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Abstract

When finally processed to provide the function for which the latex was selected — binding, protecting, finishing — components such as surfactant, costabilizer or initiator become generally useless, not to say detrimental. In this study, we show that miniemulsion photopolymerization provides a suitable method to create latex without the apparent addition of these three compounds. Indeed, UV-driven monomer self-initiation can create initiating radicals without the aid of initiator, the fast in situ photogenerated polymer can hinder Ostwald ripening with the assistance of external costabilizer, and finally UV-transparent clay can replace conventional surfactant to ensure colloidal stabilization. Each strategy has been developed individually before being combined together to end up with a unique miniemulsion procedure free of initiator, costabilizer and surfactant. Such approach paves the way to a simplified and environmentally improved pathway towards aqueous polymer dispersions.

Keywords: miniemulsion, photopolymerization, UV light, cotabilizer-free, Pickering

Introduction

In industry, producing emulsion polymers is mostly a question of formulation using a variety of vinyl monomers, radical initiators, surface-active agents, and in some cases costabilizers, all specific to different applications [1,2]. Clearly, the result of this increased number of components compared to bulk or solution systems is a higher level of complexity. As compensation, emulsion polymerization processes have hopefully unique advantages, including water-based products, thermal and viscosity control, high molecular weight and reaction rates attained simultaneously. Except for monomer eventually converted into polymer, most of these compounds have ironically little value or practical use for the final purpose, although their role are particularly significant for latex synthesis and colloidal stability [3]. In most applications, the polymer particles are indeed coalesced without purification step, and the nonvolatile initiator residues and stabilizer molecules entrapped in the functional polymer may have a detrimental effect on film formation and final properties. There are very few applications, such as drug carrier or medical diagnosis, in which the polymer dispersions must remain in the liquid form.

While heterogeneous polymerization processes seem inherently multi-component, our study demonstrates that latexes can be produced without the apparent addition of initiator, costabilizer and surfactant. In contrast to more common approaches in which a single component is removed only (e.g. surfactant-free emulsion polymerization involving no added surfactant), a method capable of eliminating at the same time all these compounds would be a milestone in that respect. To carry out this challenge, miniemulsion polymerization represents a suitable model process because these three components are generally considered as essential features in the formulation [4,5]. In miniemulsion polymerization, a surfactant/costabilizer mixture is used to stabilize submicrometric monomer droplets (50 – 500 nm) which are polymerized in presence of a radical initiator. In contrast to conventional emulsion polymerization, there is ideally neither micelle, nor need for monomer transport through the aqueous phase. Such reaction conditions are meant to promote a nucleation inside small monomer droplets.

In this work, the role and impact played by each component — initiator, costabilizer and surfactant — has been firstly discussed thoroughly. Second, a suitable and stepwise elimination strategy has been devised. To get rid of each compound one after the other, we rely on a photoinduced radical polymerization having three specific features:

i. The direct UV excitation ($\lambda < 300$ nm) of many acrylate monomer miniemulsions is able to promote their self-initiation, thereby avoiding the use of radical initiator.

ii. When the photopolymerization takes place just after emulsification and at a sufficiently fast rate, a high polymer volume fraction is rapidly generated inside the monomer droplet. As a result, Ostwald ripening could be overcome, obviating the need for an external costabilizer.

iii. Above 200 nm, UV light is poorly absorbed and scattered by nanometric particle stabilizers such as Laponite clay or silica. Hence, these inorganic species are suitable candidates for Pickering-stabilized miniemulsion photopolymerization in which the solid particles adhering to the surface of the monomer droplets replace conventional surfactant molecules.

Materials and Methods

Materials

Methyl methacrylate (MMA), methyl acrylate (MA), *n*-butyl acrylate (BA), *n*-butyl methacrylate (BMA), vinyl acetate (VA), acrylic acid (AA) were purchased from Aldrich without further purification. 3,3,5-trimethyl cyclohexanol acrylate (TCA) was purchased from Sartomer Europe. Stearyl acrylate (SA, Aldrich) or hexadecane (HD, Aldrich) was employed as costabilizers. Sodium dodecyl sulfate (SDS, Aldrich) was used as surfactant. For Pickering miniemulsion preparation, hydrophilic RD Laponite was provided by Rockwood Additives.

