Novel technologies and chemistries for waterborne coatings

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Introduction

Over the past decade, we have developed an integrated approach to the study of novel materials, methods, and processes for the production of waterborne coatings. This approach is based on a combination of conventional and free radical chemistries, micro-, mini-, and macro-emulsion polymerization, and different reactor and dispersion technologies. In this article, we will show that an integrated approach is one of the more effective ways of developing synergies for the production of waterborne-coating materials. Examples will include approaches to develop high-solids content products, translucent latexes, self-assembling materials, organic and inorganic hybrid latexes, as well as economic means of generating polymerizable miniemulsions for the implementation of these advances in a commercially feasible manner.

Hybrid and composite coatings: inorganically loaded films

The incorporation of inorganic colloids in polymer particles during their synthesis allows us to enhance their properties. Typically their synthesis requires the presence of surfactant molecules for the colloidal stability of the latex. However, there is an increasing

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interest in removing this type of stabilizer for a number of environmental and quality-related reasons. One possibility for the replacement of conventional stabilizers is the use of cerium oxide nanoparticles (CeO_2). We have developed a strategy based on the use of RAFT chemistry, and demonstrated that the incorporation of CeO_2 nanoparticles in surfactant-free polymer films opens up new opportunities, particularly in the field of anti-UV films with improved mechanical properties.

Conventional free-radical polymerization

Nowadays, researchers are developing polymer films with new properties by combining organic matter or polymers with inorganic colloids (nanoparticles, fibers, nanotubes, etc.). One way to prepare such composite films includes the incorporation of inorganic colloids in polymer particles during their synthesis, thereby creating nanocomposite latexes. Upon film formation, those colloids spread uniformly, requiring smaller quantities of both polymer and the inorganic modifier, and thereby enhancing product properties at the lowest possible cost. Those latexes are made through polymerization processes in dispersed aqueous media such as emulsion polymerization.[1] This has been extensively investigated in the case of materials such as silica particles and clays, and it has been demonstrated that there are benefits in terms of improved mechanical properties.[2–4] Clearly, different improvements in terms of material properties could be obtained by expanding our research to different inorganic colloids.

The production of these materials often requires the presence of surfactant molecules for the colloidal stability of the latex. However, there is an increasing interest in eliminating conventional surfactants and stabilizers in certain cases, not only because they can occasionally have a deleterious effect on film properties (surfactant migration in materials leading to the

degradation of their adhesive and mechanical properties), but also due to environmental concerns (treatment of aqueous effluents, toxicity). One alternative to the use of conventional surfactants is Pickering stabilization. With this method, particles are stabilized by inorganic particles located at, or very near, the water/oil interface. One such material is cerium oxide (CeO_2). In addition to being able to provide some measure of stability to colloidal systems, CeO_2 nanoparticles also display both a strong absorption to UV light and a high scratch resistance, making them useful candidates in the development of hybrid films.[5–7]

Until now only limited studies have been conducted on those particles. They have been mainly combined with polymerization techniques in miniemulsion and conventional emulsion, both using significant amounts of surfactant.[8] Their incorporation into polymer films free of molecular surfactant opens up new opportunities in the field of coatings and in particular would allow the formation of anti-UV films with improved mechanical properties.

Our goal was to develop a process that could be used for the production of film-forming latex particles incorporating CeO_2 in the absence of any molecular surfactant. CeO_2 nanoparticles are dense, cationically charged, nanocrystalline particles with a strong tendency towards aggregation and sedimentation, making their compatibilization with a polymer matrix quite challenging. Several strategies have been explored in our group. The first one relies on the use of the CeO_2 nanoparticles as solid stabilizers for miniemulsion polymerization.[9] The key feature is the use of an auxiliary comonomer in order to increase the chemical affinity of cerium oxide with the monomer droplets and subsequent polymer particles. Since carboxylic groups strongly interact with the surface of CeO_2, methacrylic acid (MAA) was chosen as this comonomer. Stable methyl methacrylate (MMA) miniemulsions were successfully prepared using a fixed MAA concentration of 1.9 μmol/m^2 based on CeO_2 and various CeO_2 contents. The use of MAA as a comonomer proved to be crucial to induce the interaction between the monomer droplets of MMA and the CeO_2 nanoparticles. Indeed only the miniemulsions prepared in the presence of both CeO_2 and MAA were stable affording nanometer-size monomer droplets.

In a different vein, the formation of stable composite latex particles armored with CeO_2 was next investigated by polymerizing the Pickering-stabilized MMA miniemulsions using different amounts of CeO_2, ranging from 20 to 35 wt%, and 2,2′-azo-bis-isobutyramidine dihydrochloride (AIBA) as cationic initiator. In all cases, partial coalescence at low conversion (<10%) was observed as evidenced by the decrease in the ratio of the number of particles to the number of droplets. In addition, the conversion was always limited to ca. 85%, concomitant with a loss of stability of the latex for CeO_2 contents lower than 35 wt%. These stability issues were likely related to the screening of the cationic charges present on CeO_2

nanoparticles upon polymerization. TEM images showed mostly spherical particles with a diameter ranging from 100 to 400 nm and homogeneously covered with CeO_2 (c.f. Fig. 1). In addition, a buckled morphology was observed for particles larger than 200 nm. This further supports the idea that there is a presence of residual monomer at the end of the polymerization.

The influence of the monomer composition was investigated using BA, either alone or in combination with MMA. All of these experiments were run at 35 wt% of CeO_2. Stable monomer emulsions were obtained in every case, showing the versatile use of CeO_2 as Pickering stabilizer for droplets of various hydrophobic monomers. Nevertheless, as one would expect, the droplet size increased with the hydrophobicity of the oil phase. This increase in size can be attributed to the increased interfacial tension with a more hydrophobic monomer phase, as well as to influence of the wettability of the solid stabilizer. In all cases, the obtained latexes showed no sign of destabilization, suggesting that the hydrophobic/hydrophilic nature of the monomer(s) is an important parameter affecting the stabilizing capability of CeO_2. In conclusion, the polymerization of Pickering miniemulsions stabilized by CeO_2 nanoparticles proved to be an efficient strategy to form armored composite latex particles which may find applications in coating technology.

