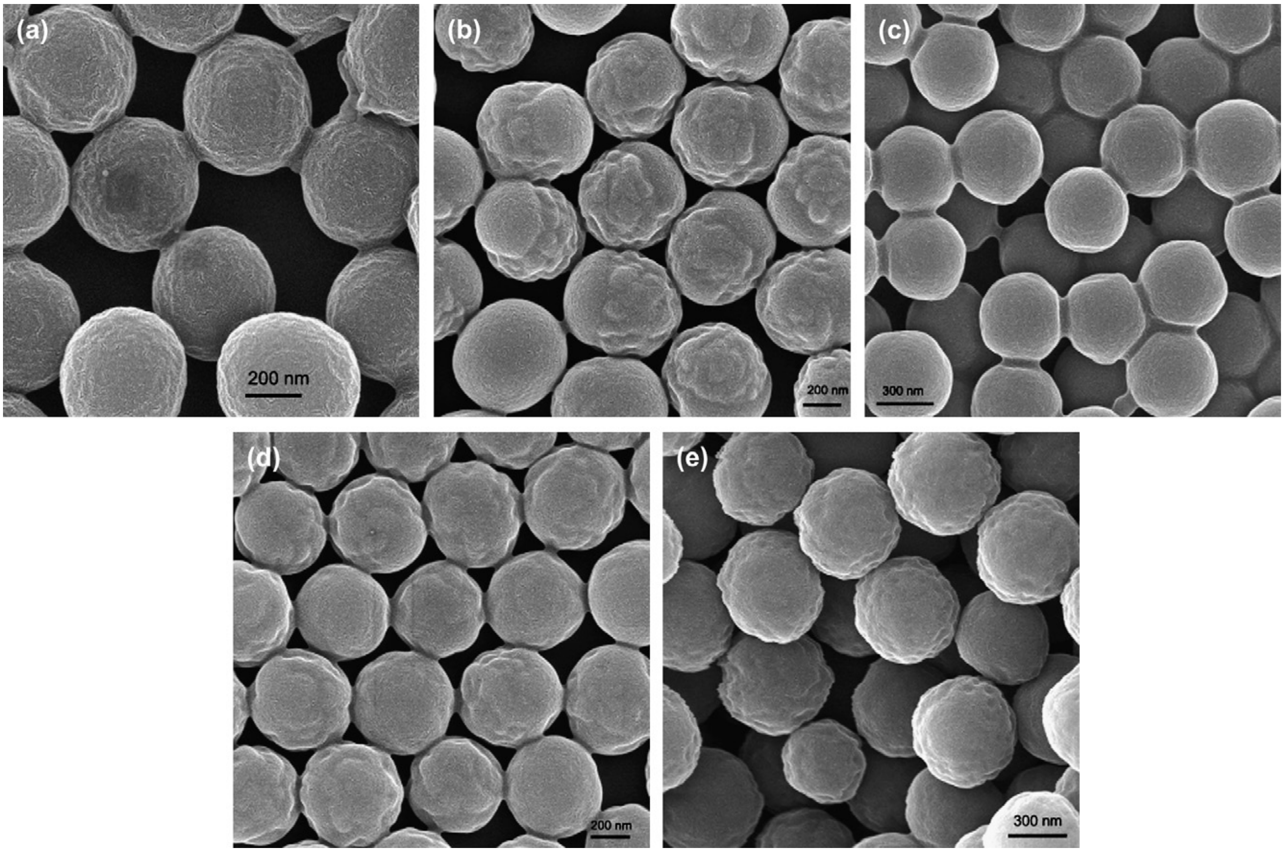


Fig. 7. SEM images of the functionalized latex particles obtained after crosslinking of the core and shell by (a) shot addition of BPOEA and DVB to 70% P(S + DVB) seed latex (run 12); (b) shot addition of S, BPOEA and DVB to 70% P(S + DVB) seed latex (run 13); (c) and (d) starved addition of the monomers of cases (a) and (b), respectively (runs 14 and 15), and (e) starved addition of S, BPOEA and DVB to 100% P(S + DVB) seed latex (run 16).

