

Article

Synthesis of Covalently Cross-Linked Colloidosomes from Peroxidized Pickering Emulsions

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Abstract: A new approach to the formation of cross-linked colloidosomes was developed on the basis of Pickering emulsions that were stabilized exclusively by peroxidized colloidal particles. Free radical polymerization and a soft template technique were used to convert droplets of a Pickering emulsion into colloidosomes. The peroxidized latex particles were synthesized in the emulsion polymerization process using amphiphilic polyperoxide copolymers poly(2-*tert*-butylperoxy-2-methyl-5-hexen-3-ine-*co*-maleic acid) (PM-1-MAc) or poly[N-(*tert*-butylperoxymethyl)acrylamide]-*co*-maleic acid (PM-2-MAc), which were applied as both initiators and surfactants (inisurfs). The polymerization in the presence of the inisurfs results in latexes with a controllable amount of peroxide and carboxyl groups at the particle surface. Peroxidized polystyrene latex particles with a covalently grafted layer of inisurf PM-1-MAc or PM-2-MAc were used as Pickering stabilizers to form Pickering emulsions. A mixture of styrene and/or butyl acrylate with divinylbenzene and hexadecane was applied as a template for the synthesis of colloidosomes. Peroxidized latex particles located at the interface are involved in the radical reactions of colloidosomes formation. As a result, covalently cross-linked colloidosomes were obtained. It was demonstrated that the structure of the synthesized (using peroxidized latex particles) colloidosomes depends on the amount of functional groups and pH during the synthesis. Therefore, the size and morphology of colloidosomes can be controlled by latex particle surface properties.

Keywords: pickering emulsion; covalently cross-linked colloidosomes; polyperoxide inisurf; emulsion polymerization; peroxidized latex particles

1. Introduction

It is difficult to overestimate the importance of colloidal systems in current polymer technology and the development of polymer materials, including nanomaterials. As a result, constant efforts are being made in commonly used industry emulsion and suspension polymerization techniques to improve existing processes and to develop new advanced polymers and polymer materials [1,2]. These polymerization processes usually use templates from liquid droplets stabilized by molecular surfactants to yield tailored solid polymeric nanomaterials (nanoparticles).

Over the past decade, considerable attention has focused on surfactant-free systems [3,4], as they provide an opportunity to reduce the environmental impact of polymer materials. More specifically, of considerable interest are Pickering emulsions, which are stable colloidal systems of two immiscible liquids, one of which is dispersed in the other with the assistance of solid particles [5–7].

The phenomena of particle surface activity were first described by Pickering and Ramsden [8,9]. Several decades later, Velev [10,11] proposed a mechanism for the self-assembly of colloidal particles at the liquid–liquid interface. It was established that Pickering emulsions exhibit superior kinetic and thermodynamic stability compared to conventional emulsions. The stabilization mechanism of colloidal particles is based on the reduction of interfacial tension, which is similar to molecular surfactants; however, compared to surfactant molecules, colloidal particles are significantly larger, and that imparts specifics to the emulsification process and stability profile [12,13]. Using a Pickering emulsion opens up a broad range of opportunities not only for improving the properties and performance of already existing polymer colloids but also for developing new polymer composite materials and nanomaterials [14].

Colloidal structures obtained as a result of fully or partially solidifying droplets of Pickering emulsion are generally referred to as colloidosomes. There are reports in the literature of the synthesis of various types of colloidosomes, including “hairy” colloidosomes [15], “sensitive” colloidosomes [16,17], and “carbon nanotubosomes” [18]. The formation of covalently cross-linked colloidosomes via free radical and condensation polymerization mechanisms has been reported [19–21] to be an effective approach for the fabrication of various colloidosome morphologies, such as core-shell and capsule-like morphologies [20,22]. Due to the ability to finely tune colloidosome properties (density of particle packing at the surface, shell thickness and porosity, core type, composition, etc.), these structures can be engineered to efficiently encapsulate (absorb) and deliver (release) various cargos in a controlled fashion [23]. Reports have shown that colloidosomes can be employed as effective encapsulation tools for drug delivery or for the protection of components in the food and cosmetics industries [24–27].

In this study, peroxidized latex particles, i.e., latex particles with peroxide groups localized at their surface, were applied in the synthesis of cross-linked colloidosomes. The latexes were synthesized using amphiphilic polyperoxide copolymers that acted as initiators and surfactants (inisurf) simultaneously in the emulsion polymerization process. The amphiphilic polyperoxide copolymers employed in colloidosome synthesis, poly(2-*tert*-butylperoxy-2-methyl-5-hexen-3-ine-*co*-maleic anhydride) (PM-1-MA) and poly[N-(*tert*-butylperoxymethyl)acrylamide]-*co*-maleic anhydride (PM-2-MA), were developed in the authors’ groups. PM-2-MA contains primary-tertiary peroxide groups in the macromolecules, whereas PM-1-MA has ditertiary peroxide groups. These peroxide groups have different reactivity and thermal stability levels.

It was expected that the presence of carboxyl and peroxide functional groups (both derived from inisurf molecules) on the latex particles’ surfaces would provide: (i) the required surface properties of particles (hydrophilic-lipophilic balance, HLB), sustaining a Pickering emulsion mechanism for synthesis of colloidosomes [10]; (ii) the initiation of free radical reactions, polymer formation, grafting, and cross-linking within Pickering emulsion droplets; and (iii) an opportunity to further functionalize colloidosomes in post-polymerization reactions.