Controlled free-radical polymerization

A different strategy was used to explore the potential of controlled radical polymerization, more specifically of the reversible addition-fragmentation chain transfer (RAFT) technique[10] to encapsulate CeO_2 particles within poly(methyl methacrylate-*co*-butyl acrylate) latex particles. This approach has been used previously for the encapsulation of TiO_2[11] or Gibbsite[12] platelets, and employs hydrophilic living copolymers synthesized
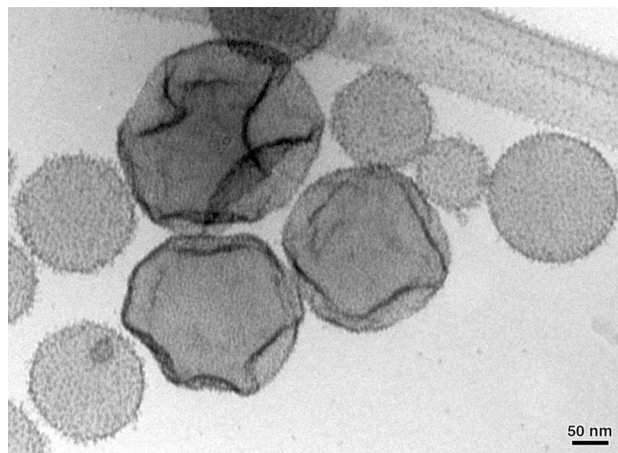

Fig. 1: TEM image of a quench-frozen suspension of PMMA particles stabilized by 35 wt% CeO_2 nanoparticles using methacrylic acid as a comonomer

by RAFT (referred to as macroRAFT agents) which are adsorbed onto the inorganic particles and then reactivated to polymerize a hydrophobic monomer under starved-feed conditions. The idea is that the second polymerization stage can be used to form an encapsulating shell. The underpinning idea is to favor the growth of the hydrophobic polymer from the surface of the inorganic particles. The macroRAFT agent not only contributes to the colloidal stability of the system (before the polymerization for the aqueous dispersion of the inorganic particles, and during the emulsion polymerization) but also favors the encapsulation by establishing a strong covalent link between the inorganic particles and the polymer.

Different homo- and copolymers based on (meth)acrylic acid (and *n*-butyl (meth)acrylate) were first synthesized in solution using trithiocarbonate compounds as RAFT agent (recall that the carboxylic comonomers can be used to alter the surface properties of the cerium oxide). After adsorption of the macroRAFT agents onto their surface, CeO_2 nanoparticles were engaged in the emulsion polymerization of methyl methacrylate and/or *n*-butyl acrylate in order to form the encapsulating shell. The influence of the composition, length, and concentration of the macroRAFT agent as well as that of the monomer mixture used in the emulsion step were investigated. Figure 2 shows the composite latex particles obtained using poly(BA-*co*-AA)-modified CeO_2 nanoparticles in the emulsion copolymerization of an MMA/BA mixture (80/20 by weight).[13]

These two strategies open new perspectives for a safe and efficient incorporation of CeO_2 nanoparticles into film-forming formulations in the absence of molecular surfactant. The resulting composite latexes could find applications in the field of waterborne UV and/or scratch-resistant coatings.
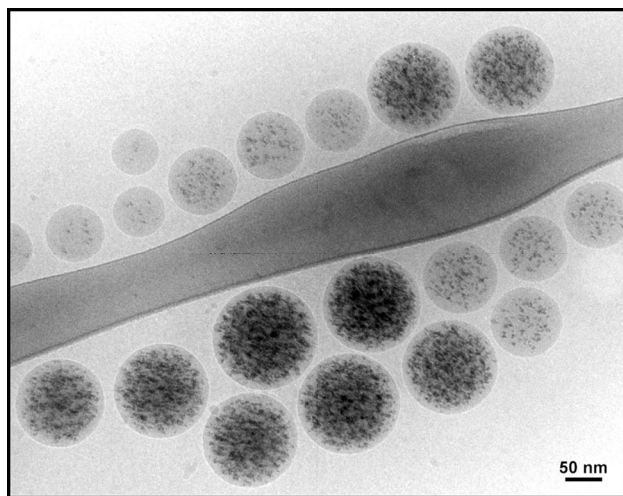
Fig. 2: Cryo-TEM image of the composite latex particles obtained using poly(BA-*co*-AA) as macroRAFT agent in the emulsion polymerization of MMA/BA mixture (80/20 by weight)

Self-assembly and morphology control

In addition to conventional free-radical processes and chemistries, we have been exploring the use of RAFT and nitroxide mediated polymerization (NMP) polymerization methods to investigate the control of morphologies. These methods can be used to make structured micelles, to promote self-assembly of waterborne objects with novel morphologies such as fibers, cylinders or vesicles, or even cholesterol-based liquid crystal structures.

Since the advent of controlled/living free-radical polymerization (CRP) based on reversible deactivation of the propagating radicals, the design of complex macromolecules is much simpler and a myriad of macromolecular buildings have been made possible under very simple synthetic conditions. Considered as one of the most developed industrial tools to produce polymers under free-radical conditions, aqueous emulsion polymerization accordingly witnessed considerable efforts in directly transposing CRP to dispersed polymerization systems. However, despite the very nice research studies that have been carried out in this field,[14–16] the obtained latexes did not meet the expectations originally put in this transposition. Indeed, control over the chain length and over a large range of macromolecular architectures was not possible mainly because of stability issues due to the presence of monomer droplets and the partitioning of the controlling molecules among the different phases.

An alternative based on the use of controlling macromolecules soluble in the water phase seems, however, to outline interesting features. Indeed, those macromolecules obtained by CRP performed in water can be reactivated to form block copolymers after the polymerization of a second batch of monomer. When dissolved in water, their reactivation in the presence of a hydrophobic monomer may lead, under certain conditions, to simultaneous chain growth and self-assembly of the resulting amphiphilic block copolymer into nano-objects that can be assimilated to latex particles. Indeed, beyond a critical molar mass of the growing hydrophobic block, the formed amphiphilic block copolymer chains self-assemble into nanoparticles[17] (Fig. 3), where the chain extension and concomitant particle growth continue within the hydrophobic particle core until complete monomer consumption. The final product is thus an in situ-created suspension of self-assembled nano-objects. Although these nano-objects may differ from a proper latex that can be obtained under conventional emulsion polymerization conditions (size, molar mass of the polymer chains…), the size and shell density can be governed by the hydrophobic/hydrophilic ratio and the structure, molar mass, and initial concentration of the water-soluble precursor. Due to the versatility of the controlled radical polymerization, this strategy allows us to define and functionalize perfectly both the outer hydrophilic shell and the inner hydrophobic core.

This method which follows a *polymerization-induced self-assembly mechanism* allows the development of
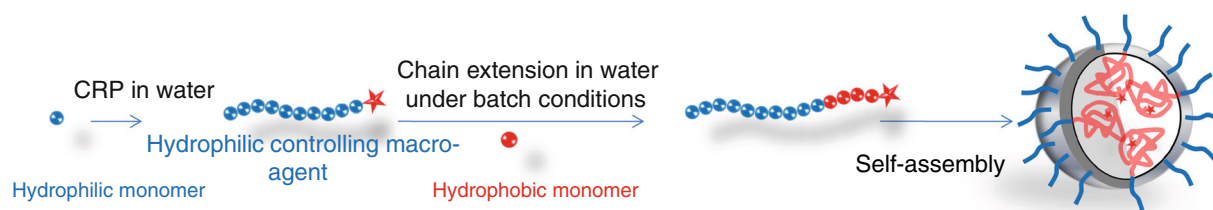
Fig. 3: Elaboration of nanoparticles by in situ self-assembly of amphiphilic block copolymers

self-stabilized particles in the complete absence of surfactant and under experimental conditions that are similar to conventional emulsion polymerization (high-solids content, temperature…).[17] The pioneering work in this area was depicted by Ferguson et al.[18] who employed a very short-poly(acrylic acid) (PAA)-living polymer obtained by one of the most powerful CRP techniques: the RAFT process. This PAA macroRAFT was chain extended with a hydrophobic monomer. This monomer was slowly fed into the reactor to avoid the formation of droplets and to form an amphiphilic block copolymer able to self-assemble into frozen micelles. This method was the first example of successful surfactant-free emulsion polymerization, based on self-assembled amphiphilic block copolymers formed in situ, leading to very small particles ($D < 100$ nm) self-stabilized by the hydrophilic PAA block of the constituting block copolymers. From the self-assembly point of view, it indeed allowed for the first time to consider the formation of spherical nano-objects under non-conventional conditions (high concentration of block copolymers, high final solids contents, water as only solvent/nonsolvent). Our group invested a great deal of energy in simplifying as much as possible the way to implement such systems. Preformed macromolecular hydrophilic RAFT agents were further employed[17] and we achieved an additional step forward by performing the particle synthesis in a one-pot process.