Table 4
NMR analysis and comparison of the initial (expected) and final mole ratios of the monomer units before and after polymerization; d_{TEM} = average diameter calculated from TEM micrographs, SSA = specific surface area

Run	Initial mole ratio of S + DVB to BPOEA	Initial mole ratio of S to DVB	Initial moles of BPOEA/g of latex	Mole ratio of S + DVB to BPOEA from NMR	Mole percent of BPOEA from NMR	Moles of BPOEA/g of latex from NMR	d_{TEM}, nm	SSA, m^2/g	Conversion, %
1	5.0	−	1.3×10^{-3}	11.5	0.079	6.9×10^{-4}	920	6.04	72
4	8.1	−	9.1×10^{-4}	16.3	0.058	5.1×10^{-4}	745	7.50	81
13	11.5	45	6.9×10^{-4}	25.4	0.038	3.4×10^{-4}	520	10.83	83
14	8.8	29	8.5×10^{-4}	10.9	0.084	7.2×10^{-4}	500	11.10	81
15	11.6	44	6.8×10^{-4}	17.8	0.053	4.7×10^{-4}	560	10.01	85
16	11.6	42	6.8×10^{-4}	17.6	0.054	4.8×10^{-4}	530	10.57	88

polymerization are similar to those of run 1. Similar results were also observed in the literature by Zukoski et al. [40]. On the other hand in run 3, the copolymer chains are richer in styrene and therefore more compatible with the polymer seed. Accordingly, the so-formed nuclei produced by homogenous nucleation can either form secondary particles or adsorb on the surface of the seed particles, but due to the increased compatibility, the formation of the 'strawberry' morphology observed in run 2 is avoided.

The generated morphologies are totally different when the formation of seed particles is allowed till 70% conversion of the monomer. The fact that the seeded particles are not fully polymerized can affect the final result in different ways. First, the unreacted styrene makes the effective ratio of styrene to BPOEA to increase with respect to the value in the second charge of monomers. Second, the seeded particles are already swollen with styrene, which makes the monomer interphase partitioning much faster. Finally, it can be assured that the surface of the seed is 'softer' than in the case of fully polymerized particles and, thus, more prone to coalescence. These three facts can be used to explain the results of runs 4−7 in Table 1. Shot addition of the monomers led to the generation of no secondary particles in the system (runs 4 and 5, Fig. 3). It is worth noting that in these systems, interphase monomer equilibration is much faster than monomer consumption by polymerization. Accordingly, in run 5 most of the styrene added

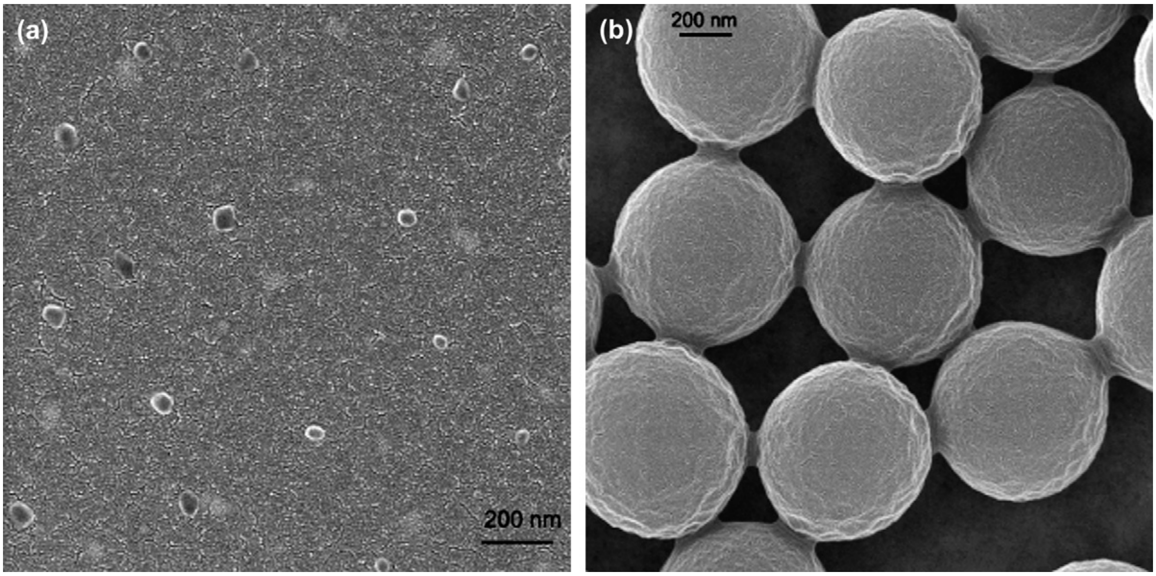


Fig. 8. SEM images representing the particles obtained after copolymerization of S and BPOEA in the absence of any preformed seed particles with S to BPOEA in mole ratio of (a) 1:1 (run 17) and (b) 3:1 (run 18).

with the shell forming monomer mixture is used to swell the seed particles and it is thus subtracted from the newly forming particles thus making run 5 very similar to run 4. In both cases, we expect therefore the formation of chains richer in BPOEA, which being very unstable precipitate on the seed surface, and do not lead to secondary nucleated particles. This effect, together with the softer surface of the seed particles, which is favoring the coalescence or adsorption of the nuclei produced by homogenous nucleation, can explain the absence of secondary particles and the smooth surface of the resulting particles in runs 4 and 5.