The Pickering emulsion was composed of an oil phase from a monomer mixture, an initiator (AIBN), and a hydrophobic solvent hexadecane (HD) that was emulsified in an aqueous phase where the peroxidized latex particles, which exclusively acted as surface-active ingredients, were located. Once a Pickering emulsion was formed, it was heated to initiate free radical polymerization inside each oil droplet, yielding hollow (HD-filled) colloidosomes (Figure 1).

It was demonstrated that the presence of functional groups on latex particle surfaces plays a crucial role in the stability of a Pickering emulsion (by controlling the HLB) and determines its success in colloidosome synthesis. By utilizing the peroxide functional groups of latex particles, colloidosomes can be further modified to obtain a covalently cross-linked shell and hollow (liquid) core.

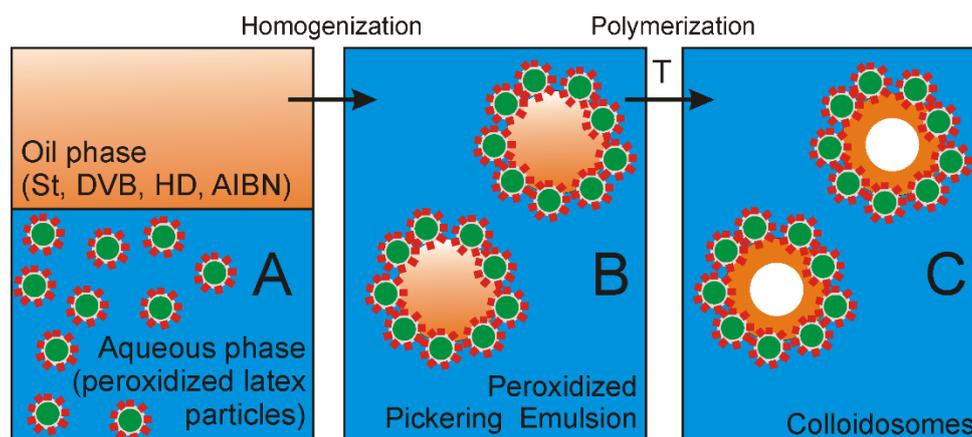


Figure 1. Schematic of the colloidosomes synthesis: (A) Aqueous and oil phases before homogenization; (B) Pickering emulsion; (C) Colloidosomes (polymeric shell covered with grafted peroxidized latex particles and solvent-filled hollow interior).

2. Materials and Methods

Styrene (St), butyl acrylate (BA), divinylbenzene (DVB) (Sigma-Aldrich, St. Louis, MO, USA), hexadecane (HD) (Alfa Aesar, Ward Hill, MA), 2,2'-azobis-isobutyronitrile (AIBN) (Aldrich, St. Louis, MO, USA) were used. Amphiphilic copolymers poly(2-*tert*-butylperoxy-2-methyl-5-hexen-3-ine-*co*-maleic anhydride) (PM-1-MA) or poly[N-(*tert*-butylperoxymethyl)acrylamide]-*co*-maleic anhydride (PM-2-MA) were synthesized as described elsewhere [28–30]. All monomers were purified by vacuum distillation. Other reagents and water (Milli-Q, 18 M Ω) were used as received.

Emulsion polymerization was carried out to synthesize peroxidized latex particles. Briefly, 10 wt.% emulsions of styrene in an aqueous solution of PM-1-MAc (6–10 wt.% per styrene) at pH 10 or PM-2-MAc (1–7.5 wt.% per styrene) at pH 5.5–9.5 were prepared in a 50 mL single-neck round-bottom flask by magnetic stirring at 1200 rpm for 30 min. The emulsions were purged with argon under constant stirring for 20 min and subsequently placed in an oil bath heated to 85 °C. The polymerization was conducted under constant stirring to a conversion of 95%–98%. At the end of the reaction, the latexes were cooled and placed into a 5 mL dialysis bag (50 kDa molecular cut-off) to remove the non-grafted inisurf. The bag was submerged into a 2000 mL beaker filled with distilled water adjusted to pH 9.5 using NaOH. At intervals of 24 h, the water in the beaker was replaced to ensure a constant high concentration gradient to improve the dialysis process. After 14 days, the peroxidized latexes were removed from the dialysis bag and stored at 4 °C.

The resulting polymer was then either (i) stored at 4 °C or (ii) precipitated by a freeze-thaw cycle and washed repeatedly with 0.1 N NaOH and hexane to remove non-reacted materials. The resulting polymer was collected, dried at room temperature, and stored at 4 °C to be used for further analysis.

Volume mean particle size and zeta-potential measurements were performed in dilute aqueous dispersions of latex particles using Malvern Zetasizer Nano-ZS90 at 25 °C. The final numbers represent an average of a minimum of five individual measurements.

A potentiometric titration (back titration using 0.1 N HCl as a titrant) of peroxidized latexes was used to calculate the amount of carboxyl groups (originated from PM-1-MAc or PM-2-MAc) on the surface of latex particles.

A thermal analysis of peroxidized latexes was used to calculate the amount of peroxide groups on the surface of latex particles. For this purpose, latex samples (15 mg) were heated at an underlying heating rate of 10 °C/min to 400 °C in air using a TA Instruments Q500 (TA Instruments, New Castle, DE, USA).

Gas-liquid chromatography was used to calculate the content of the peroxide monomer 2-*tert*-butylperoxy-2-methyl-5-hexen-3-ine (PM-1) units in both the copolymer PM-1-MA and the

peroxidized polystyrene latex particles. A quantitative analysis of the products of a complete decomposition of the PM-1 units was carried out using a Selmihrom chromatograph with columns ($3 \times 3000 \text{ mm}^2$) filled with an absorbent Inerton super (0.125–0.16 mm fraction) modified with 5 wt.% of Carbowax 40 M. The concentration of acetone and 2-methyl-2-propanol—the peroxide group decomposition products—was determined using chloroform as an internal standard.