In this frame, we first employed RAFT polymerization to synthesize the hydrophilic RAFT-controlling macroagent directly in water starting from a hydrosoluble monomer.[19,20] We managed to conduct up to complete conversion and under very well controlled conditions the RAFT homopolymerizations of acrylic acid (AA)[19] and methacrylic acid (MAA)[19,21] and the copolymerization of MAA with methyl ether poly(ethylene glycol)methacrylate (PEOMA) (19 ethylene oxide units) under acidic pH (<4). In the same reactor, styrene (S) was added and the batch emulsion polymerization was further successfully conducted in the presence of the formed macroRAFT without any purification. From a pure synthetic point of view, this polymerization-induced self-assembly process was shown to be a simple and efficient tool to produce PAA-*b*-PS, PMAA-*b*-PS, and P(MAA-*co*-PEOMA)-*b*-PS amphiphilic block copolymers more efficiently than a strategy that would employ organic solvents. In all the cases, these reactions led to very small spherical

block copolymer nanoparticles that were further studied for their colloidal properties.[20,21]

In a way similar to the post-polymerization self-assembling of amphiphilic block copolymers at very low concentrations (<1% wt), this process should allow one to reach various morphologies such as vesicles, elongated micelles, and nanofibers, however, directly via CRP in aqueous emulsion at high concentrations (>30% wt).[17] The previous conditions were thus slightly modified to further study the possibility of achieving these morphologies by varying the pH and the targeted PS polymerization degree (Fig. 4). At pH 5, using P(MAA-*co*-PEOMA) as hydrophilic macro-RAFT and styrene as hydrophobic monomer, the transition from spheres to fibers to vesicles was observed. This transition was found to be the direct consequence of the mass ratio of the hydrophilic and hydrophobic blocks upon polystyrene chain growth and depending on the target final degree of polymerization of the PS block. This indicated that the conformation and hydrophilicity of the stabilizing block (segregation strength) is also an important parameter.

Methyl methacrylate (MMA) was further employed as hydrophobic monomer under different pH conditions with the same P(MAA-*co*-PEOMA) macro-RAFT agent. The systems led to spherical micelles, fibers, and then vesicles when the molar mass of the hydrophobic block was increased, this irrespective of the pH of the aqueous phase contrary to the case of styrene (Fig. 5; transition not observed at pH 3.5). The results were interpreted on the basis of an influence of the polymerization kinetics, especially in the early stage of the reaction in the aqueous phase.[22]

Eventually, NMP was employed in the same strategy by using a preformed copolymer of MAA and 4-styrene sulfonate (SS). This copolymer was obtained by NMP carried out in DMSO in the presence of BlocBuilder as controlling agent. The small percentage (less than 10%) of SS employed for the starting monomer composition ensured the control growth of the chains and allowed for the generation of well-defined P(MAA-*co*-SS) macroalkoxyamines that can further be used to initiate the polymerization of MMA in water. Again, during this second step, a small fraction of a styrenic monomer (here styrene) was required to ensure the control of the hydrophobic block. After a sufficient molar mass of the P(MMA-*co*-S) was reached, the resulting amphiphilic P(MAA-*co*-SS)-
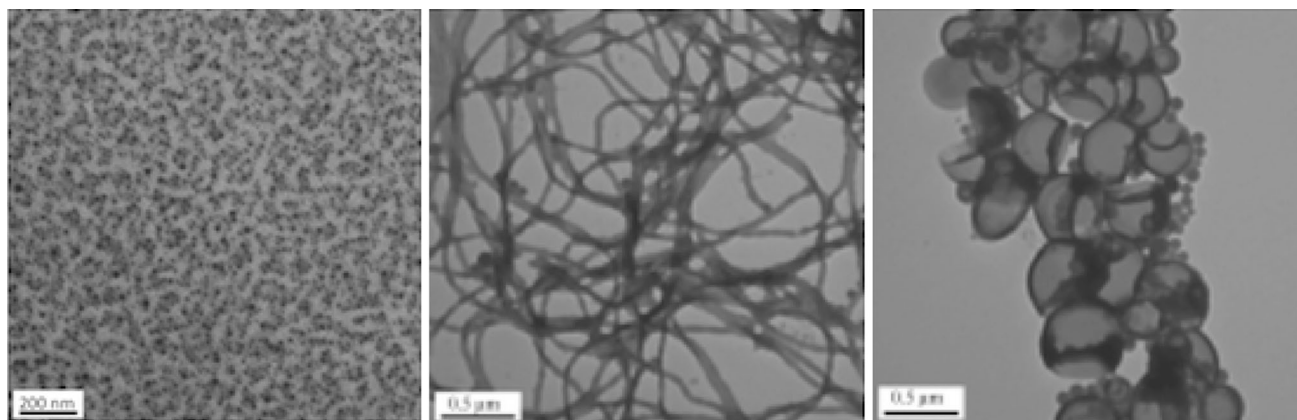
Fig. 4: TEM images, dispersion pictures of the P(MAA-*co*-PEOMA)-*b*-PS block copolymers obtained via RAFT-mediated polymerization at pH 5
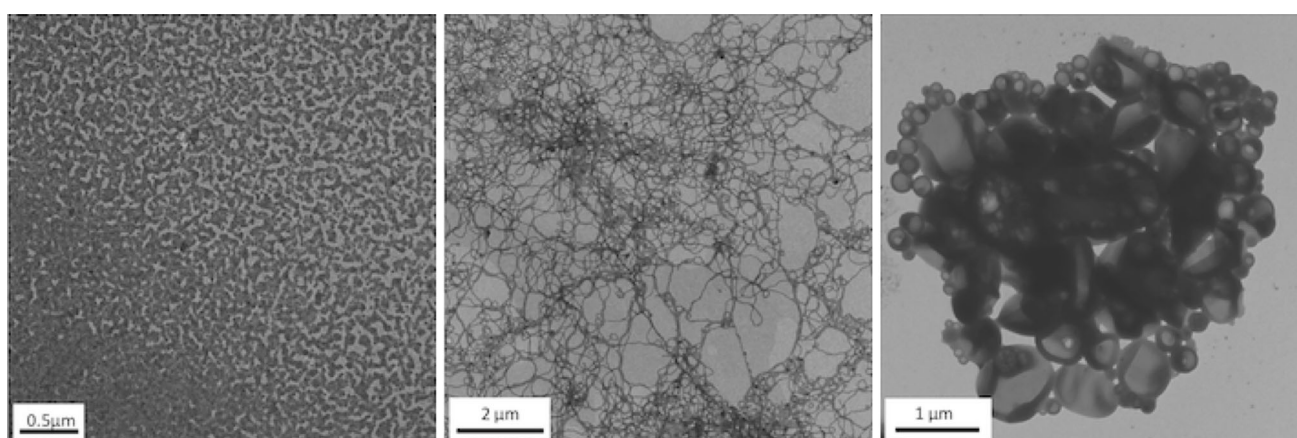

