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Feature Article

Water-soluble SG1-based alkoxyamines: A breakthrough in controlled/living free-radical polymerization in aqueous dispersed media

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This feature article is dedicated to Professor Jean-Pierre Vairon for his 70th birthday.

Abstract

This feature article describes the application of nitroxide-mediated controlled/living free-radical polymerization in aqueous dispersed systems such as miniemulsion and emulsion polymerizations. It mainly focuses on the acyclic nitroxide SG1 with derived alkoxyamines and aims to show how the recent development of new water-soluble species has allowed a true emulsion polymerization process to be successfully implemented and block copolymers to be created directly in latex particles.

Keywords: Alkoxyamine; Nitroxide-mediated controlled/living free-radical polymerization; Emulsion polymerization

1. Introduction

In the last 15 years, the field of free-radical polymerization has undergone an important renewal with the discovery of controlled/living free-radical polymerization (CRP). The most important methods are based either on a reversible termination mechanism or on a reversible chain transfer reaction. Among those techniques, the first, and probably the easiest to apply, is nitroxide-mediated polymerization (NMP) [1−3]. Most of the early works in NMP were devoted to polymerization in homogeneous conditions, i.e. bulk or solution systems, with TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) or derivatives as the mediator [2,4]. The latter, however, exhibit the major disadvantage of being applicable to a limited range of monomers, such as styrenics. New efficient nitroxides and alkoxyamines were later proposed by several groups, which allowed the range of monomers to be continuously broadened [5−10]. In our group we decided to focus on NMP in heterogeneous aqueous media in order to form ‘‘living’’ submicron latex particles, the main target being emulsion polymerization, which is a process of very high academic and industrial interest [11,12]. The purpose of this paper is to relate the development of the method from the first results obtained in miniemulsion systems toward the most recent achievements in true emulsion polymerization. Such an accomplishment was made possible by the development of water-soluble alkoxyamines based on the nitroxide SG1 (*N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)]nitroxide) [9]. By describing the various logical and chronological steps before we reached the goal, we emphasize the important kinetic and mechanistic parameters that had to be understood and controlled and we hope that the reader will be convinced of the numerous benefits of NMP in non-homogeneous systems. This article should not be considered as a comprehensive review; more complete information on the domain can be found in dedicated papers, in which the application of NMP to aqueous heterogeneous systems is fully described [13−15]. It is also interesting to mention that the other CRP techniques have been carried out in aqueous dispersed media by several

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groups and a brief discussion on this topic will be given at the end of this article.

2. Aqueous miniemulsion and emulsion polymerizations

Radical polymerization in aqueous dispersed media represents one of the most important industrial processes for the production of synthetic polymers. It leads to the formation of polymer particle suspensions and includes a variety of systems which differ from each other in multiple points such as the initial state of the polymerization recipe, the mechanism of particle formation, the size of the polymer particles and the kinetics of polymerization. Within the framework of this review, we will exclusively focus on the two most-studied techniques for CRP in aqueous dispersed media: emulsion [16–20] and miniemulsion [21–29] polymerizations, which have been well described in several books and review articles.

Emulsion polymerization is undoubtedly the more widespread of the two processes; it is widely used in industry and has been extensively studied in academic laboratories for many years. Considering a typical batch emulsion polymerization, the initial state is mainly composed of large droplets (>1 μm) of hydrophobic monomer(s) and of a large number of monomer-swollen micelles (Fig. 1a) and it leads to a stable suspension of submicron-size particles (also called latex). Following the use of a water-soluble radical initiator, which is usually a charged molecule, latex particles are obtained according to a complex nucleation mechanism that can be either micellar (the oligoradicals formed in the aqueous phase enter the swollen micelles) or homogeneous (precipitation of the oligoradicals), depending on the surfactant concentration and on the water solubility of the monomer(s). The unique feature of the emulsion polymerization process is that the polymerization takes place in small particles and monomer is provided to the polymerization locus *via* diffusion through the aqueous phase from the large droplets, which only act as monomer reservoirs. Nucleation and polymerization in the monomer droplets are not considered because of their large size and small number, resulting in a very low probability of capture of the oligoradicals generated in the aqueous phase. In contrast, if oligoradicals were generated in the oil phase (oil-soluble initiator), nucleation would not only take place in the monomer-swollen micelles but also in the large monomer droplets leading to latex destabilization.