Pickering emulsions were formed by mixing 28 g of an aqueous phase (containing 0.3–1 wt.% of peroxidized latex particles) with 2 g of an oil phase (consisting of HD, St and/or BA, DVB, and 0.06 g AIBN initiator). The mixtures of oil and aqueous phases were homogenized at 10,000 rpm in a pulsating regime (1 pulse consisting of 60 s of homogenizing +20 s of rest time) for 8 min using a T25 Ultra-Turrax homogenizer equipped with an S 25 N–25 G dispersing element (IKA, Wilmington, NC, USA).

The obtained Pickering emulsions were transferred into a 50 mL single-neck round-bottom flask, purged with argon for 20 min, and subsequently polymerized at 80 °C with magnetic stirring at 1200 rpm for 24 h. After polymerization, colloidosomes were isolated from the reaction mixture, thoroughly washed with an acetone/ethanol (1:1) mixture, and stored either under an H₂O or HD layer or in dry state.

Pickering emulsion stability was evaluated as a volume portion of an emulsified oil phase that does not float at room temperature in 15 min after homogenization.

Digital images of latex particles were obtained using JEOL JSM-6490LV scanning electron microscopy (JEOL USA, Inc., Peabody, MA, USA).

3. Results and Discussion

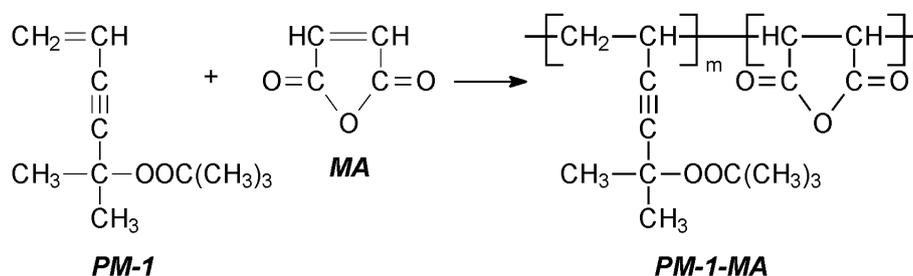
The main goal of this work was to develop a fabrication route for colloidosome synthesis on the basis of Pickering emulsions stabilized using peroxidized latex particles.

To achieve this goal, two objectives were set: (i) to synthesize colloidosomes using peroxidized latex particles and (ii) to investigate the ways that the presence of hydrophilic functional groups on latex particle surfaces impacts Pickering emulsion stability.

Thus, the synthesis of colloidosomes from Pickering emulsions involves the following steps: (i) synthesis of peroxidized latex particles as reactive building blocks in the colloidosome formation; and (ii) localization of the peroxidized latex particles at the interface, i.e., formation of an oil-in-water Pickering emulsion and the synthesis of colloidosomes using the peroxide groups at the interface.

3.1. Synthesis and Characterization of Peroxidized Latexes

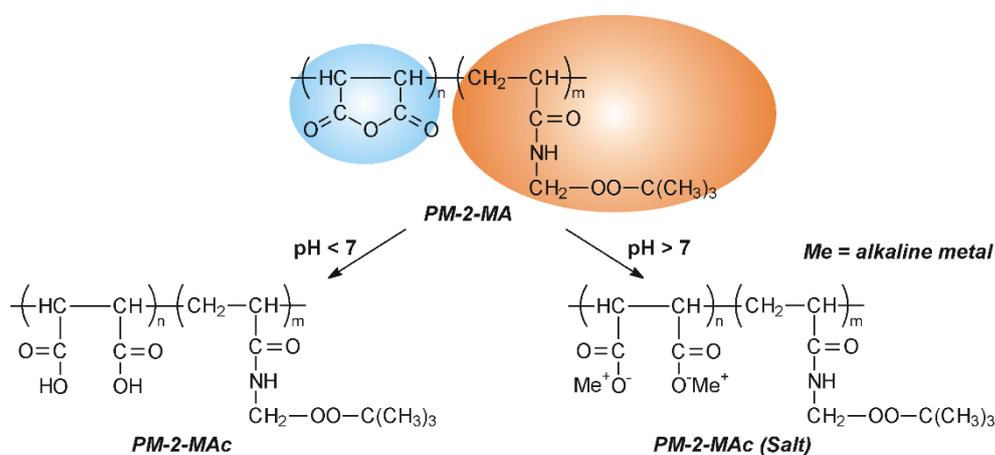
An amphiphilic PM-1-MA copolymer used as an inisurf was synthesized through a free-radical copolymerization of a peroxide monomer 2-*tert*-butylperoxy-2-methyl-5-hexen-3-ine (PM-1) with maleic anhydride (Scheme 1).



Scheme 1. Synthesis of PM-1-MA containing peroxide and anhydride groups.

The subsequent hydrolysis of the synthesized PM-1-MA copolymer leads to the formation of a surface active initiator (inisurf) with carboxyl groups (at pH < 7) or carboxylate (salt) groups (at pH > 7) (Scheme 2).

An inisurf PM-2-MAC with carboxyl groups or carboxylate (salt) groups was formed via the hydrolysis of the PM-2-MA copolymer at different pH levels (Scheme 4).



Scheme 4. Inisurf formation by hydrolysis of an amphiphilic PM-2-MA copolymer at different pH levels (blue and orange represent the hydrophilic and hydrophobic moieties of PM-2-MA, respectively).