Preparation of monomer miniemulsions

i. Photoinitiator-free miniemulsions

6 g of monomer based on a mixture (MMA/BA/AA: 49.5:49.5:1 wt %) or a single compound (MMA, MA, BMA, BA, VA or TCA) was mixed with 0.24 g of SA (or HD in the case of VA miniemulsion) to form the organic phase. Separately, an aqueous phase was prepared by dissolving 0.21 g or 0.045 g of SDS in 14 g of distilled water; for each instance the surfactant concentration was respectively 3.5 or 0.75 wt % with respect to monomer. Both phases were mixed together and magnetically stirred during 10 minutes at 600 rpm. The resulting coarse initiatorless dispersion was then emulsified under sonification (Branson Sonifier 450 W/L) for 5 minutes at 90 % amplitude while maintaining the stirring.

ii. Costabilizer-free miniemulsions

The same procedure was applied with an organic phase without costabilizer (SA), and still without initiator.

iii. Surfactant-free miniemulsions

Pickering miniemulsions were prepared as described below. An organic phase was first prepared with 2 g of monomer (MMA or BA) with or without SA (0.08 g). The aqueous phase containing 0.2 g of Laponite RD dispersed in 20 g of water was obtained after vigorous magnetic stirring during to yield an optically transparent solution. Both phases were mixed. After magnetic stirring during 10 minutes at 600 rpm, sonification (Branson Sonifier 450 W/L) was applied for 5 minutes at 90 % amplitude while maintaining the stirring.

Miniemulsion photopolymerization

Photopolymerization of the different monomer miniemulsions was carried out in a 500 µm or 1 cm quartz rectangular cell (170 µL or 340 µL) without nitrogen bubbling. Note that stirring was not possible with the thinnest cuvettes. Irradiation was applied vertically through the polychromatic focused light of a medium-pressure Hg-Xe arc lamp (Hamamatsu L8252, 365 nm reflector, 200 W) coupled to a flexible light-guide. Such spot light source covers a broad continuous spectrum spanning from short-wavelength UV to infrared (185 – 2000 nm). Adverse effects from heat (IR radiation) were removed thanks to a 365 nm elliptical cold reflectors, at maximum power, radiometric measurements revealed respectively a total irradiance of 50 mW cm^{-2} below 300 nm (noted $I_{<300nm}$). See Figure S1 of the supplementary material for a schematical representation of the irradiation set-up.

Methods

Miniemulsions stability were measured by multiple-light scattering (MLS) to determine the reflectance of the miniemulsion during aging. Miniemulsions were filled in a 20 mL glass vial and analyzed 4 hours without stirring. MLS (Turbiscan MA, Formulaction) was used to determine the reflectance evolution which is directly related to the average droplet size and concentration evolution over time [6-8]. The photopolymerization kinetics were followed by Real Time–Fourier Transform Near Infrared (RT-FTNIR, Bruker IFS 66). The characteristic harmonic absorption modes of acrylate or vinyl compounds in the NIR range were exploited to determine monomer conversion. For acrylate and methacrylate-based monomers, the C-H combination band at 6169 cm^{-1} was used [9,10] while CH_2 second overtone band at 4484 cm^{-1} was chosen for VA [11]. Average miniemulsion droplet diameters (D_d) and latexes particle diameters (D_p) were obtained by Dynamic Light Scattering (DLS, Malvern Zetasizer Nano). Samples were diluted 100 times in distilled water before analysis. For monomer miniemulsions produced without costabilizer, a dilution-induced destabilization prevented determination of their average droplet size. Latexes obtained by surfactant-free photopolymerization were observed by TEM (Philips CM200 working at 200 kV) and SEM (Philips XL-30 FEG). Before analysis, latexes were diluted at 1 wt % in distilled water. Droplets of the resulted solutions were deposited on TEM grids or SEM stubs and then dried on air. Before analysis, the SEM samples were also sputtered with gold.

Results and Discussion

1. Initiator-free photopolymerization

The main issue related to the use of radical initiators is partial efficiency. On average only one half of the decomposing initiator molecules yield polymer chains. The rest may react differently and form by-products in significant amount, exceeding recommended toxicity thresholds. For instance, the oil-soluble

azobutyronitrile (AIBN) undergoes cage recombination to form tetramethylsuccinonitrile, a potentially toxic material [12]. Incorporated as chain end, the initiator fragments are also likely to change the film properties. For example, the ubiquitous water-soluble peroxydisulfate initiator generates sulfate ester chain ends promoting corrosion phenomena. In addition, initiator residues entrapped in the polymer can impart odor, color and decreased durability. The photosensitivity caused by photoinitiator residue is thus a major issue for outdoor applications [13,14].