The latex particles are generally stabilized by a low molar mass surfactant, which can be either ionic, nonionic or a mixture of both. Amphiphilic copolymers can also be used instead and offer the advantage of being better anchored at the particle surface and of providing efficient electrosteric stabilization when the hydrophilic component is a polyelectrolyte. The surfactant can also take part in the polymerization process [30,31], i.e. initiation (so-called inisurfs), propagation (so-called surfmers) or chain transfer (so-called transurfs), which strongly improves the anchoring and avoids release of the molecules during the application. Alternatively, surfactant-free latexes can be produced either by taking advantage of the charged fragments of the initiator at the chain-ends as the sole stabilizer (in this case, large particles are obtained and low solids content have to be targeted), or by adding a hydrophilic comonomer leading to the *in situ* production of amphiphilic chains by copolymerization [20].

When the starting monomer phase is divided into submicronic droplets by a high shear device (ultrasonicator or microfluidizer), the droplets become small enough so that they can compete for the radical entry and become the primary locus of polymerization, hence acting as bulk nanoreactors (Fig. 1b). This process is called miniemulsion and offers some important advantages over emulsion polymerization: (i) it avoids the complex nucleation step encountered in the conventional emulsion polymerization, (ii) the system exhibits only two phases throughout the polymerization reaction (the aqueous phase and the monomer/polymer particles), (iii) either an oil-soluble or a water-soluble initiator can be used and (iv) the final latex is theoretically a 1:1 copy of the initial droplets, allowing a direct control over the number of particles, although not always achieved in practice. Miniemulsion can thus be seen as a simplified model for emulsion polymerization. Nevertheless, miniemulsion polymerization is mainly devoted to laboratory-scale experiments and is not easily applicable in industrial conditions. Like emulsion polymerization, miniemulsion systems require the use of a surfactant

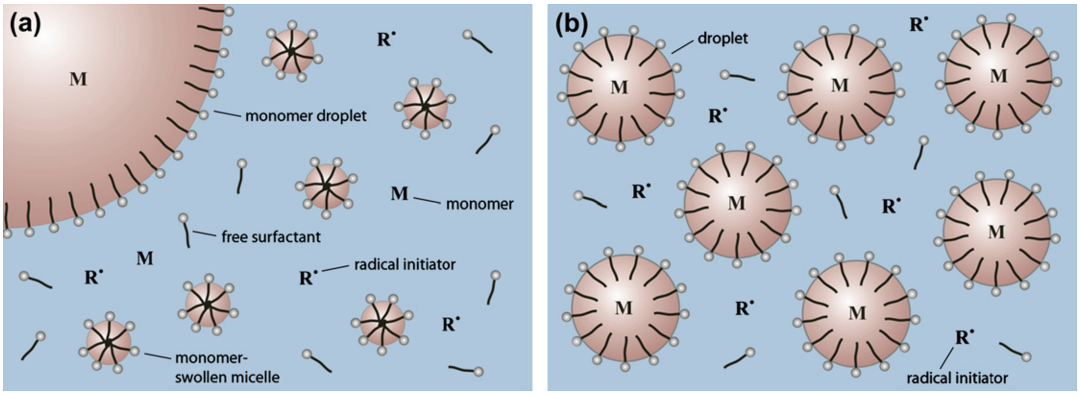
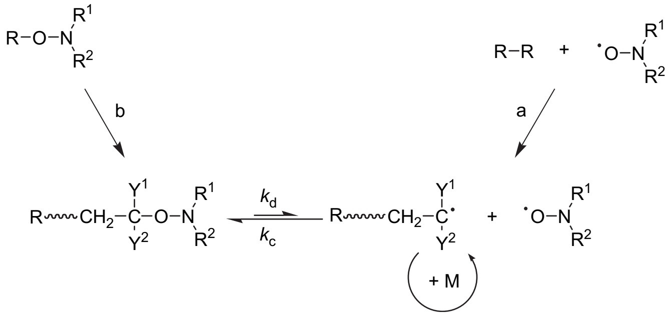


Fig. 1. Initial state of aqueous polymerization in emulsion (a) and in miniemulsion (b).

(either a low molar mass species or an amphiphilic copolymer) to stabilize the monomer droplets and the latex particles against coalescence and flocculation; the alternative of using a water-soluble comonomer in the absence of emulsifier is not applicable as the initial monomer droplets would not be stabilized. Additionally, it is important to introduce a hydrophobic additive in the monomer phase to enhance stabilization of the submicronic droplets against Ostwald ripening.