Fig. 5: TEM images, dispersion pictures of the P(MAA-*co*-PEOMA)-*b*-PMMA block copolymers obtained via RAFT-mediated polymerization at pH 3.5

b-P(MMA-*co*-S) block copolymers self-assemble into various morphologies (spheres, vesicles, micelles) depending on the final targeted molar mass of P(MMA-*co*-S).[23]

Translucent latexes by controlled microemulsion polymerization

Microemulsion polymerization has been demonstrated to be a promising technique for the synthesis of nanolatexes. However, microemulsion polymerization commonly suffers from the high amounts of emulsifier that are required to obtain the initial thermodynamically stable mixture of monomer in water. After polymerization, only a small fraction of the available amount of emulsifier is required for maintaining the colloidal stability of the synthesized nanolatex. Consequently, polymer nanolatexes synthesized by microemulsion polymerization typically consist of polymer colloids co-existing with emulsifier micelles. In general,

the emulsifier micelles outnumber the polymer colloids by 1000:1, which illustrates the poor nucleation efficiency in microemulsion polymerization. Furthermore, as the emulsifier often acts as a contaminant in many of the intended applications of nanolatexes (especially in the biomedical area), the commercial implementation of microemulsion polymerization remains limited. Increasing the nucleation efficiency therefore remains a re-occurring topic in microemulsion polymerization.[24–26]

We have reported on a new methodology for the synthesis of nanolatexes from emulsion polymerization using an extremely hydrophobic cobalt(II) complex,[27] i.e., bis[(difluoronoryl)-diphenylglyoximato]cobalt(II) (COPhBF). In addition to molecular weight control, catalytic chain transfer polymerization (CCTP) can also be used in dispersed phase free-radical polymerization for its potential to enhance the particle nucleation efficiency.[27] CCTP is a controlled radical polymerization technique that utilizes certain low-spin cobalt(II) complexes like COPhBF for the synthesis of polymer of predetermined molecular weight and a

polydispersity index of approximately 2. Molecular weight control in CCTP is achieved by transferring the radical activity of a propagating chain, via the active cobalt(II) complex, to a monomer molecule. This generates monomeric radicals which have the tendency to desorb to the aqueous phase, thereby lowering the growth rate of the polymer particles while promoting the nucleation of new polymer particles.[28] Consequently, more polymer particles can be nucleated which promotes a more efficient usage of the available amount of emulsifier.

Since we were able to demonstrate that CCTP can be successfully implemented for the microemulsion polymerization for molecular weight control,[29] we thought that it could also be exploited for the synthesis of even smaller colloids than possible with CCTP in emulsion polymerization (i.e., <20 nm).[30] We compared the polymerization of several different monomers: MMA, ethyl methacrylate (EMA), styrene (S), butyl methacrylate (BMA), and ethyl hexyl methacrylate (EHMA). In the absence of COPhBF, the microemulsion polymerizations of MMA, EMA, S, BMA, and EHMA resulted in colloidally stable, monodisperse latexes containing polymer particles of approximately 40 nm. Furthermore, the particle-size distributions (PSDs) were fairly narrow with polydispersity indexes (PDI) ≤ 1.2. As the concentration of COPhBF increases, the average particle diameter $d_{p(N)}$ decreases for the microemulsion polymerizations of S, BMA, and EHMA. For example, the $d_{p(N)}$ of the poly(BMA) nanolatexes decreased from 40.3 nm to 13.1 and 4.6 nm in the presence of 0.0, 2.0, and 10.0 ppm COPhBF, respectively.

Optical transparency is a common characteristic of nanolatexes. The transmittance of the undiluted nanolatexes of PMMA made using this technique (as measured by UV–Vis spectroscopy) is presented in Fig. 6, and the latexes themselves in Fig. 7. The latexes synthesized in the absence of COPhBF display a fair amount of transmittance over the recorded wavelength range of 400–800 nm. This can be attributed to the relatively small average particle diameters (19 nm ≤ $d_{p(V)}$ ≤ 50 nm).

Our results[27,29,30] have led us to conclude that nanolatexes can be successfully synthesized using CCTP in microemulsion polymerization. However, for the more hydrophilic monomers (i.e., MMA and EMA) CCTP proved less (or not) effective when compared to the more hydrophobic monomers (i.e., S, BMA, and EHMA). In microemulsion polymerization the water-solubility of the monomer proves to be key parameter governing the synthesis of the nanolatexes. Furthermore, the synthesis of nanolatexes is dependent on two parameters: (i) the water-solubility of the monomer and (ii) the performance of the monomer in CCTP. For relatively hydrophilic monomers the relatively high aqueous phase monomer concentration in combination with significant rates of radical desorption result in a shift from predominantly micellar nucleation to more homogeneous nucleation and subsequently increased particle flocculation. For more hydrophobic monomers micellar nucleation remains the primary
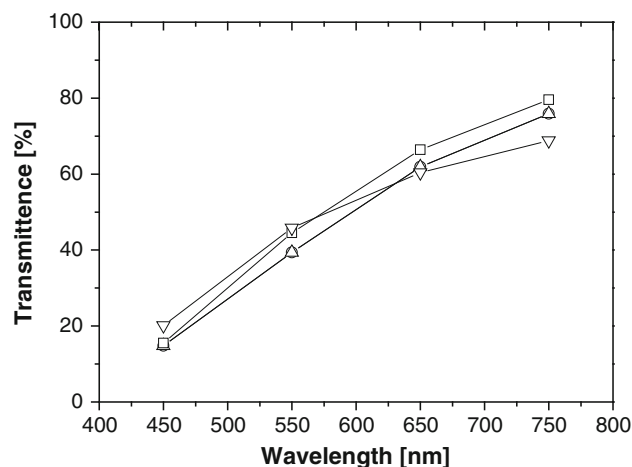

Fig. 6: Transmittance of the micro-poly(methyl methacrylate) latexes with varying solids contents. Solids content: △, 10 w/w%; ○, 20 w/w%; □, 30 w/w%; and ▽, 40 w/w%
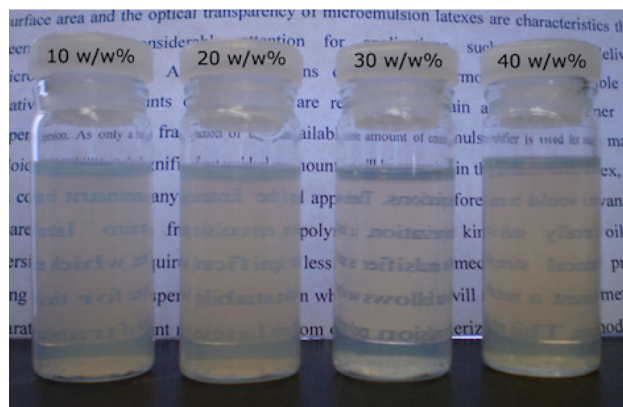

Fig. 7: Optical appearance of the microlatexes with varying solids contents

nucleation mechanism, which is a prerequisite for the formation of nanolatexes.