UV-driven self-initiation of acrylate monomers has recently emerged as an elegant initiatorless approach to create latexes based on methyl methacrylate or butyl acrylate [15]. Mechanistically, the formation of initiating radicals via hydrogen transfer from a photogenerated diradical intermediate (Flory mechanism) was proposed as a likely explanation for experimentally observed spontaneous initiation under UV exposure [16]. However, it was still unclear whether such a method can be generalized to a wide range of radically polymerizable monomers: acrylate, methacrylate and vinyl propionate [17]. Figure 1 is the conversion-time plot for a series of initiator-free monomer miniemulsions with 30 wt % monomer content ($C_{monomer}$) stabilized by SDS (3.5 wt %) and SA (4 wt %). Typically, a spectroscopic cell containing the miniemulsion was exposed to the polychromatic spot light of a Hg-Xe lamp. For all the miniemulsions (MMA, VA, BA, MA, TCA, BMA and MMA/BA/AA) a complete conversion is achieved in less than 20 min exposure ($I_{<300nm}$ = 50 mW cm^{-2}). As a result, these conversion profiles show self-initiated miniemulsion photopolymerization as a versatile and effective method to polymerize a wide range of very conventional monomers. Discrepancies between reaction rates are the result of differences in monomer reactivity (affecting rate constants, but also the self-initiation mode and rate) and initial droplet size (40-210 nm) [18,19]. Despite this complex interplay, there is a general trend indicating that the rate-determining factor is the propagating radical reactivity. It seems that the reactivity increases in the order of increasing radical reactivity, following the order: acrylate > vinyl acetate > methacrylate. A drawback arising from photoinitiator removal is a continuous radical generation through spontaneous UV initiation, leading to broader molecular weight distribution. The number average molar mass (M_n) were in the range of 10000 - 200000 g mol^{-1}, and the polydispersity indices (PDI) were generally broad yet monomodal, with PDI typically in the range 2.5 - 4.

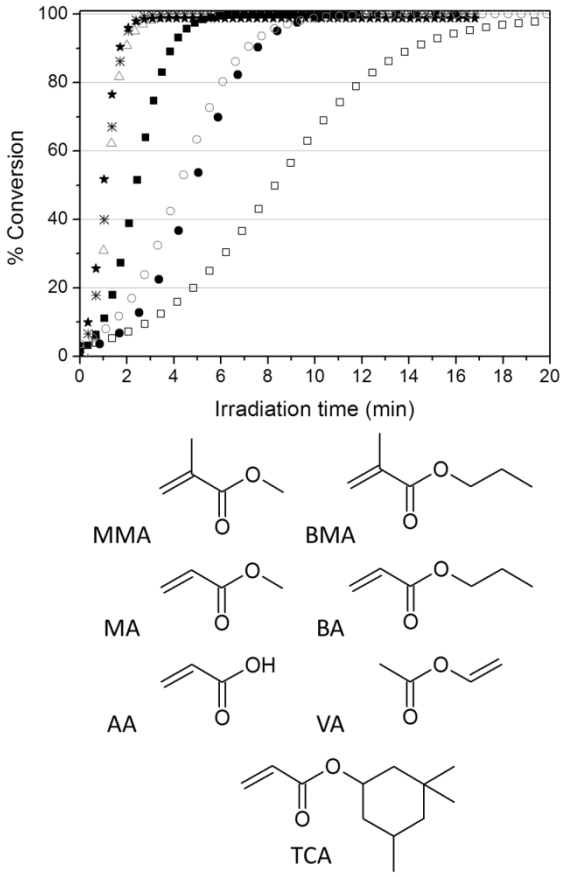


Figure 1. Conversion profiles of various miniemulsions photopolymerized by monomer self-initiation, the average droplet diameter determined by DLS is given in brackets: MMA (□, 77 nm), VA (■, 85 nm), BA (△, 100 nm), MA (★, 71 nm), TCA (✳, 210 nm), BMA (○, 112 nm) and MMA/BA/AA: 49.5:49.5:1 wt % (●, 75 nm). SA or HD = 4 wt % / $C_{monomer}$, SDS = 3.5 wt % / $C_{monomer}$, $C_{monomer}$ = 30 wt %. Optical path = 500 µm.