On the other hand, in the case of runs 6 and 7, the system behavior is significantly different, mainly due to the significant presence of secondary nucleation. This traces back to the fact that the slow (delayed) monomer addition procedure leads to a ratio of styrene to BPOEA in the reaction system higher than in the case of shot addition. This fact might have helped the secondary particles to reach faster a size where they are colloidally stable. Accordingly, the difference between runs 4 and 5 and runs 6 and 7 can be explained in terms of competition between the rate of growth of the secondary particles and their rate of coalescence to the seed. In both cases, however, smooth surface is observed for the resulting particles, thus confirming the role of styrene in making the two polymers more compatible.

The presence of the crosslinker even in very small amounts led to significant changes in the resulting particles. Also in this case different morphologies were produced using different operating conditions (runs 12–16 in Table 1), but in all cases no secondary nucleation was observed (Fig. 7). Divinylbenzene is known to enhance the colloidal instability of the forming particles and reduce the swelling of the polystyrene seed particles by the second batch of monomers. This leads to the formation of a large number of nuclei, which being colloidally unstable, keep on coalescing with the polystyrene particles. As observed above, this phenomenon seems to be enhanced when styrene is present in the shell forming monomer batch (runs 13 and 15, Fig. 7b and d, respectively). This may confirm the role of styrene in producing nuclei which are initially more stable.

5. Conclusions

In this work, the functionalization of seed polymer particles with a functional acrylic monomer carrying an ATRP initiator moiety (BPOEA) was studied. Many different reaction conditions have been investigated and it has been found that the system exhibits a complex behavior which may lead to unexpected results. For example, in order to control the density of the ATRP initiator on the seed surface, one would naturally change the ratio between styrene and the functional acrylic monomer in the shell forming monomer mixture which is added to the seed particles. However, this is found to strongly change the final particle morphology and to affect the formation of secondary set of particles. Both of these may have undesired consequences on the final particle application properties. A screening of different reaction conditions has been done by changing the conversion in the seed particles at which the mixture containing BPOEA is added, the composition of this mixture and its modality of addition. It has been found that the presence of unreacted monomer in the seed is often beneficial to the success of the reaction. This 'reservoir' of monomer is probably favoring the compatibility between the polymers and the coalescence of the newly formed chains onto the seed particles. The occurrence of these two phenomena is clearly more difficult when fully polymerized seed particles are used. The presence of a crosslinker both in the seed and in the monomer mixture containing BPOEA induces a lower stability in the system, which eliminates secondary nucleation in all the cases analyzed. However, in some conditions, irregular morphologies have been observed, which might represent a non-homogenous distribution of ATRP initiator on the surface. We should also note that the addition of a crosslinking agent is not only beneficial in reducing the occurrence of the previous phenomena, but also in improving the properties of the final particles, which are then more rigid, less prone to swelling and have ATRP initiator groups irreversibly bound on their surface. In conclusion, if crosslinked material is desired then the functionalization procedure should be one step process with delayed addition of the shell forming monomers as surface roughness was enhanced by the shot addition of these monomers. If non-crosslinked material is required, then the good results are obtained by the shot addition of shell forming monomers to the 70% polymerized polystyrene seed particles. The control of the density of functional groups can be achieved by changing the styrene/BPOEA mole ratio in the shell generating monomer mixture added to the polystyrene seed.