3. General features of nitroxide-mediated controlled/living free-radical polymerization (NMP)

Nitroxide-mediated polymerization represents one of the most well-established techniques in CRP [3]. NMP is based on a reversible termination reaction between a growing (macro)-radical and a free nitroxide to form a (macro)alkoxyamine (Scheme 1). The alkoxyamine obtained from the trapping reaction is the predominant species, namely the "dormant species", which can regenerate the propagating radical and the nitroxide by homolytic cleavage at elevated temperature. This equilibrium presents the advantage of being a purely thermal process where neither catalyst nor bimolecular exchange is required. The polymerization kinetics are governed by both this activation–deactivation equilibrium and the persistent radical effect [32]: the existence of early irreversible terminations between the propagating radicals leads to a build-up in free nitroxide concentration, which consequently allows the reversible termination to be favoured throughout the polymerization reaction. A typical NMP can be set up following two different pathways: (i) either *via* the use of a *bicomponent* initiating system, that is to say a conventional radical initiator in conjunction with a free nitroxide in order to form the (macro)alkoxyamine *in situ* (Scheme 1a), (ii) or *via* the direct use of a preformed alkoxyamine, in which case the initiating system is termed *monocomponent* (Scheme 1b). However, the use of a bicomponent initiating system does not permit accurate control over the number of growing chains and the concentration of free nitroxide because the free-radical initiator efficiency is generally ill-defined. Thus, it has some strong repercussions on the kinetics and the control over the polymer characteristics. In contrast, the monocomponent pathway allows this problem to be avoided as long as the efficiency of the alkoxyamine remains close to 1.

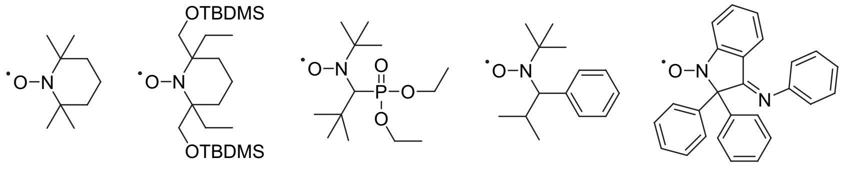


Scheme 1. Activation–deactivation equilibrium in nitroxide-mediated controlled/living free-radical polymerization. Bicomponent initiating system (a) and monocomponent initiating system (b).

Based on the initial work of Solomon and Rizzardo [1,33,34], nitroxide-mediated polymerization was further developed by Georges and coworkers [2] when they reported the bulk polymerization of styrene at 123 °C in the presence of TEMPO (**N1**, Scheme 2) as a control agent. However, TEMPO was mainly efficient with styrenic monomers (only a sterically hindered TEMPO derivative (**N2**) recently developed by Studer and Knoop [10] was able to afford a good control of the polymerization of *n*-butyl acrylate) and an important breakthrough came with the discovery of efficient acyclic nitroxides for the controlled polymerization of a much broader range of monomers. Indeed, *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)]nitroxide (SG1, **N3**, also called DEPN) [7,9] and *N*-*tert*-butyl-*N*-[1-phenyl-2-(methylpropyl)]nitroxide (TIPNO, **N4**) [6,8] are able to control the polymerization of styrenics [8,9], alkyl acrylates [8,9], acrylic acid [35,36], acrylamides [37,38], and dienes [39,3]. For methacrylic esters, a particular nitroxide (DPAIO, **N5**) had to be designed for the purpose of forming living homopolymers [40]; alternatively SG1 could be readily used to produce living poly(methyl methacrylate)- or poly(methacrylic acid)-rich polymers *via* a simple copolymerization approach with a very small amount of styrene [41–43].

4. Bicomponent initiating systems in (mini)emulsion polymerizations

An easy way of conducting NMP in miniemulsion or emulsion, without significantly altering the experimental process, is to use the aforementioned bicomponent initiating system. In other words, the radical initiator is kept the same as in a classical free-radical polymerization recipe and the selected free nitroxide is added to the reaction medium. For polymer to be well controlled, it is important then to select the nitroxide as a function of its solubility in the monomer phase. Indeed, whatever the initiation locus, the major part of the propagation



N1 **N2** **N3** **N4** **N5**

Scheme 2. Structure of various nitroxides used as efficient control agents in NMP.

reaction should take place in the monomer-swollen polymer particles, where the activation and deactivation mechanisms should occur simultaneously. With SG1, this requirement is actually fulfilled as the molecule is perfectly soluble in all hydrophobic monomers and partitions between the monomer phase and the aqueous phase [44].