2. Costabilizer-free Photopolymerization

In contrast to initiator, the use of costabilizer is specific to miniemulsion (or microemulsion) preparation. Ideally highly hydrophobic and low molecular weight, the costabilizer is meant to slow the diffusional degradation, i.e. the transfer of monomer from the smaller droplets to the larger droplets [20,21]. Any removal of monomer from the droplet will cause indeed an increase in costabilizer volume concentration, thereby resulting in an increase in free energy. Hence, costabilizers are efficient in preventing or retarding Ostwald ripening, thus maintaining a relatively stable droplet size distribution [22]. Usually long-chain alkanes such as hexadecane are employed; but these compounds may cause plasticizing effect or leach out after film formation [23,24]. To circumvent these deleterious effects, reactive costabilizers such as SA [25] or preformed polymer [26,27] were often employed. Nevertheless, the best alternative would be to remove completely the costabilizer molecule.

To give insight into the role of the costabilizer, the stability of two model initiatorless monomer miniemulsions (MMA/BA/AA: 49.5:49.5:1 % wt) containing respectively 0.75 and 3.5 wt % SDS was first probed by monitoring the evolution of the diffuse reflectance *R* (the fraction of incident light scattered back by the sample) during four hours following the emulsification stage. As shown in Figure 2, the miniemulsions prepared with SA as costabilizer (full symbol) exhibit a steady profile ([SDS] = 0.75 wt %) or only slight variations ([SDS] = 3.5 wt %) during the two first hours, suggesting that an equilibrium is progressively reached between osmotic and Laplace pressure at this composition [28]. Consistent with these results, reliable and stable average droplet sizes of respectively 75 and 40 nm were obtained by DLS measurements. The slightly poorer stability of the smallest miniemulsion was assigned to the higher surfactant concentration that may facilitate the monomer transport through the aqueous phase, thus enhancing Ostwald ripening [29]. In each instance, the removal of costabilizer (open symbol) has a significant impact on the temporal evolution of *R*. The strong decrease in *R* provides indirect evidence that change in droplet size distribution has actually occurred. This clearly shows Ostwald ripening, by contrast to coalescence, as the main instability source in this system. Unlike the previous costabilized miniemulsions, a lower SDS concentration leads to stronger signs of destabilization in the first 20 minutes of ageing. After 3 hours, a phase separation eventually even takes place irrespective of the initial SDS concentration.

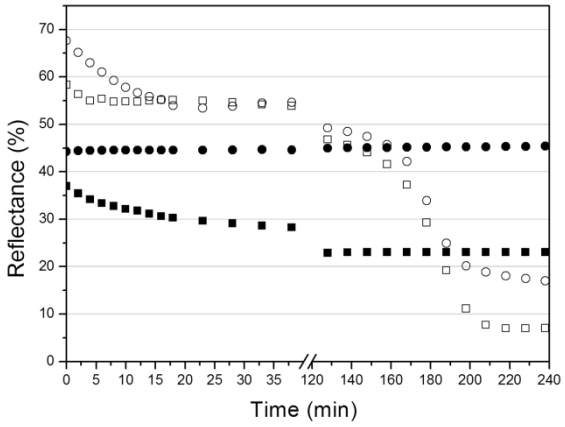


Figure 2. MMA/BA/AA (49.5:49.5:1 wt %) miniemulsion stability (Turbiscan® data) assessed by measuring the reflectance in the middle of the sample vial during 4 hours following the emulsification stage. The monomer miniemulsions are prepared with 3.5 wt % (square) or 0.75 wt % of SDS (circle). Full and open symbol are for miniemulsions produced with or without SA (4 wt % / $C_{monomer}$) respectively. $C_{monomer}$ = 30 wt %, no photoinitiator.

While these results illustrate the importance of thermodynamic equilibrium and costabilizer addition, they also highlight that monomer diffusion is a kinetic process that takes some times to occur. The underlying idea is that a very fast polymerization process promoting the in situ generation of water-insoluble polyacrylate polymer, in a minimum time and at sufficient concentration, may successfully hinder the extent

of Ostwald ripening in this system. In a thermally induced process, such objective has proved hard to achieve because diffusional degradation is enhanced by high temperature and the significant time needed to heat the dispersion [3]. By contrast, a photopolymerization process proceeding at ambient temperature, and immediately after monomer miniemulsion preparation, may promote the fast generation of initiating radicals, thus helping to achieve rapidly a high polymer volume fraction in the monomer droplets. Although polymer is not regarded as a good hydrophobic agent, its efficiency can be significantly enhanced when used at high volume fraction [30,31].