References

[1] Lahann J, Mitragotri S, Tran TN, Kaido H, Sundram J, Choi IS, et al. Science 2003;299:371–4.
[2] Sidorenko A, Minko S, Schenk-Meuser K, Duschner H, Stamm M. Langmuir 1999;15:8349–55.
[3] Chaudhury MK, Whitesides GM. Science 1992;256:1539–41.
[4] Nagasaki Y, Kataoka K. Trends Polym Sci 1996;4:59–64.
[5] Fytas G, Anastasizdis SH, Seghrouchni R, Vlassopoulos D, Li J, Factor BJ, et al. Science 1996;274:2041–4.
[6] Mansky P, Liu Y, Huang E, Russell TP, Hawker CJ. Science 1997;275:1458–60.
[7] Mir Y, Auroy P, Auvray L. Phys Rev Lett 1995;75:2863–6.
[8] Prucker O, Ruhe J. Macromolecules 1998;31:592–601.
[9] Prucker O, Ruhe J. Macromolecules 1998;31:602–13.
[10] Zhao B, Brittain WJ. J Am Chem Soc 1999;121:3557–8.
[11] Wu T, Efimenko K, Genzer J. Macromolecules 2001;34:684–6.
[12] Milner ST. Science 1991;251:905–14.
[13] Jordan R, Ulman A, Kang JF, Rafailovich MH, Sokolov J. J Am Chem Soc 1999;121:1016–22.
[14] Ingall MDK, Honeyman CH, Mercure JV, Bianconi PA, Kunz RR. J Am Chem Soc 1999;121:3607–13.
[15] Zhao B, Brittain WJ. Macromolecules 2000;33:8813–20.
[16] Kim J, Bruening ML, Baker GL. J Am Chem Soc 2000;122:7616–7.
[17] Sun T, Wang G, Feng L, Liu B, Ma Y, Jiang L, et al. Angew Chem Int Ed 2004;43:357–60.
[18] You YZ, Hong CY, Pan CY, Wang PH. Adv Mater 2004;16:1953–7.
[19] D'Agosto F, Charreyre M-T, Pichot C, Gilbert RG. J Polym Sci Part A Polym Chem 2003;41:1188–95.
[20] Lamb D, Anstey JF, Fellows CM, Monteiro JM, Gilbert RG. Biomacromolecules 2001;2:518–25.
[21] Lamb D, Anstey JF, Lee DY, Fellows CM, Monteiro MJ, Gilbert RG. Macromol Symp 2001;174:13–27.
[22] Wang XS, Jackson RA, Armes SP. Macromolecules 2000;33:255–7.
[23] Nishikawa T, Ando T, Kamigaito M, Sawamoto M. Macromolecules 1997;30:2244–8.
[24] Coca S, Jasieczek C, Beers KL, Matyajaszewski K. J Polym Sci Part A Polym Chem 1998;36:1417–24.
[25] Gaynor SG, Qiu J, Matyajaszewski K. Macromolecules 1998;31:5951–4.
[26] Qiu J, Gaynor SG, Matyajaszewski K. Macromolecules 1999;32:2872–5.
[27] Matyajaszewski K, Miller PJ, Shukla N, Immaraporn B, Gelamn A, Luokala BB, et al. Macromolecules 1999;32:8716–24.
[28] von Werne T, Patten TE. J Am Chem Soc 2001;123:7497–505.
[29] Husseman M, Malmstrom EE, McNamara M, Mate M, Mecerreyes D, Benoit DG, et al. Macromolecules 1999;32:1424–31.
[30] Huang WX, Kim JB, Bruening ML, Baker GL. Macromolecules 2002;35:1175–9.
[31] Kizhakkedathu JN, Norris-Jones R, Brooks DE. Macromolecules 2004;37:734–43.
[32] Kizhakkedathu JN, Takacs-Cox A, Brooks DE. Macromolecules 2002;35:4247–57.
[33] Kizhakkedathu JN, Brooks DE. Macromolecules 2003;36:591–8.
[34] Kizhakkedathu JN, Goodman D, Brooks DE. In: Matyajaszewski K, editor. Advances in controlled/living polymerization. ACS symposium series 854. Washington, DC: American Chemical Society; 2003. p. 316.
[35] Matyajaszewski K, Gaynor SG, Kulfan A, Podwika M. Macromolecules 1997;30:5192–4.
[36] Du YZ, Ma GH, Ni HM, Nagai M, Omi S. J Appl Polym Sci 2002;84:1737–48.
[37] Cho I, Lee KW. J Appl Polym Sci 1985;30:1903–26.
[38] Sundberg DC, Casassa AP, Pantazopoulous J, Muscato MR, Kronberg B, Berg J. J Appl Polym Sci 1990;41:1425–42.
[39] Juang MS, Krieger IM. J Polym Sci Polym Chem Ed 1976;14:2089–107.
[40] Zukoski CF, Saville DA. J Colloid Interface Sci 1985;104:583–6.
[41] van Herk AM, Gilbert RG. In: van Herk AM, editor. Chemistry and technology of emulsion polymerization. Oxford: Blackwell Publishing; 2005. p. 46–78.
[42] Guo X, Weiss A, Ballauff M. Macromolecules 1999;32:6043–6.
[43] Guerrini MM, Charleux B, Varion JP. Macromol Rapid Commun 2000;21:669–74.
[44] Kim DJ, Heo JY, Kim KS, Choi IS. Macromol Rapid Commun 2003;24:517–21.