Amphiphilic PM-1-MAC and PM-2-MAC copolymers (Schemes 2 and 4) were used as inisurfs in emulsion polymerization to synthesize peroxidized latex particles. To provide particles with surface activity and the ability to stabilize a Pickering emulsion in colloidosome synthesis, these particles must exhibit amphiphilic behaviors, i.e., combine hydrophilic and hydrophobic molecular moieties at the surface. In the case of peroxidized latexes, hydrophilic properties are provided by the hydrolysis of PM-1-MA or PM-2-MA maleic anhydride groups (Scheme 2 and blue area in Scheme 4) and form the carboxyl groups of PM-MAC at pH < 7 or PM-MAC (salt) at pH > 7 inisurf macromolecules, whereas non-polar fragments of the peroxide monomers in the copolymer (Scheme 2 and orange area in Scheme 4) and polystyrene (core material of latex) provide hydrophobic properties to the particle's surface.

To investigate the ability to vary the nature of the peroxide groups and the amount of carboxyl groups on the surface of latex particles, and thus their reactivity and surface activity, a series of peroxidized latexes were synthesized at pH 10 using PM-1-MAC at various concentrations (6, 8, and 10 wt.% based on monomer weight) and at pH 5.5, 7.5, and 9.5 using PM-2-MAC at various concentrations (0.3, 1, 2.5, 5, and 7.5 wt.% based on monomer weight).

The water soluble copolymers PM-1-MAC and PM-2-MAC exhibit surface activity that decreases the surface tension at the water-air interface to 30–40 mN/m. In an aqueous medium, they form micellar structures, which are able to solubilize hydrophobic substances [28]. This allows for the application of PM-1-MAC and PM-2-MAC as polymeric surfactants in emulsion polymerization. The peroxide groups in the polymeric surfactant macromolecules enable their ability to initiate free radical processes [31–33]. The amphiphilic nature of the PM-1-MAC and PM-2-MAC macromolecules with the hydrophilic units of maleic acid and the hydrophobic units of the peroxide monomer facilitates the stabilization of latex particles in emulsion polymerization. The solubilization of the styrene monomer in emulsion polymerization followed by the formation of adsorption layers at the surface of latex particles occurs due to hydrophobic interactions and the hydration of ionized carboxylate groups oriented towards an aqueous phase (Figure 3). The stability of the latex particles is achieved due to the combination of steric and electrostatic stabilization [28].

An advantage of the application of PM-1-MAC and PM-2-MAC as polymeric inisurfs is the presence of peroxide groups in the hydrophobic PM units, which are regularly distributed along the macromolecules. During thermolysis, the peroxide groups decompose to form *tert*-butoxy and macroradicals, which are able to initiate radical reactions of styrene polymerization [28,34].

The combination of the PM-1-MAC and PM-2-MAC macroradicals with the growing polystyrene chains leads to the attachment of the PM-1-MAC and PM-2-MAC macromolecules to the surface of latex particles and to the formation of the polyperoxide PM-1-MAC and PM-2-MAC layers covalently grafted to the polystyrene particle surface (Figure 3).

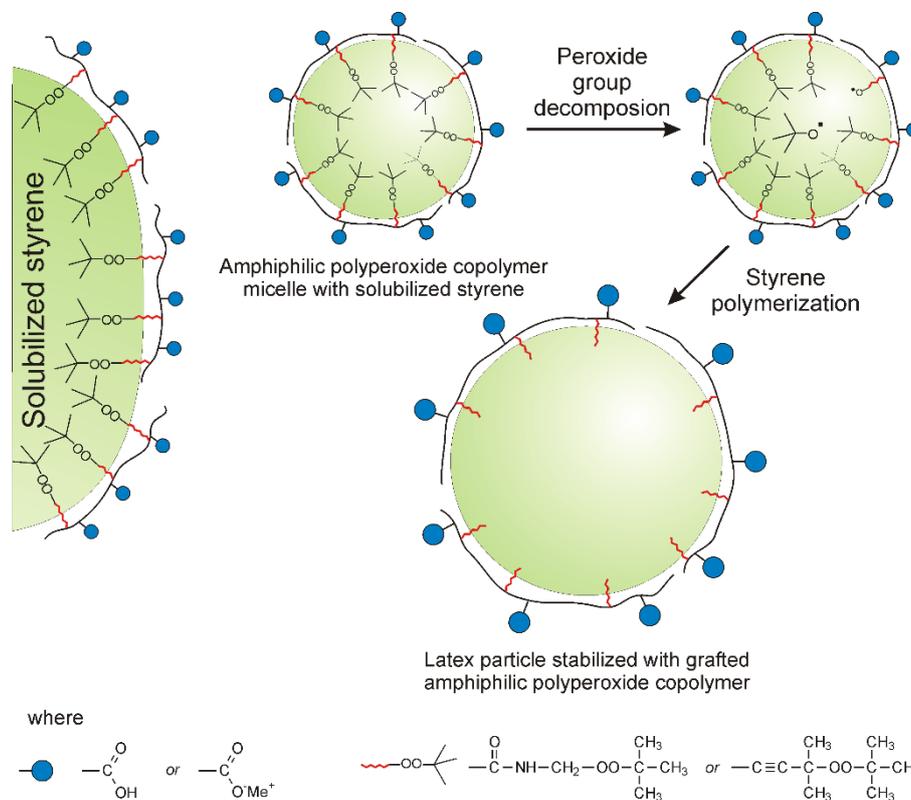


Figure 3. Emulsion polymerization of styrene using PM-1-MAC and PM-2-MAC as polymeric inisurfs.

The emulsion polymerization of styrene in the presence of PM-1-MAC resulted in polystyrene latex particles with peroxidized surfaces and average diameters in the range of 165 nm to 220 nm (Table 1).