To examine the viability of a miniemulsion photopolymerization without costabilizer, the same two miniemulsions ([SDS] = 0.75 and 3.5 wt %) were photopolymerized upon varying the elapsed time between the end of emulsification and the beginning of irradiation, subsequently noted Δt. During Δt, the miniemulsions were left at ambient temperature without stirring. Lengthening Δt may increase the odds of destabilization by diffusional degradation, in particular for systems without costabilizer. Figure 3 shows the evolution of particle size obtained after 20 minutes of irradiation (a duration sufficient to obtain a full conversion irrespective of the droplet size, see Figure 1) for different values of Δt ranging 5 min and 1 h. As expected, in the case of the SA-based miniemulsions (full symbols), the particle diameter obtained are similar regardless of Δt (and display a good correspondence with the initial droplet size), which is consistent with a good metastability. This result supports SA as an effective costabilizer, able to make the polymerization course relatively insensitive to Δt. By contrast, the particle size evolution looks completely different when the costabilizer is removed (open symbols). In this case, the particle sizes match those of their costabilized counterparts provided Δt is small enough. For the 3.5 % SDS miniemulsion having a slower monomer diffusion rate (see backscattering data in Figure 2), the agreement is maintained until 20 min. By contrast, the 0.75 % SDS miniemulsion that degrades more rapidly must be irradiated more rapidly within the following 5 min to achieve a particle size similar to its costabilizer-based analogue. In the same way, Figure 4 compares the particle size distribution of these two SA-free latexes (open symbol) produced after different with that of a reference costabilized miniemulsion (full symbol). We clearly see that the particle size distribution broadening and shift towards higher sizes compared to the reference experiment occurs for smaller Δt values with the less stable miniemulsions.

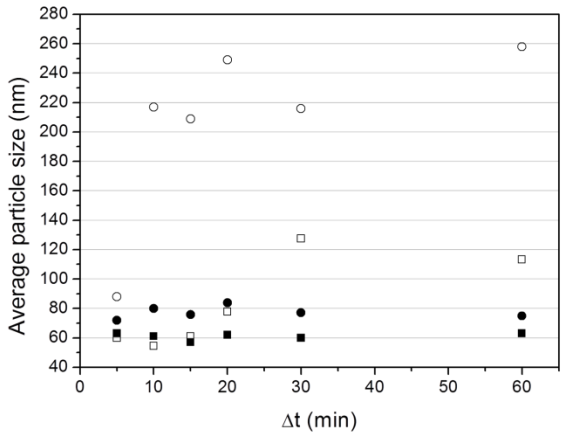


Figure 3. Influence of *Δt* (delay between emulsification and irradiation) on the average particle size of polymerized MMA/BA/AA miniemulsion in presence of 3.5 wt % (square) or 0.75 wt % (circle) SDS. Full and open symbol are for miniemulsions produced with or without SA (4 wt % / $C_{monomer}$) respectively. $C_{monomer}$ = 30 wt %, organic phase composition: MMA/BA/AA (49.5:49.5:1 wt %), irradiation time = 20 min, $I_{<300nm}$ = 50 mW cm^{-2}, conversion = 100 %, no photoinitiator.