Many publications were devoted to NMP in miniemulsion, using a bicomponent initiating system with TEMPO or derivatives as the nitroxide. For instance, the nature of the TEMPO substituents has been selected in order to adapt the hydrophilicity of the nitroxide to the polymerization process. These investigations were performed at elevated temperatures (typically above 100 °C), mainly with styrene as the monomer. The conclusions were not very different from ours and are described in several review articles [13–15].

4.1. Miniemulsion polymerization

In our early works devoted to miniemulsion polymerization, we selected two types of initiating systems: 2,2′-azobisisobutyronitrile (AIBN) as an oil-soluble initiator and persulfate/metabisulfite ($K_2S_2O_8$/$Na_2S_2O_5$) as a water-soluble redox couple [45]. The purpose was to work in low temperature conditions, i.e. below 100 °C. With styrene as a monomer, the SG1-mediated polymerization temperature could be set at 90 °C. Hexadecane was used as a hydrophobe to stabilize the monomer droplets against Ostwald ripening and sodium dodecyl sulfate (SDS) was the surfactant; high shear was applied *via* ultrasonication. In both cases, the optimal SG1 over initiator molar ratio was 1.2, which represented the best compromise between fast kinetics and acceptable control over molar mass and molar mass distribution. Whatever the type of initiator, the addition of SG1 to the polymerization system led to a drastic decrease of the polymerization rate, due to the establishment of the activation–deactivation equilibrium; the more the SG1, the slower the polymerization.

Using AIBN as an oil-soluble initiator in miniemulsion systems with 10 wt% or 20 wt% of styrene in water, the polymerization reached approximately 50% conversion within 8 h, not very different from a comparable bulk reaction. The conversion *vs* time plots exhibited a characteristic shape, with first an induction period, then a relatively fast polymerization and finally a plateau at incomplete conversion, with very slow conversion increase (Fig. 2). The induction period corresponded to the time required for consumption of free SG1 by the continuously formed oligoradicals generated from AIBN. Only when concentration of free nitroxide reached a small enough value could the polymerization start, in agreement with the activation–deactivation equilibrium-based kinetics. After this minimum in SG1 concentration (i.e. maximum in polymerization rate), the system was governed by the persistent radical effect, which led to a continuous increase of the SG1 concentration and to a concomitant decrease of the polymerization rate. At 90 °C, the thermal autoinitiation of styrene is too slow to create propagating radicals in sufficient concentration to consume the nitroxide excess. The expected linear increase in the number-average molar mass (M_n) with monomer conversion was nevertheless observed (Fig. 2), but the polydispersity index was systematically larger than in bulk (i.e. $M_w/M_n = 1.6–1.7$ at final stage instead of 1.3). With SDS as a surfactant, the miniemulsion polymerization led to stable latexes with diameter in the 150–220 nm range, but with a broad particle size distribution (Fig. 3).