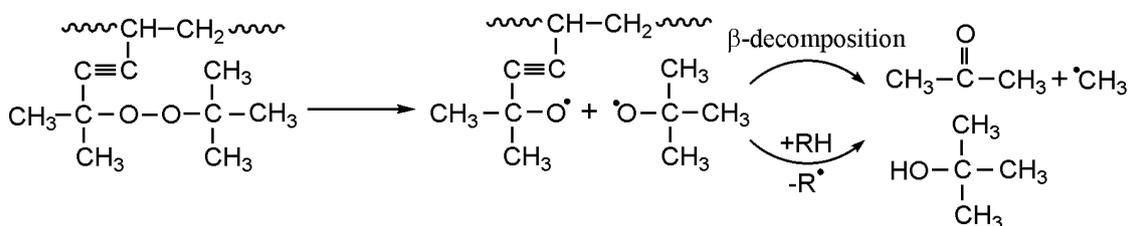
Table 1. Physico-chemical characteristics of latex particles synthesized using varying concentrations of PM-1-MAC in the emulsion polymerization of styrene at pH 10.

Sample of the Peroxidized Latex Particles	Synthetic Conditions for Peroxidized Latexes (Latex Particles)			D_h (nm) ²	Content of the PM-1 Units in a Sample (%) ³
	Initial [PM-1-MAC] (%)	T (°C)	Conversion (%) ¹		
polySt-PM-1-MAC-1	6	70	97	181	3.2
polySt-PM-1-MAC-2	8	70	98	180	3.2
polySt-PM-1-MAC-3	10	70	97	166	2.8
polySt-PM-1-MAC-4	6	80	99	212	2.6
polySt-PM-1-MAC-5	8	80	97	207	2.8
polySt-PM-1-MAC-6	10	80	98	218	1.7

Notes: ¹ Using solid content determination; ² Using dynamic light scattering; ³ Using gas-liquid chromatography.

The presence of the peroxide groups in the grafted PM-1-MAC macromolecules was proven by the thermogravimetric analysis of the polystyrene latex. Weight loss at 150–220 °C accompanied by a well-pronounced exothermic effect is characteristic of the decomposition of the ditertiary peroxide groups of PM-1 [28,31,35].

The ratio of the low-molecular-weight products (i.e., acetone and 2-methyl-2-propanol) of the peroxide group decomposition (Scheme 5) was determined using gas-liquid chromatography, which enabled quantifying the PM-1 units in the peroxidized polystyrene latex (Table 1). The presence of the PM-1-MAC chains in the polystyrene latex confirms a covalent grafting of the PM-1-MAC macromolecules to the surface of the polystyrene latex particles.



Scheme 5. Decomposition of the peroxide PM-1 units.

Varying concentrations of the synthesized PM-2-MAC copolymer were used in a series of emulsion polymerizations of styrene at pH 9.5 (Table 2). The expectation was that the PM-2-MAC would act as an inisurf during the polymerization process, initiating polymerization by generating free radicals at elevated temperatures and ensuring micelle formation and the stabilization of growing polymer particles.

Table 2. Physico-chemical characteristics of latex particles synthesized using varying concentrations of PM-2-MAC in the emulsion polymerization of styrene at 85 °C and pH 9.5.

Initial [PM-2-MAC] (%) ¹ /-OO- (mmol/g)	[PM-2-MAC] Localized at the Latex Particle Surface (%) ²	D_h (nm)	PDI	ζ -Potential (mV)	-OO- Localized at the Surface (mmol/g) ^{2,3}
1.0/0.05	0.73	196	0.050	-58 ± 2.1	0.04/0.01
2.5/0.13	1.76	162	0.015	-57 ± 1.9	0.09/0.07
5.0/0.27	3.99	146	0.041	-54 ± 2.0	0.21/0.19
7.5/0.40	6.21	155	0.033	-54 ± 1.8	0.32/0.29

Notes: ¹ In reaction feed, per styrene monomer; ² Using potentiometric titration (as no decomposition occurs);

³ Using thermogravimetric analysis (considering decomposition).

Figure 4A illustrates the size variations of the peroxidized particles obtained at 85 °C as a function of pH and initial PM-2-MAC concentration. In general, the size of latex particles decreases with an increasing PM-2-MAC concentration and with a decreasing pH. The latter can be explained by the fact that a higher concentration of inisurf naturally results in a larger number of micelles (nucleating sites for particle growth in emulsion polymerization); thus, a greater number of smaller particles is formed. The HLB of inisurf macromolecules depends on the pH of the solution. At a higher pH, inisurf macromolecules are more hydrophilic, and thus more are required to form a micelle (the opposite is true for a lower pH). Consequently, the pH changes the total number of micelles in polymerization and results in variations in latex particle numbers and sizes (Figure 4A).

As shown in Tables 1 and 2, the inisurf macromolecules at elevated temperatures undergo covalent attachments (grafting) to latex particle surfaces during polymerization. A potentiometric titration of peroxidized latexes was performed to determine the amount of carboxyl groups on the particles' surfaces. The obtained data reveal that only 60%–80% of carboxyl groups in grafted macromolecules are indeed located on the particle surface. Thus, a significant part of the anhydride groups was localized in the particle core during the synthesis and may not have undergone hydrolysis. Figure 4B shows the zeta potential measurements of peroxidized latexes and provides information regarding the overall effect of inisurf concentration and pH on a particle's charge. The data show that the amount of carboxyl groups on the surface of latex particles depends almost linearly on the concentration of

the inisurf (Figure 5B); however, the density of the functional groups on the surface differs based on inisurf concentrations, possibly due to changes in latex particle sizes (Figure 5A).