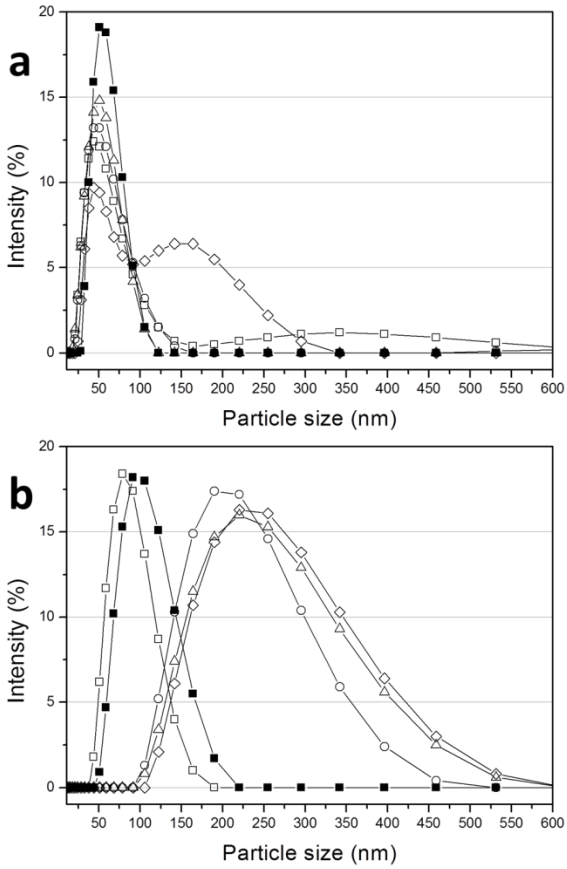


Figure 4 Evolution of the particle size distribution as a function of the elapsed time between the emulsification and the beginning of irradiation (*Δt*) for two costabilizer-free miniemulsions: **a**. [SDS] = 3.5 wt % and **b**. [SDS] = 0.75 wt %. *Δt* = 5 min (□), 10 min (○), 20 min (△) and 60 min (◇). For comparison,

a SA-based miniemulsion is shown with a full symbol. $C_{monomer}$ = 30 wt %, organic phase composition: MMA/BA/AA (49.5:49.5:1 wt %), irradiation time = 20 min, $I_{<300nm}$ = 50 mW cm^{-2}, no photoinitiator.

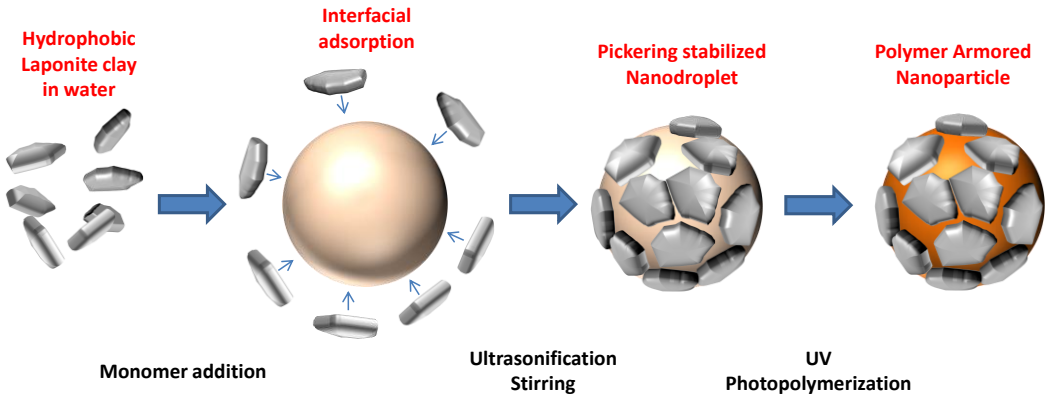
We have attempted to extend this concept of costabilizer-free miniemulsion photopolymerization to a range of different monomer compositions while keeping both the SDS concentration (0.75 wt % / $C_{monomer}$) and Δt value (5 min) constant. Table 1 compares, when possible, the difference of average particle size achieved with or without costabilizer as qualitative marker of destabilization. From these size data, it can be concluded that the feasibility of a costabilizer-free pathway requires a fast photoinduced polymerization, and more importantly a relatively slow diffusional degradation process. Using monomers yielding a low interfacial tension such as MMA, MA and VA, relatively small droplets (< 80 nm) can be generated. Indeed, it is well-known that the smaller the droplets, the more stable the miniemulsion towards settling and creaming [32]. In this case, the particle size distribution turns out to be slightly affected by the absence of costabilizer (see Figure S2). By contrast, the miniemulsions based on more hydrophobic monomers such as BA, BMA or TCA show a larger discrepancy, suggesting that significant destabilization has occurred. This result may seem surprising because Ostwald ripening rates is known to be reduced upon decreasing the solubility of the oil (monomer) in the continuous phase, thus improving the physical stability of the nanoemulsions. Our assumption is that the lower stability encountered with hydrophobic monomer miniemulsions may not only originate from Ostwald ripening, but also from coalescence. As compared to more hydrophilic monomer miniemulsions prepared under the same conditions, these miniemulsions are slightly larger in size ($\geq$ 100 nm), and are thus less susceptible to diffusional degradation than hydrophilic monomer-based miniemulsions. On the other hand, a higher packing density of surfactant is required to stabilize these more hydrophobic oil droplets. Therefore, the rate of droplet coalescence may be more significant because there is insufficient surfactant. A last intriguing feature of this system is the fact that faster polymerization rates were obtained systematically when removing the costabilizer (see irradiation time to reach full conversion in Table 1). The low N_p/N_d ratio observed in all the monomer systems suggests that only a fraction of monomer droplets are actually nucleated. Thus, one possible mechanism for particle growth is through monomer diffusion from non-nucleated droplets. Obviously, monomer transport will be enhanced for costabilizer-free monomer droplets compared to conventional costabilized miniemulsions, thus affording acceleration of the polymerization.