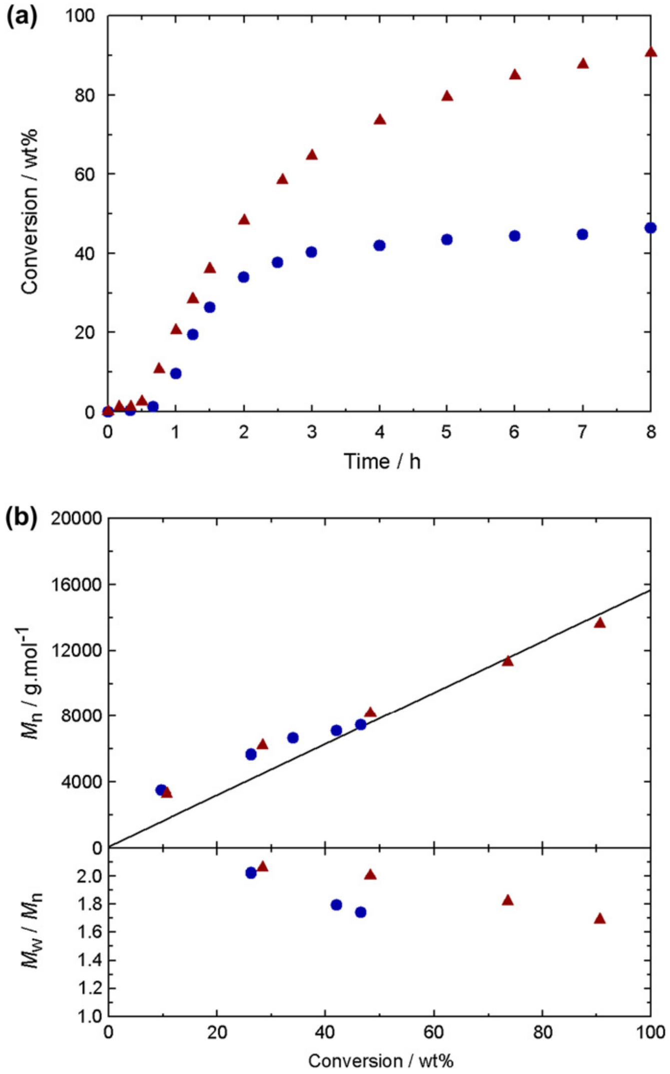


Fig. 2. Miniemulsion polymerization of styrene at 90 °C, using SG1 as a nitroxide mediator and either AIBN as an oil-soluble radical initiator or persulfate/metabisulfite as a water-soluble radical initiator. Styrene/water = 10 wt%; $[SDS]_0 = 15$ mmol L^{-1}_{water}; $[SG1]_0/[initiator]_0 = 1.2$; $[NaHCO_3]_0 = 9$ mmol L^{-1}_{water}; hexadecane = 5 wt% based on styrene; high molar mass polystyrene = 1 wt% based on styrene. Evolution of monomer conversion with time (a) and evolution of M_n and M_w/M_n with monomer conversion (b). $[AIBN]_0 = 0.037$ mol $L^{-1}_{styrene}$ and pH = 8.6 (●); $[K_2S_2O_8]_0 = [Na_2S_2O_5]_0 = 4.5$ mmol $L^{-1}_{water} = 0.037$ mol $L^{-1}_{styrene}$ and pH = 6.6 (▲).

With the water-soluble persulfate/metabisulfite initiator system [46], polymerization was significantly faster than with AIBN and the final conversion was much higher, but the molar mass distribution was broader, even though the linear increase in M_n with monomer conversion was still observed (Fig. 2). An increase of the SG1 over initiator molar ratio induced a decrease of the polymerization rate together with a narrowing of the molar mass distribution. The

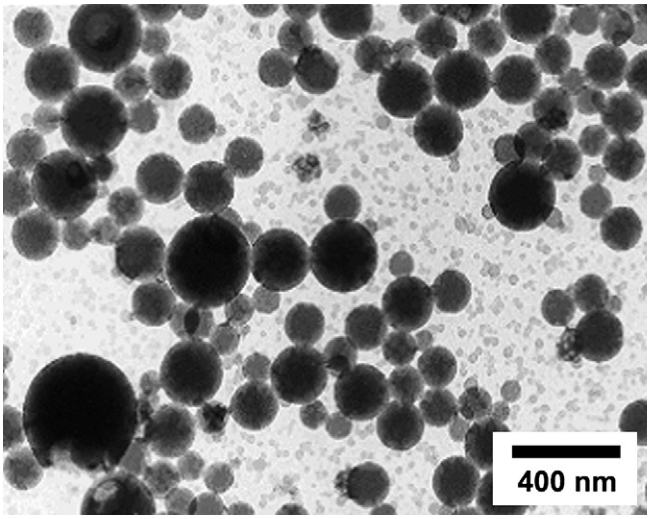


Fig. 3. Transmission electron microscopy (TEM) image of the final latex obtained from a 10 wt% solid SG1-mediated miniemulsion polymerization of styrene at 90 °C initiated by AIBN.