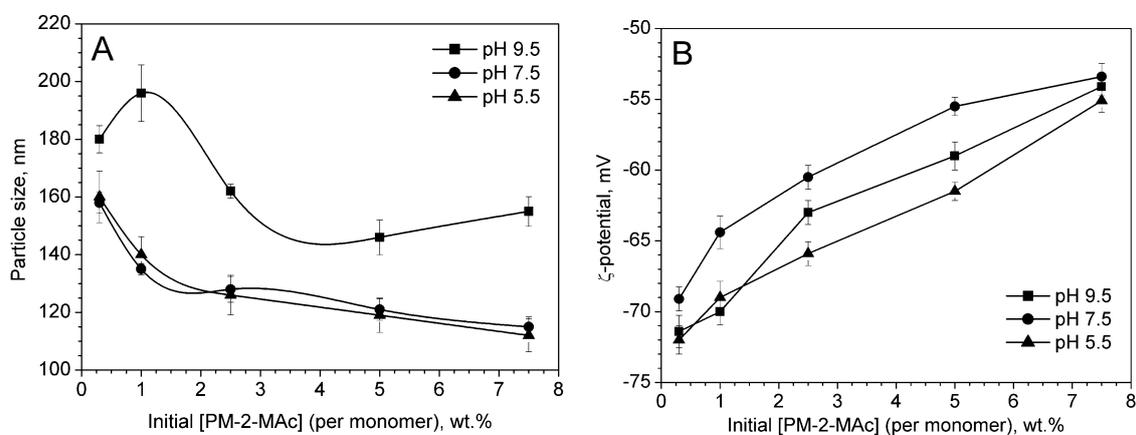


Figure 4. (A) Diameter and (B) ζ -potential variations of peroxidized latex particles synthesized at 85 °C at different pH levels and PM-2-MAC concentrations.

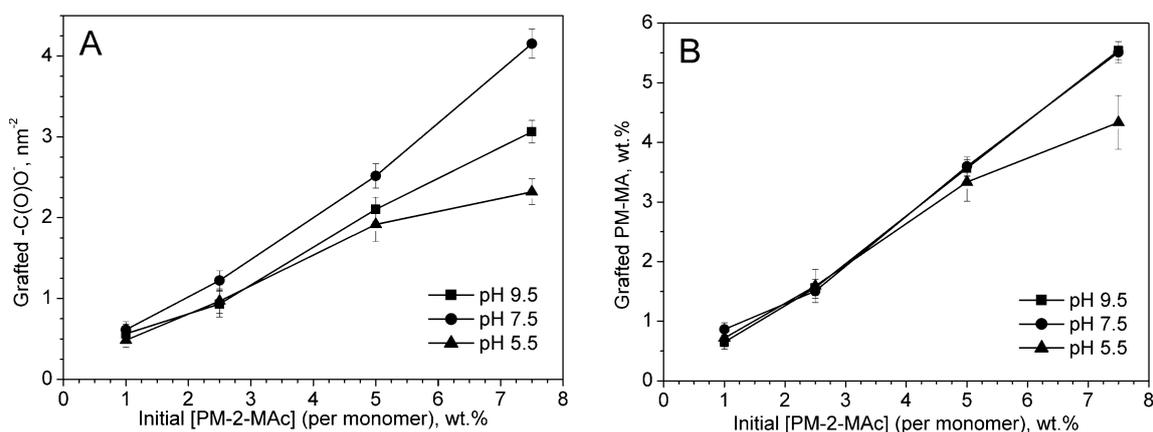


Figure 5. Amount of: (A) carboxyl groups; and (B) PM-2-MAC copolymers on peroxidized latex particles synthesized at different pH levels.

The observed changes of zeta potential with respect to pH during synthesis can be explained by the fact that part of the anhydride groups is not accessible for hydrolysis, as was determined by the potentiometric titration.

Thus, it was observed that increasing the inisurf concentration in latex synthesis results in a significantly smaller size of the resulting particles and a larger amount of carboxyl groups on the surface. The size of the particles is determined by the pH during emulsion polymerization, and it is also affected by the amount of carboxyl groups on the surface of particles.

As a result, a variable amount of carboxyl groups on the surface of peroxidized latex particles allows for control over particle surface properties (including HLB).

During the next step, a colloidosome synthesis was attempted using peroxidized latex particles.

3.2. Colloidosome Preparation

In this study, the “soft template” approach [10] was used in which liquid droplets of Pickering emulsion serve as templates for cross-linked colloidosomes synthesis (Figure 1).

To synthesize colloidosomes, a combined initiation mechanism was applied, i.e., initiation in a bulk template (with AIBN) and initiation from the surface of the peroxidized latex particles (with the

inisurf). Depending on the composition of a monomer mixture, polystyrene, poly(butyl acrylate), or poly(styrene-*co*-butyl acrylate) (all polymers cross-linked with divinylbenzene) were formed in the bulk template during polymerization. The formed polymers are insoluble in hexadecane. As a result, their macromolecules were localized at the interface and were involved in the formation of the colloidosomes' polymer walls (Figure 1C). The peroxide groups localized at the interface (on the surface of peroxidized latex particles) in turn generate free radicals, which participate in radical reactions of initiation, chain transfer, and combination. Due to the above-mentioned radical processes, polymer chains from the monomers and the divinylbenzene cross-linker grew both in the bulk template and from the interface. This resulted in the formation of intermolecular cross-links and the covalent immobilization of the latex particle, which acted as a Pickering stabilizer, within the colloidosome walls.