Table 1 Kinetic and colloidal properties obtained by initiatorless photopolymerization of various monomer miniemulsions with or without costabilizer. Δt = 5 min, $C_{monomer}$ = 30 wt %, [SDS] = 0.75 wt %, [Costabilizer] = 4 wt %.

Organic phase	Costabilizer	$t_{100\%}$ (min)	D_d (nm)	D_p (nm)	N_p/N_d
MMA	SA	20	77±5	99±5	0.37
MMA	-	17	-	92±5	-
BA	SA	6	100±5	124±5	0.41
BA	-	10	-	-	-
MA	SA	4	71±5	105±5	0.24
MA	-	3	-	104±5	-
BMA	SA	11	112±5	110±5	0.83
BMA	-	-	-	176±5	-
VA	HD	4	85±5	150±5	0.14
VA	-	2	-	78±5	-
TCA	SA	4	210±5	169±5	1.5
TCA	-	2	-	345±5	-

3. Surfactant-free photopolymerization

To preserve film properties, the concentration of surfactant is generally minimized in a latex formulation. Several studies reported indeed problems of toxicity [33], adhesion [34], wettability [35], morphology [36] originating from surfactant residue in the polymer film. Recently, two surfactant-free approaches have been developed involving initiator radicals imparting surface-active properties or adsorbed solid nanoparticles. Obviously, this latter route, often referred as Pickering polymerization, appears the better option since our ultimate goal remains to remove the surfactant. Radical polymerization of Pickering stabilized miniemulsions has been reported by a number of authors including notably clay particles [37] as stabilizer such as Laponite [38] or Montmorillonite [39] but only through a thermal process. Our original photoinduced Pickering polymerizations were conducted with a MMA or BA organic phase devoid of initiator but including a costabilizer. In the aqueous phase, SDS was replaced by Laponite clay to induce a Pickering stabilization of the monomer miniemulsion [40]. Solid particles of Laponite consisting of 25 - 35 nm diameter disks with a thickness of 1 nm [41,40] are advantageously transparent to UV light ($\lambda > 200$ nm) and poorly scattering, thereby having limited impact on light penetration. In addition, Laponite clay may improve mechanical and thermal properties of many polymeric films. Scheme 1 summarizes the basic preparative steps leading to armored nanolatex via photopolymerization.



Scheme 1. Armored nanoparticles synthetized by Pickering miniemulsion photopolymerization.

As reported in the literature [40], the clay platelets were first dispersed in the aqueous phase at a concentration of 1 wt % to avoid the formation of gel before addition of the monomer phase. Pickering-stabilized monomer miniemulsions based on BA (D_d = 266 nm) and MMA (D_d = 271 nm) were successfully prepared. Reflectance measurements showed that the stability is maintained for 4 hours without creaming or sedimentation (Figure S3). It is assumed that the solid particles adhere spontaneously to droplets' surface to ensure a colloidal stability. UV irradiation during 30 min yielded fully polymerized polyBA (D_p = 210 nm) and polyMMA (D_p = 248 nm) latexes. The morphology of the armored polymer particles was confirmed by TEM and SEM characterization (Figure 6). Mostly exfoliated platelets are seen in the TEM picture exhibiting a high concentration of adsorbed particles at the particle surface. However, excess of Laponite is also visible, suggesting the need to find an optimal clay concentration. In addition, SEM observation shows the presence of adsorbed platelets distorting the spherical morphology of the polymer particles. In a last proof of concept experiment, a Laponite-stabilized MMA miniemulsion was produced without costabilizer and initiator. In this case, larger latexes with average diameter of 357 nm were produced that revealed by a similar morphology through electron microscopy characterization (Figure 7).