conversion *vs* time plot exhibited a marked induction period, due to the formation of water-soluble alkoxyamines, which were progressively transferred into the monomer phase upon growth by monomer addition. With SDS as a surfactant, the average particle diameter was in the 150–250 nm range, and again the particle size distribution remained rather broad. The only fundamental difference between the SG1-mediated miniemulsion polymerizations carried out with the oil-soluble radical initiator and with the water-soluble one was the polymerization rate. The latter was particularly enhanced in acidic conditions and simultaneously the initiator efficiency was very low (Fig. 4). It was further demonstrated that SG1 was unstable in the presence of the two components of the initiating system, especially at low pH [44], but the stability was improved when pH was increased above 6. Degradation of SG1 induced by side reactions with the initiating system was then believed to be responsible for the decrease of the deactivator concentration and hence the increase of the polymerization rate. In neutral conditions, the polymerization rate was slower but the average molar mass was better controlled by the initial monomer over initiator concentration ratio. The use of a bicomponent initiating system composed of a water-soluble radical initiator together with free nitroxide was thus a very simple way of achieving CRP in miniemulsion. From a practical viewpoint, very few parameters had to be changed with respect to a classical polymerization recipe. Nevertheless, because kinetics and control of molar mass were very sensitive to small changes in nitroxide concentration, control was fairly difficult to achieve and the concentrations of each component and the experimental conditions (such as pH in particular) had to be very carefully adjusted.

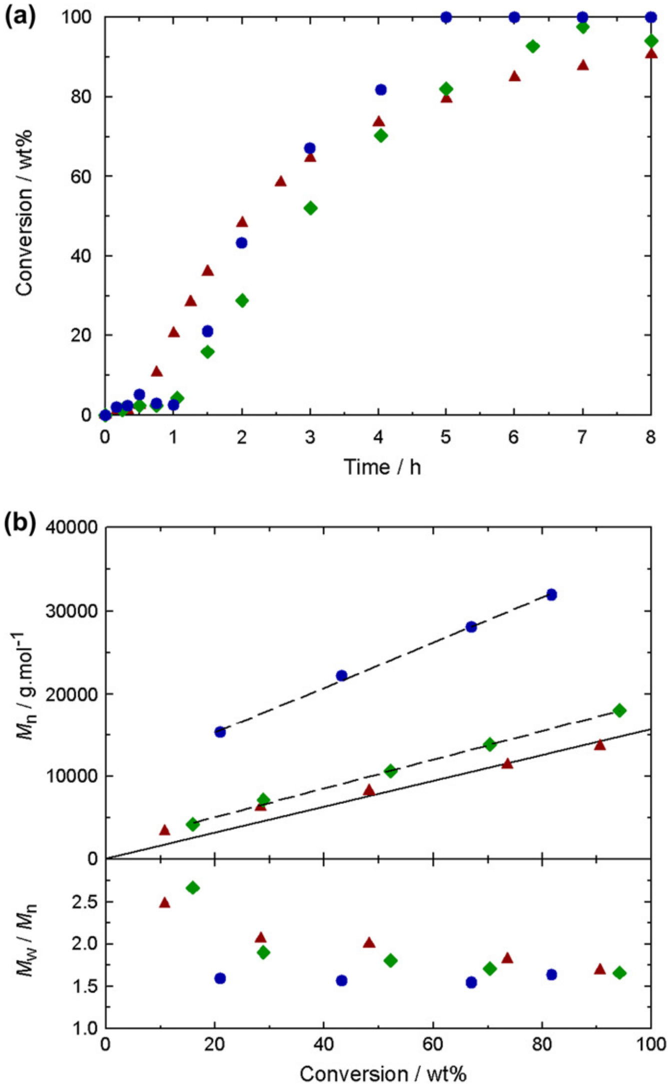


Fig. 4. Miniemulsion polymerization of styrene at 90 °C and various pH, using SG1 as a nitroxide mediator and persulfate/metabisulfite as a water-soluble radical initiator. Styrene/water = 10 wt%; $[K_2S_2O_8]_0 = [Na_2S_2O_5]_0 =$ 4.5 mmol L^{-1}_{water}; $[SG1]_0/[initiator]_0 = 1.2$; $[SDS]_0 = 15$ mmol L^{-1}_{water}; hexadecane = 5 wt% based on styrene; high molar mass polystyrene = 1 wt% based on styrene. Evolution of monomer conversion with time (a) and evolution of M_n and M_w/M_n with monomer conversion (b). $[NaHCO_3]_0 = 9.0$ mmol L^{-1}_{water} and pH = 6.6 (▲); $[K_2CO_3]_0 = 4.4$ mmol L^{-1}_{water} and pH = 4.8 (◆); $[K_2CO_3]_0 = 3.0$ mmol L^{-1}_{water} and pH = 2.9 (●).