Processes for the production of miniemulsions

As mentioned above, miniemulsions have recaptured the attention of both academics and industrial producers of polymers because of the ease with which one can incorporate a wide range of organic and inorganic materials into the final polymeric product. Monomer-in-water miniemulsions are typically generated by the direct emulsification of monomer (referred to as the oil phase, O) and water (W), followed by subsequent miniemulsification using some form of mechanical homogenization to reduce the droplet size to the miniemulsion range (~50–500 nm). This can be done using some form of intense mixing such as rotor stator mixers, high pressure homogenizers, or static mixers.[31,32] If the surfactant

system is not optimized, El-Jaby et al.[31] showed that it could take well over 1 h to create polymerizable mini-emulsions using a rotor stator mixer. A reduction of this emulsification time could lead to more commercially useful processes. There are different ways of achieving this goal, and we will rapidly look at two of them here: the use of in situ surfactants to improve the efficiency of the stabilization of droplet interfaces; and catastrophic phase inversion to use ''thermodynamics'' to do the emulsification.

In situ surfactants

Typically, miniemulsification processes lose significant amounts of energy to heat, reversible rupture, and droplet coalescence. As a consequence, only a small fraction of the mechanical energy is effectively used for droplet-size reduction (an exception to this is the use of static mixers, which appear to be less prone to heat losses). produce tremendous amounts of heat because of the way they generate droplets (cavitation, followed by implosion of the microbubbles that can lead to local temperatures on the order of several thousand K for fractions of a second). This is not feasible onCertain techniques, like ultrasonication, an industrial scale, so we have begun to look to other techniques, and in particular the use of static mixers.[31,33,34] An earlier study from our group showed that significant amounts of the energy input to the emulsification step is used very inefficiently; over 95% of energy used to form droplets is lost when the droplets coalescence. Therefore, the reduction of droplet coalescence (or faster stabilization) is a key issue.

Regardless of the mechanical device used for homogenization, the surfactant will play two related roles in the process: reduction of interfacial tension, which allows us to divide the oil phase up into small droplets; and stabilization of the newly generated oil–water interface. It has been shown that the surface tension equilibrates within 1–10 times the characteristic diffusion times of surfactant in solution, which means that adsorption of the surfactant is the rate controlling step in the stabilization process.[35] A certain amount of droplet coalescence is inevitable in a mixed system, as stability of the new surfaces is highly dependent on the rate of surfactant transport within the emulsion and adsorption kinetics of the surfactant on the formed droplets. After repeated breakage cycles, an equilibrium between droplet breakage and coalescence will be established and the system will reach a minimum droplet size once the surfactant has had enough time to diffuse to the surface. The homogenization process could therefore be improved by using a surfactant that instantaneously stabilizes newly formed surfaces, thus reducing the time to reach a stable droplet size.

We demonstrated the efficiency and robustness of the in situ generation of potassium stearate (KSA) for the production and polymerization of miniemulsion droplets. We first compared the performance of in situ generated KSA (steric acid in the oil phase, KOH in the water phase) to its preformed equivalent (i.e., purchased as KSA and dissolved directly in the reaction medium) in terms of homogenization time using a rotor–stator. We also investigated the effect of varying process parameters, such as surfactant concentration and solids content, on the droplet size/stability and the evolution of particle size.

As an example, we ran two emulsifications using the rotor–stator and formulations FM 1 and 2 (Fig. 8). Formulation FM 1 contained stearic acid in the organic phase and potassium hydroxide in the aqueous phase; if complete neutralization is attained, this would produce 9.0 mmol of potassium stearate. Formulation FM 2 contained 9.0 mmol of the preformed equivalent potassium stearate.

Figure 8 shows that droplets prepared with preformed KSA decreased in size with homogenization time, eventually reaching equilibrium in approximately 40 min. Droplets prepared with in situ KSA reached a similar droplet size in approximately half the time (20 min), supporting the idea that in situ surfactants stabilize droplets faster than preformed surfactants. In other words, during homogenization, the neutralization of surfactant at the interface stabilizes newly formed surfaces faster compared with transport and adsorption of a preformed surfactant. This in turn reduces the amount of coalescence during homogenization and therefore the time to reach a minimum stable droplet size.

Miniemulsions were subsequently polymerized using KPS. In all cases, conversion reached 90–95% within 2 h of polymerization. Droplet diameters (D_V) were measured and used to calculate the ratio of N_P/N_D. Miniemulsions consisting of 15.5 mmol of in situ KSA polymerized in a controllable manner, i.e., with a nearly one to one mapping of droplets to particles
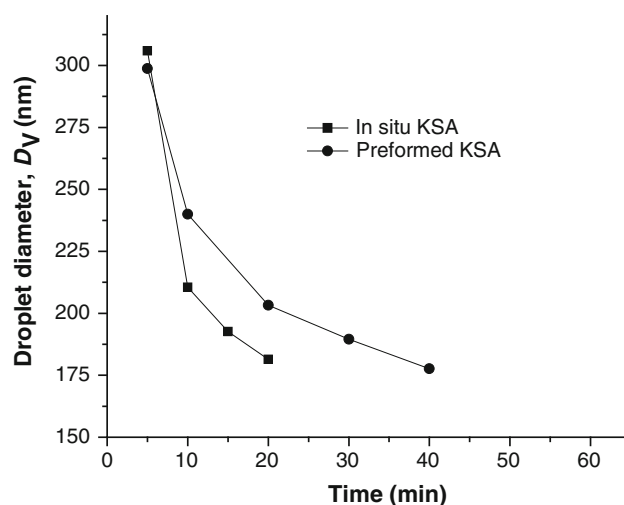
Fig. 8: Droplet-size evolution for droplets prepared with a rotor–stator (3000 RPM) using equal amounts (9.0 mmol) of either preformed KSA or in situ KSA

(N_P/N_D = 1 within ±5%) and with a constant mean particle diameter. Miniemulsions containing 20.6 and 25.8 mmol in situ KSA showed evidence of secondary nucleation in the form of a 10–20% increase in the number of particles relative to the number of droplets.

As the solids content increases from 40 to 60%, the droplet diameter increases from 130 to 185 nm since it becomes somewhat more challenging to manage to stabilize the additional interface and prevent coalescence. All miniemulsions were stable (little variance in droplet size) for several hours. When subsequently polymerized using KPS, conversion reached 90–95% within 2 h of polymerization. A nearly one to one copy of droplets to particles (N_P/N_D = 1 within ±5%) was again obtained, indicating minimal secondary nucleation and excellent stabilization of the interface. In fact, it turns out that since the surfactant is generated *at the interface* and it is not in the water phase (in any appreciable amount), secondary nucleation is actually much less prevalent in systems with the two-part, in situ surfactant system.