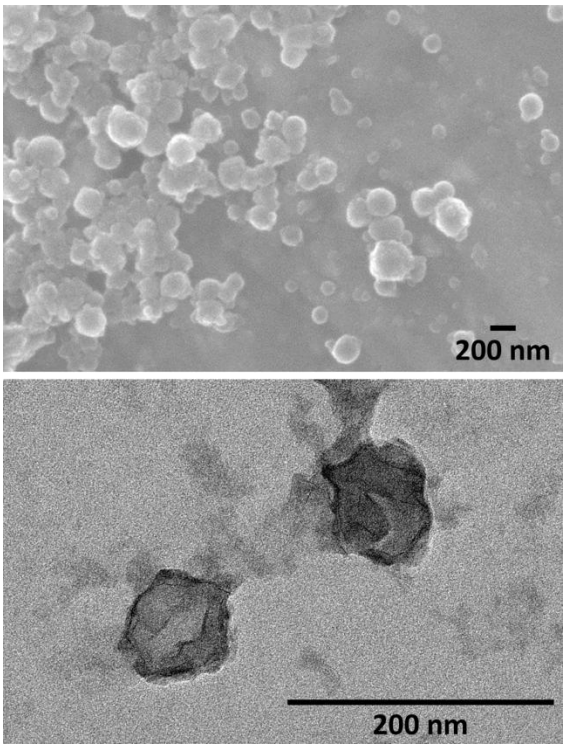


Figure 6. SEM (top) and TEM (bottom) images of armored particles produced by Pickering-stabilized MMA miniemulsion photopolymerization without initiator. $C_{monomer}$ = 9 wt %, [SA] = 4 wt %, [Laponite RD] = 1.43 wt %, irradiation time = 30 min, $I_{<300nm}$ = 50 mW cm^{-2}.

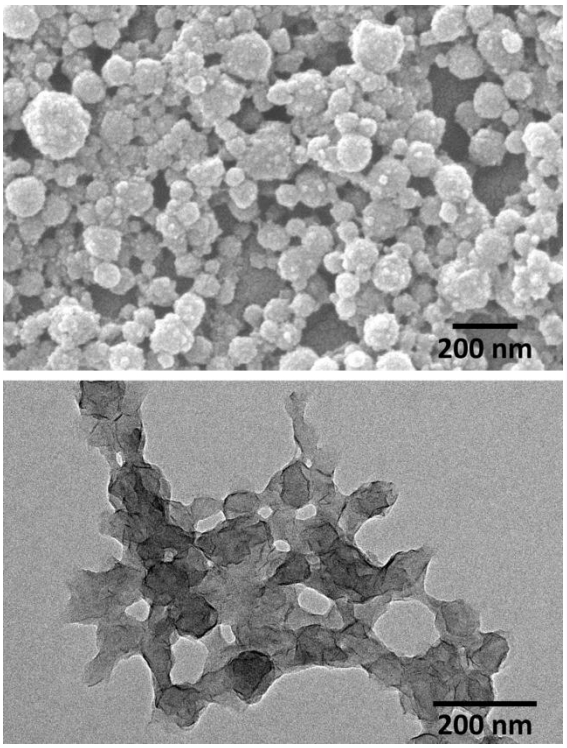


Figure 7. SEM (top) and TEM (bottom) pictures of armored particles produced by Pickering-stabilized MMA miniemulsion photopolymerization without initiator and costabilizer. $C_{monomer}$ = 9 wt %, [Laponite RD] = 1.43 wt %, irradiation time = 30 min, $I_{<300nm}$ = 50 mW cm^{-2}.

Conclusion

We showed that the elimination of many components generally judged to be essential in a miniemulsion polymerization process became possible via a photoinduced radical polymerization. To get rid of the initiator, a short wavelengths irradiation (< 300 nm) emitted by a conventional medium-pressure Hg lamp was found to be sufficient to self-initiate a wide range of acrylate, methacrylate and vinyl monomer miniemulsions without particular restriction in terms of structure. Secondly, a fast photoinduced polymerization achievable at room temperature enabled to polymerize costabilizer-free miniemulsions without significant destabilization process. For monomer miniemulsions exhibiting a relatively slow diffusion rate, equivalent particle sizes were thus obtained compared to homologues containing a costabilizer such as SA or HD. To use the polymer formed in situ as costabilizer is advantageous because it obviates the dissolution of an external preformed polymer in the organic monomer phase, resulting generally in a viscosity increase and the impairment of droplet breakup efficiency. Finally, we proved that a costabilizer- and initiator-free photopolymerization can be combined with Pickering-stabilized miniemulsion in a way to avoid the use of surfactant.

These studies must be pursued at larger scale than spectroscopic cells to show their viability in photoreactors which are well-known and used in various industrial technologies including water purification or preparative organic chemistry. In addition, the systematic comparison of film properties with those of regular latex comprising surfactant, costabilizer and initiators is worth investigating too. These two steps are essential in the assessment of the new technology for industrial applications.

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