The formation and stability of a Pickering emulsion depend on the latex particles' surface activity (surface HLB). Therefore, the ability to control the HLB of the particle surface is crucial. To confirm that peroxidized latex particles can be used in Pickering emulsion formation for covalently cross-linked colloidosome synthesis, a series of Pickering emulsions was prepared.

First, the formation and stability of a series of formulated Pickering emulsions were studied as a function of pH (Figure 6). It was found that there is an optimum pH range in which superior Pickering emulsion stability can be achieved. Notably, at pH < 3 and pH > 9, no emulsion formation was observed, which can be explained by either an absence (pH < 3) or an excessive amount (pH > 9) of ionized carboxyl groups on the latex particles' surfaces, causing the particles to coagulate due to a detrimental HLB change of inisurf macromolecules that act as particle stabilizers.

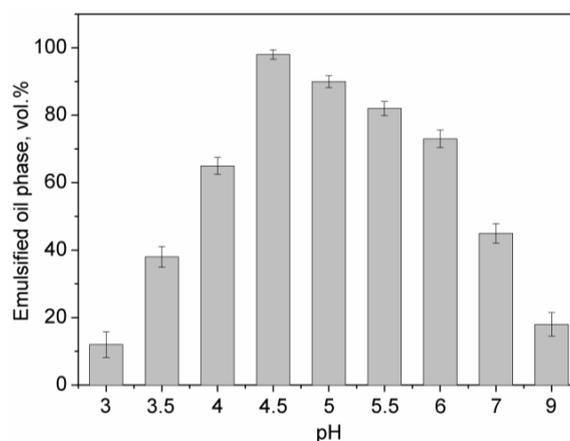


Figure 6. Fraction of remaining emulsified oil phase of Pickering emulsions prepared at various pH levels (recorded after a 24 h rest period).

Immediately after formation, a Pickering emulsion “creams” by floating an emulsified oil phase on top of an excessive aqueous phase. This effect can be explained by the different densities of the aqueous and oil phases (a large size prevents droplet suspension). At this point, the formulation quality can be assessed by inspecting the aqueous phase for the presence of excessive latex particles. Opalescence and turbidity would signify an inefficient use of latex particles. By adjusting the pH, shear rate, and concentration of latex particles, it is possible to form a clear (particle-free) aqueous phase, indicating that all particles are involved in droplet stabilization.

For the synthesis of colloidosomes, latexes developed at pH 7.5 at 85 °C in the presence of 1 wt.% (based on monomer weight) inisurf PM-2-MAc were chosen. It was the assumption that while having a smaller amount of carboxyl groups, these latexes exhibit sufficient surface activity to stabilize a Pickering emulsion.

After formulating a Pickering emulsion, polymerization was conducted at 80 °C to yield hollow colloidosomes decorated with peroxidized latex particles. Table 3 presents data on the properties of the synthesized colloidosomes. The obtained results indicate that several morphological characteristics

of colloidosomes can be controlled by variations in oil phase compositions (e.g., monomer/HD ratio) and the pH levels of the aqueous phase.

Table 3. Synthetic conditions and properties of colloidosomes based on PM-2-MAC.

Sample	pH	Oil Phase Composition (wt.%)				Colloidosome Dimensions	
		St	DVB	HD	AIBN	D (μm)	Shell (μm)
CS1	7.5	28	12	57	3	10 ± 8	1.7 ± 0.4
CS4	3.5	28	12	57	3	10 ± 4	1.3 ± 0.3
CS3	4.5	28	12	57	3	15 ± 3	1.5 ± 0.4
CS2	4.5	14	6	77	3	10 ± 2	0.8 ± 0.2

At the same time, the size of colloidosomes can be adjusted using the pH of the aqueous phase and the homogenization parameters (pulse length, sonication intensity), whereas shell thickness depends on the total initial concentration of monomers. Figure 7 shows SEM images of different colloidosomes (Table 3) synthesized using peroxidized latex particles.

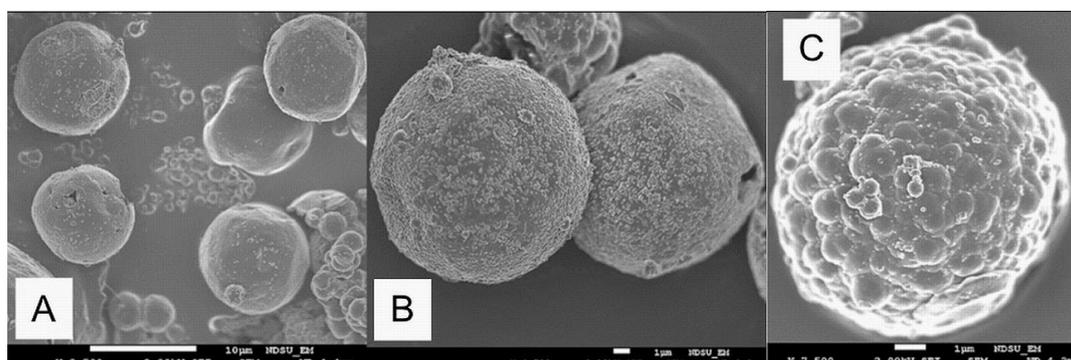


Figure 7. SEM photographs of colloidosomes synthesized from peroxidized (inisurex PM-2-MAC) latex particles: (A) CS2; (B) CS3; (C) CS1.

Although the surface charge of latex particles is essential for the electrostatic stabilization of droplets in a Pickering emulsion, it can also be disruptive if it is too large. Notably, unlike other samples, the colloidosomes prepared at pH 7.5 did not feature smooth surfaces covered with grafted latex particles. Their outer surfaces showed signs of phase separation during synthesis and an obvious lack of latex particles, which is possibly due to an excessive particle charge at pH 7.5.