Continuous reactors using in situ surfactant

The ability to continuously generate miniemulsions that could be immediately polymerized would have a number of advantages, including eliminating the need to store and transport intermediate emulsions, and to exploit the numerous advantages inherent in a continuous process. The choice of reactor is important in this context, and while many options are open, the use of continuous stirred tank reactors (CSTR) is not recommended because the wide residence time distribution would lead to the inclusion of unpolymerized droplets in the exit stream. For this reason, either (semi-)batch reactors or continuous tubular reactors seem to be better choices since all of the particles in the reactor will have the same residence time. In order to exploit the advantages of a continuous system, we used a linear flow tubular reactor. Linear tubular reactors are simple to design and construct, can operate for an extended period of time with very little maintenance, and have large surface area to volume ratio which allows for efficient heat removal. Previous studies have demonstrated successful polymerization of miniemulsions using tubular reactors on a laboratory scale.[36]

Using a linear flow tubular reactor and the in situ surfactant system which provides a very efficient and rapid emulsification step, we developed a process whereby miniemulsions are continuously produced and polymerized on a laboratory scale. A schematic illustration of the set up is shown in Fig. 9. The organic and aqueous phases are introduced into the emulsification vessel and emulsified using three banks of seven elements each of Sulzer SMX static mixers. This requires somewhat less than 30 s to emulsify a kilogram of a mixture of water and monomer (FM1 = 43 wt% monomer). An initial emulsification step is used to fill up a holding tank situated between the

emulsification loop and the reactor, and to fill the reactor itself. Once both the reactor and the holding tank are full, a second gear pump is used to pump the stable miniemulsion from the holding tank through the tubular reactor at a flow rate of ~12 g/min (this corresponds to a residence time of 1 h in the tube). Given the difference between the residence time of the reactor and the time required to generate the emulsion, it is rather straightforward to occasionally open the T-valve between the emulsification loop and the holding tank to ensure that the latter always contains enough emulsion to keep the tubular reactor full. The tubular reactor process was compared to a batch polymerization also operated with excess initiator and at 80°C. Both the continuous and the batch processes were initiated using water-soluble KPS. The conversions, droplet diameters (DV), and the final particle sizes were all but identical for both the batch and tubular processes. This has a wide range of implications, both in terms of the ability to control product quality as well as the efficiency of production and control of the reaction kinetics and conversion.

Polymerizable miniemulsions by phase inversion

As mentioned above, one of the major challenges that faces the generation of miniemulsions on industrial scale is high energy consumption, and until recently, the need for high shear to produce droplets of appropriate size. From this point of view, the phase inversion method could provide a promising alternative for the generation of miniemulsions. Catastrophic phase inversion (CPI) as an emulsification method has received recent interest for its ability to produce emulsions at high-solids content (≥50 w/w%) with droplet sizes on the order of microns.[37,38] When compared to direct (or conventional) emulsification, CPI typically generates smaller droplet sizes and less energy is required to produce droplets of a given size.[38] In addition, the efficiency of the CPI processes only increases with increasing solids content, e.g., an increasing amount of oil phase. However, as CPI can only produce droplets in the micrometer range, mechanical homogenization devices are still required if droplets in the miniemulsion size range (100–500 nm) are desired.

We found that the CPI technique was quite useful for generating high-solids content O/W emulsions, where the oil phase consists of a polymerizable monomer and co-stabilizer for the miniemulsification process. Subsequently the O/W emulsions are subjected to mechanical homogenization to generate stable polymerizable miniemulsions. We showed that CPI in combination with simple mechanical homogenization is a promising route to obtain high-solids content latex-based products in a commercially viable manner.[39] In fact, we were able to obtain high-solids content dispersions of up to 80 w/w% monomer-in-water emulsions prepared by catastrophic phase
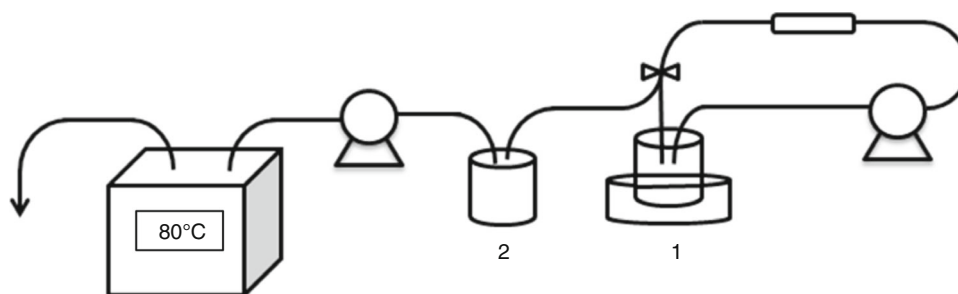
Fig. 9: Continuous emulsification/polymerization process set up for the production of miniemulsions. Set up consists of the homogenization and a separate reservoir (tank 2), pump and water bath for the polymerization process

inversion followed by miniemulsification with a rotor–stator mixer. The subsequent miniemulsification of these monomer-in-water emulsions proves to be almost four times more energy efficient than is possible with direct miniemulsification using the same mixers and recipes. The highly concentrated miniemulsions thus obtained can be successfully (and rapidly) diluted to different solids contents for polymerization, without compromising the droplet-size distribution, and used to produce colloidally stable latexes.

We investigated this with a relatively simple system: the initial continuous phase (oil phase, O) consists of the monomer methyl methacrylate (MMA) and octadecyl acrylate (ODA), a long-chain acrylate that acts as a polymerizable co-stabilizer, or hydrophobe in the mini-emulsification process. The dispersed phase (water, W) consists of water with the dissolved surfactant, typically sodium dodecylbenzene sulfonate (SDBS). Catastrophic phase inversion can be induced by the gradual addition of the dispersed phase. Gradual addition of the dispersed phase slowly alters the overall composition of the emulsion and as such the inversion line can be crossed, resulting in CPI. CPI can also be triggered by the instantaneous addition of the dispersed phase followed by continuous stirring. We examined both approaches but found that the most efficient manner to achieve CPI is by a combination of instantaneous addition and continuous stirring. The water phase is added instantaneously to the oil phase and CPI is induced by the continuous alteration of the agitation speed between 50 and 250 rpm. The rationale for this CPI protocol is as follows: to our experience, the gradual addition of the water phase yielded comparable results in terms of the droplet-size distribution (DSD) of the O/W emulsion, however, the instantaneous addition proved to result in faster phase inversion. Furthermore, alteration of the agitation speed between 50 and 250 rpm also decreased the time to reach phase inversion.