4.2. Batch emulsion polymerization

With the requirement that a water-soluble initiator had to be used, the same persulfate/metabisulfite system was applied in a batch emulsion polymerization process, stabilized with SDS only at 90 °C, i.e. in the absence of hexadecane and without ultrasonication. The initial nitroxide over initiator molar ratio and the pH were found to affect the conversion rate and the molar mass in the same way as in miniemulsion polymerization. Nevertheless, when comparing the kinetics of similar miniemulsion and emulsion polymerizations, it appeared that the induction period was longer for the emulsion polymerization system (Fig. 5). This could be assigned to the nucleation mechanism, which is fundamentally different in both systems (droplet nucleation in miniemulsion *vs* micellar nucleation in emulsion). The evolution of molar masses with monomer conversion was not notably different in both processes, but the

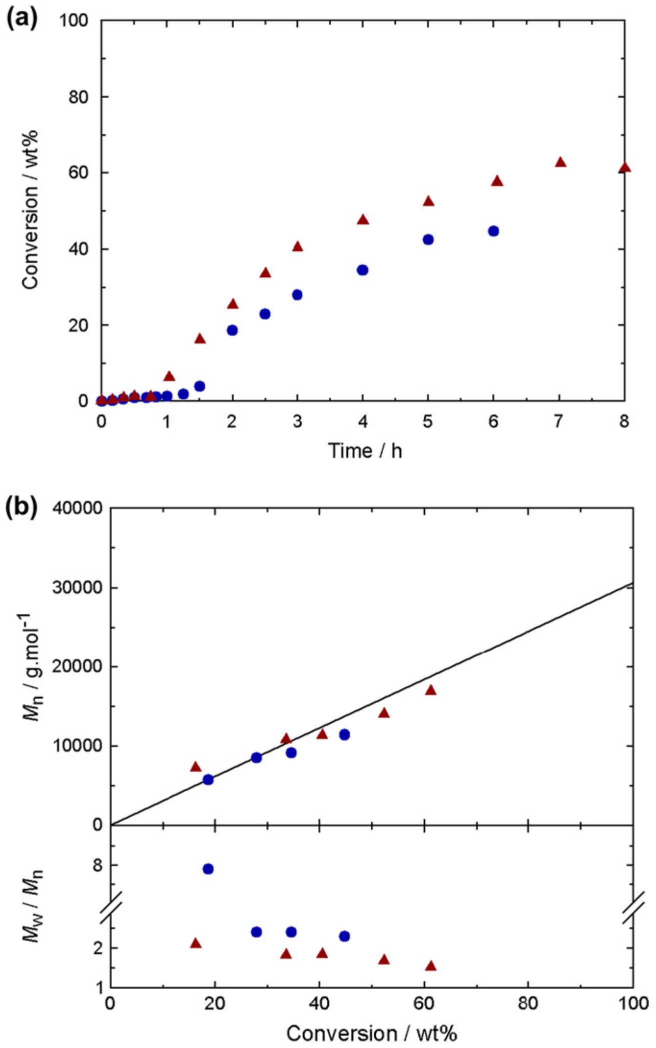


Fig. 5. Emulsion polymerization (●) of styrene at 90 °C *vs* miniemulsion polymerization (▲). Styrene/water = 20 wt%; $[K_2S_2O_8]_0 = [Na_2S_2O_5]_0 = 4.5\ \text{mmol}\ L_{\text{water}}^{-1}$; $[SG1]_0/[\text{initiator}]_0 = 1.2$; $[SDS]_0 = 15\ \text{mmol}\ L_{\text{water}}^{-1}$; $[NaHCO_3]_0 = 9\ \text{mmol}\ L_{\text{water}}^{-1}$; for the miniemulsion process: hexadecane = 5 wt% based on styrene; high molar mass polystyrene = 1 wt% based on styrene. Evolution of monomer conversion with time (a) and evolution of M_n and M_w/M_n with monomer conversion (b).

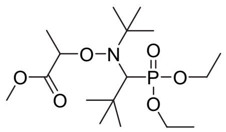
molar mass distribution was significantly broader in emulsion (M_w/M_n typically above 2). Another important feature of the emulsion polymerization was the stability issue, since a significant amount of coagulum (approximately 5–10 wt% based on the overall monomer) was usually observed, whereas the average particle size and the particle size distribution were very similar to those obtained in miniemulsion, in which no coagulum formed. This might be assigned to droplet nucleation either *via* thermal autoinitiation, although it remains rather slow at 90 °C, or *via* partition of the oligo-alkoxyamines between water and monomer due to the slow chain-growth process.