The same approach was applied for the synthesis of colloidosomes from latex particles synthesized with inisurex PM-1-MAC. The synthetic conditions and characteristics of the formed colloidosomes are summarized in Table 4.

Table 4. Synthetic conditions¹ and properties of colloidosomes based on PM-1-MAC.

Colloidosome Polymer	Monomer conc. in Oil Phase (mol/L)			Total Monomer conc. (mol/L)	Monomer/DVB Ratio (mol/mol)	Hexadecane conc. (mol/L)	D (μm)
	St	BA	DVB				
polySt-BA-1	1.3	0.7	2.0	4.0	1/1	1.66	4–20
polyBA-2	–	2.0	2.0	4.0	1/1	1.47	5–30
polyBA-3	–	1.5	1.5	3.0	1/1	1.96	10–35
polySt-4	3.0	–	1.0	4.0	3/1	1.76	1.7–6
polySt-5	2.0	–	2.0	4.0	1/1	1.67	6–18
polySt-6	2.25	–	0.75	3.0	3/1	2.18	1–3

Notes: ¹ Ratio of aqueous:oil phase as 9:1; Pickering stabilizer concentration 0.36 wt.%; reaction time 150 min.; temperature 80 °C.

As determined by SEM measurements, the diameter of the synthesized colloidosomes varied in the range of 1.3 μm to 35 μm depending on the synthetic conditions and compositions of the reactive mixture. Figure 8A shows SEM images of colloidosomes polySt-4 (Table 4). The polydispersity of the colloidosome diameter is evidently dependent on a dispersing process during the Pickering emulsion formation; the same behavior was noted in Ref. [20].

The morphology of the synthesized colloidosomes (Figure 8B) clearly shows the presence of the polymer particles within the colloidosome wall. As evidenced by Figure 8C, the colloidosome walls define an internal enclosure, or cavity. The application of divinylbenzene as a low-molecular-weight cross-linker allows for the formation of cross-linked polymers with a three-dimensional structure, namely, the formation of the spongy walls of the colloidosomes (Figure 8C). The cross-linked polymer chains then lose their mobility, which leads to a decrease in their precipitability and an increase in the wall thickness. Under certain conditions, the filling of the entire colloidosome cavity with the spongy polymer was observed (Figure 8D). On the other hand, the development of broken (or not fully formed) colloidosomes was observed when the content of the monomers in the template decreased. This indicates that the walls formed under these conditions are either not strong enough or that the cross-linking degree is low.

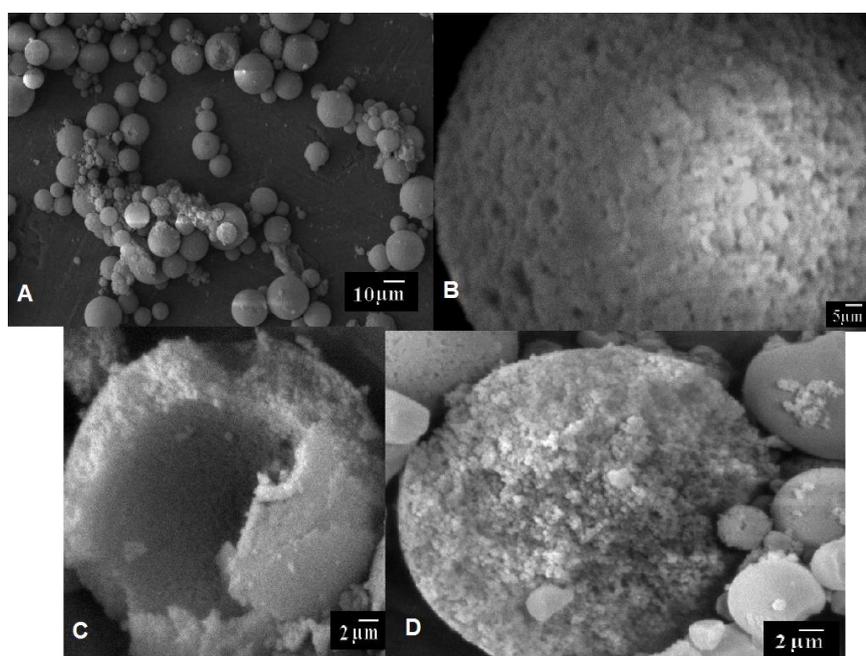


Figure 8. SEM photographs of colloidosomes synthesized from peroxidized (inisurf PM-1-MAc) latex particles: (A,B,C) polySt-4; (D) polySt-BA-1.

4. Conclusions

Pickering emulsions were first synthesized using new Pickering stabilizers: peroxidized latex particles with a grafted layer of polymeric inisurfs poly(2-*tert*-butylperoxy-2-methyl-5-hexen-3-ine-*co*-maleic acid) and poly[N-(*tert*-butylperoxymethyl)acrylamide]-*co*-maleic acid. Covalently cross-linked colloidosomes were synthesized on peroxidized particle basis. The formation of colloidosomes was achieved through the radical copolymerization of vinyl monomers in a disperse phase of the Pickering emulsion. The copolymerization was initiated both in a template bulk and from the surface of the Pickering stabilizer.

Peroxidized latex particles with variable amounts of carboxyl and peroxide groups on particle surfaces allow for the formation of Pickering emulsions and covalently cross-linked colloidosomes

with several different morphologies. It was found that the surface charge of the particles is essential for maintaining the stability of the droplets in a Pickering emulsion and thus for colloidosome formation.

The developed synthetic technique allows the fabrication of carrier colloidosome capsules free of surfactant contamination that can potentially leak out during colloidosome application.

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