The CPI process can be monitored by measuring the conductivity of the continuous phase, see Fig. 10. Initially, the oil phase acts as the continuous phase and consequently the conductivity is low. After phase inversion the aqueous phase becomes the continuous phase and as such a large increase in the conductivity is
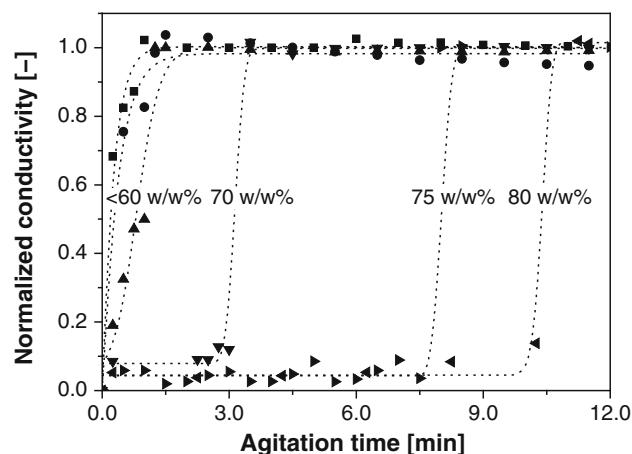
Fig. 10: CPI process for different solids contents. ●, 40 w/w%; ■, 50 w/w%; ▲, 60 w/w%; ▼, 70 w/w%; ▶, 75 w/w%; and ◀, 80 w/w%

measured as the anionic surfactant (SDBS in this case) is soluble only in this phase. A large increase in the conductivity is observed after a certain agitation time regardless of the solids content considered. In all cases, the conductivity typically increased from <5 μS cm^{-1} before inversion to approximately 1,400 μS cm^{-1} immediately afterward. Agitation times for the formulations tested were found to be between 0.5 and 12 min, increasing as the solids content increases from 40 to 80% w/w. After the CPI step, mechanical homogenization is used to miniemulsify the O/W emulsion to further reduce the O/W droplet size. The evolution of d_V during the miniemulsification in the rotor stator is presented in Fig. 11. The initial droplet sizes for the O/W emulsions, which are on the order of 1–8 μm, are successfully reduced to the miniemulsion size range and this size reduction was typically achieved within 60 min of homogenization for low solids content latexes, and less than 10 min for O/W emulsions with solids contents of 60–80 w/w%. This suggests that systems with solids contents below 60% did not actually undergo CPI, but rather were directly emulsified. On the other hand, it is useful to note that
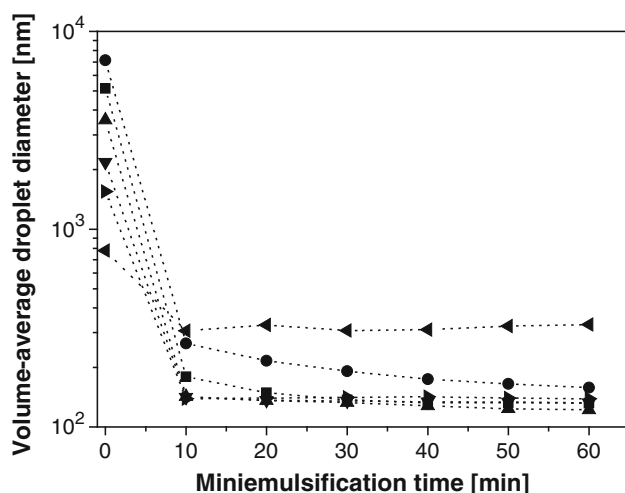
Fig. 11: Evolution of the volume-average droplet diameter of the O/W miniemulsion droplet-size distribution during mechanical homogenization in the rotor stator. ●, 40 w/w%; ■, 50 w/w%; ▲, 60 w/w%; ▼, 70 w/w%; ▶, 75 w/w%; and ◀, 80 w/w%

the O/W emulsions with solids contents of 60–80 w/w% reach the final d_v within the initial 10 min of miniemulsification. This is significant in the sense that the entire emulsification process is much more rapid (CPI step + mechanical size reduction) if we use CPI to prepare the initial dispersions than if we emulsify directly, and therefore consumes much less energy. An energy balance on the emulsification step showed that the energy consumption required to reach a stable droplet size at 70 w/w% MMA was 14% of that required to arrive at the same point with the direct emulsification of the 40 w/w% formulation. This suggests that using CPI to perform the initial size reduction of the miniemulsion is much more efficient than using mechanical agitation.

Conclusions

We have attempted to convince the reader that an integrated approach to developing different coatings formulations is a positive way to develop the potential of both novel chemistries and innovative processes.

Insight into the interaction between the chemistry, the physics and the process itself make it possible to create potentially useful products—but always with the idea that one must come up with a feasible, economically viable process to implement this new knowledge.

References

1. Bourgeat-Lami, E, Lansalot, M, "Organic/Inorganic Composite Latexes: The Marriage of Emulsion Polymerization and Inorganic Chemistry." *Adv. Polym. Sci.*, **233** 53–123 (2010)

2. Chabert, E, Bornet, M, Bourgeat-Lami, E, Cavaille, JY, Dendievel, R, Gauthier, C, Putaux, JL, Zaoui, A, "Filler–Filler Interactions and Viscoelastic Behavior of Polymer Nanocomposites." *Macromol. Mater. Sci. Eng. Part A.*, **381** 320–330 (2004)

3. Faucheu, J, Gauthier, C, Chazeau, L, Cavaille, JY, Mellon, V, Bourgeat-Lami, E, "Miniemulsion Polymerization for Synthesis of Structured Clay/Polymer Nanocomposites: Short Review and Recent Advances." *Polymer*, **51** 6–17 (2010)

4. Ruggerone, R, Plummer, C, Negrete-Herrera, N, Bourgeat-Lami, E, Manson, JE, "Mechanical Properties of Highly Filled Latex-Based Polystyrene/Laponite Nanocomposites." *Solid State Phenom.*, **151** 30–34 (2009)

5. Pattamasattayasonthi, N, Chaochanchaikul, K, Rosarpitak, V, Sombatsompop, N, "Effects of UV Weathering and a CeO₂-Based Coating Layer on the Mechanical and Structural Changes of Wood/PVC Composite." *J. Vinyl Addit. Technol.*, **17** (1) 9–16 (2011)

6. Bousseau, JN, Fauchadour, D, Tolla, B, WO2003099942A1, 2003

7. Berret, JF, Morvan, M, Sehgal, A, WO2006072743A2, 2006

8. Tissier N, "Elaboration de Matériaux Nanocomposites Inorganique/Organique Par." PhD thesis University Claude Bernard Lyon 1, 2007

9. Zgheib, N, Putaux, JL, Thill, A, D'Agosto, F, Lansalot, M, Bourgeat-Lami, E, "Stabilization of Miniemulsion Droplets by Cerium Oxide Nanoparticles: A Step toward the Elaboration of Armored Composite Latexes." *Langmuir*, **28** (14) 6163–6174 (2012)

10. Barner-Kowollik, C, *Handbook of RAFT Polymerisation.* Wiley-VCH, Weinheim (2008)

11. Nguyen, D, Zondanos, HS, Farrugia, JM, Serelis, AK, Such, CH, Hawkett, BS, "Pigment Encapsulation by Emulsion Polymerization Using Macro-RAFT Copolymers." *Langmuir*, **24** (5) 2140–2150 (2008)

12. Ali, SI, Heuts, JPA, Hawkett, BS, van Herk, AM, "Polymer Encapsulated Gibbsite Nanoparticles: Efficient Preparation of Anisotropic Composite Latex Particles by RAFT-Based Starved Feed Emulsion Polymerization." *Langmuir*, **25** (18) 10523–10533 (2009)

13. Zgheib, N, Putaux, JL, Thill, E, Bourgeat-Lami, E, D'Agosto, F, Lansalot, M, "Cerium Oxide Encapsulation by Emulsion Polymerization Using Hydrophilic MacroRAFT Agents." *Polym. Chem.*, **4** 607–614 (2013)

14. Cunningham, MF, "Controlled/Living Radical Polymerization in Aqueous Dispersed Systems." *Prog. Polym. Sci.*, **33** (4) 365–398 (2008)

15. Oh, KJ, "Recent Advances in Controlled/Living Radical Polymerization in Emulsion and Dispersion." *Polym. Sci., Part A: Polym. Chem.*, **46** (21) 6983–7001 (2008)

16. Zetterlund, PB, Kagawa, Y, Okubo, M, "Controlled/Living Radical Polymerization in Dispersed Systems." *Chem. Rev.*, **108** 3747–3794 (2008)

17. Charleux, B, Delaittre, G, Rieger, J, D'Agosto, F, "Polymerization-Induced Self-Assembly: From Soluble Macromolecules to Block Copolymer Nano-objects in One Step." *Macromolecules*, **45** (17) 6753–6765 (2012)

18. Ferguson, CJ, Hughes, RJ, Pham, BTT, Hawkett, BS, Gilbert, RG, Serelis, AK, Such, CH, "Effective ab Initio Emulsion Polymerization under RAFT Control." *Macromolecules*, **35** (25) 9243–9245 (2002)

19. Chaduc, I, Zhang, W, Rieger, J, Lansalot, M, D'Agosto, F, Charleux, B, "Amphiphilic Block Copolymers from a Direct and One-pot RAFT Synthesis in Water." *Macromol. Rapid Commun.*, **32** 1270–1276 (2011)

20. Zhang, W, D'Agosto, F, Boyron, O, Rieger, J, Charleux, B, "Toward a Better Understanding of the Parameters that Lead to the Formation of Nonspherical Polystyrene Particles via RAFT-Mediated One-Pot Aqueous Emulsion Polymerization." *Macromolecules*, **44** (10) 7584–7593 (2011)

21. Chaduc, I, D'Agosto, F, Lansalot, M, Charleux, C, "Batch Emulsion Polymerization Mediated by Poly(Methacrylic Acid) MacroRAFT Agents: One-Pot Synthesis of Self-Stabilized Particles." *Macromolecules*, **45** (15) 5881–5893 (2012)

22. Zhang, W, D'Agosto, F, Dugas, PY, Rieger, J, Charleux, B, "RAFT-Mediated One-Pot Aqueous Emulsion Polymerization of Methyl Methacrylate in Presence of Poly(Methacrylic Acid-*co*-Poly(Ethylene Oxide)Methacrylate) Trithiocarbonate Macromolecular Chain Transfer Agent." *Polymer*, **54** (8) 2011–2019 (2013)

23. Groison, E, Brusseau, S, D'Agosto, F, Magnet, S, Inoubli, R, Couvreur, L, Charleux, B, "Well-Defined Amphiphilic Block Copolymer Nanoobjects via Nitroxide-Mediated Emulsion Polymerization." *ACS Macro Lett.*, **1** 47–51 (2012)

24. Moraes, RP, Hutchinson, RA, McKenna, TFL, "High Polymer to Surfactant Polystyrene Microemulsions Using Anionic Surfactants in a Semibatch Process." *J. Polym. Sci. Part A: Polym. Chem.*, **48** 48–54 (2010)

25. Ming, W, Jones, FN, Fu, S, "Synthesis of Nanosize Poly(Methyl Methacrylate) Microlatexes with High Polymer Content by a Modified Microemulsion Polymerization." *Polym. Bull.*, **40** 749–757 (1998)

26. Sajjadi, S, "Formation of Nanoparticles by Monomer-Starved Semibatch Emulsion Polymerization." *Langmuir*, **23** 1018–1024 (2007)

27. Smeets, NMB, Moraes, RP, Wood, JA, McKenna, TFL, "A New Method for the Preparation of Translucent Microemulsion Polymer Latexes from Emulsion Polymerization." *Langmuir*, **27** 575–581 (2011)

28. Smeets, NMB, Jansen, TGT, Sciarone, TJJ, Heuts, JPA, Meuldijk, J, Van Herk, AM, "The Effect of Different Catalytic Chain Transfer Agents on Particle Nucleation and the Course of the Polymerization in Ab Initio Batch Emulsion Polymerization of Methyl Methacrylate." *J. Polym. Sci. Part A: Polym Chem.*, **48** 1038–1048 (2010)

29. Smeets, NMB, Lam, RWK, Moraes, RP, McKenna, TFL, "Catalytic Chain Transfer for Molecular Weight Control in Microemulsion Polymerization." *Polym. Chem.*, **3** 514–524 (2012)

30. Smeets, NMB, McKenna, TFL, "The Synthesis of Translucent Polymer Nanolatexes via Microemulsion Polymerization." *JCIS*, **383** 28–35 (2012)

31. El-Jaby, U, Cunningham, MF, McKenna, TFL, "Comparison of Emulsification Devices for the Production of Miniemulsions." *Ind. Eng. Chem. Res.*, **48** 10147–10151 (2009)

32. Lopez, A, Chemtob, A, Milton, J, Manea, M, Paulis, M, Barandiaran, MJ, Theisinger, S, Landfester, K, Hergeth, WD, Udagama, R, McKenna, TFL, Simal, F, Asua, JM, "Miniemulsification of Monomer–Resin Hybrid Systems." *Ind. Eng. Chem. Res.*, **47** 6289–6297 (2008)

33. El-Jaby, U, Cunningham, MF, McKenna, TFL, "Continuous Production of Miniemulsions Using In-Line SMX Elements." *AIChE J.*, **57** (6) 1585–1594 (2011)

34. Farzi, GA, Bourgeat-Lami, E, McKenna, TFL, "Miniemulsions Using Static Mixers. 2. Polymer/Silica Nanocomposite Latexes Using Static Mixers." *CJChE*, **89** 1434–1440 (2011)

35. Ferri, JK, Stebe, KJ, "Which Surfactants Reduce Surface Tension Faster? A Scaling Argument for Diffusion-Controlled Adsorption." *Adv. Colloid Interf. Sci.*, **85** 61–97 (2000)

36. Ouzineb, K, Graillat, C, McKenna, TFL, "Continuous Tubular Reactor as a Seed Reactor in Miniemulsion Polymerisation." *DECHEMA Monogr.*, **137** 293–301 (2001)

37. Sajjadi, S, Jahanzad, F, Brooks, BW, "Phase Inversion in Abnormal O/W/O Emulsions. I. Effect of Surfactant Concentration." *Ind. Eng. Chem. Res.*, **41** 6033–6041 (2002)

38. Jahanzad, F, Crombieb, G, Innesd, R, Sajjadi, S, "Catastrophic Phase Inversion via Formation of Multiple Emulsions: A Prerequisite for Formation of Fine Emulsions." *Chem. Eng. Res. Des.*, **87** 492–498 (2009)

39. Campbell, S, Larson, T, Smeets, NMB, El-Jaby, U, McKenna, TFL, "Miniemulsification by Catastrophic. Phase Inversion." *Chem. Eng. J.*, **183** 534–541 (2012)