The very first results obtained with a bicomponent initiating system were quite encouraging, but had to be improved in terms of kinetics, control over molar mass and molar mass distribution. Most importantly, it appeared that the bicomponent initiating system was not as convenient as we initially thought to finely control the kinetics and the polymer characteristics. Nevertheless, at the same time, various SG1-based oil-soluble alkoxyamines were developed and allowed a very simple miniemulsion polymerization recipe to be adapted as described below.

5. Oil-soluble alkoxyamines in miniemulsion polymerization

After having considered several bicomponent initiating systems in aqueous dispersed media, our next logical step was to investigate the use of a preformed alkoxyamine based on the nitroxide SG1 as an efficient initiator/control agent in miniemulsion polymerization. As previously mentioned, miniemulsion polymerization can be started using either oil-soluble initiator or water-soluble initiator. As a consequence, in order to induce a direct, efficient initiation in the monomer droplets analogous to bulk systems, the oil-soluble alkoxyamine derived from the 1-(methoxycarbonyl)eth-1-yl initiating radical and the SG1 nitroxide (MONAMS, Scheme 3), was selected. In other works, the authors have generally selected macromolecular alkoxyamines based on TEMPO (typically polystyrene oligomers previously obtained by bulk NMP) for the miniemulsion polymerization of styrene at 135 °C. However, the systems suffered from thermal autoinitiation, but allowed the polymerization to be correctly controlled and block copolymers with *n*-butyl acrylate to be synthesized using particular experimental conditions [47].

A theoretical study was undertaken to examine the kinetics of nitroxide-mediated CRP in miniemulsion with an oil-soluble alkoxyamine initiator, in the absence of thermal self-initiation. An important assumption was that only the alkoxyamines and the propagating radicals were compartmentalized, but not the nitroxide, i.e. its concentration reached a fast equilibration in the entire dispersed oil phase [48]. The latter assumption may strongly depend, however, on the nitroxide nature and polarity and may not apply for highly hydrophobic radicals. The polymerization kinetics was described, as a function of particle size, by analytical expressions based on the Smith–Ewart equations and on the equation obtained when the persistent radical effect is established. For large particles, the polymerization rate was found to be similar in miniemulsion and in bulk. In contrast, when particle size became smaller, the overall rate of irreversible termination could be slower in a dispersed medium than in bulk (which denotes a compartmentalization effect), depending on the concentration of free nitroxide. As a consequence, both the overall proportion of dead chains and the concentration of released nitroxide were lower (higher proportion of living chains); the polymerization was then expected to be faster and the molar mass distribution to be broader.



Scheme 3. Structure of the oil-soluble SG1-based alkoxyamine, MONAMS.

A similar study was undertaken by Butté et al. [49], Zetterlund et al. [50,51], and Tobita and Yanase [52], who applied numerical simulation, considered the compartmentalization of all species including free nitroxide and took into account the thermal self-initiation (which is relevant for nitroxide-mediated polymerization of styrene, but was not considered to play any role in small particles owing to fast recombination of the produced radicals). They reached conclusions that were in contradiction with ours, as they showed that small particles would induce a lower polymerization rate, a lower polydispersity index and a higher degree of livingness than large ones, resulting mainly from the increase of the deactivation rate in confined volumes [50]. At the present time, it is difficult to compare those results with experimental data as very small and monodisperse particles have never been reached in miniemulsion NMP. Thermal autoinitiation is very specific to styrene and its reduced rate in small particles would actually lead to an accumulation of free nitroxide (the excess nitroxide would not be consumed by deactivation of newly formed propagating radicals), leading to a decrease of the overall polymerization rate as compared with bulk polymerization.

From the experimental viewpoint, we successfully used the MONAMS alkoxyamine for the polymerization of styrene (S) at 120 °C [53,54] and *n*-butyl acrylate (BA) at 112 °C in aqueous miniemulsion [55]. Polymerization of the latter monomer was studied in great detail [56] and the important results are described below. Stabilization was provided by a mixture of SDS and Forafac ($C_8F_{17}CH_2CH_2COO^-K^+$), and 2.5 mol.% excess of free SG1 with respect to MONAMS was initially introduced to ensure a good control of the polymerization under reasonable durations. Polymerizations were rather fast and all the characteristics of a controlled system were obtained: M_n increased linearly with BA conversion in good agreement with calculated values while polydispersity indices remained low throughout the polymerization ($M_w/M_n = 1.2–1.4$). Stable latexes at 20 wt% solids were recovered with average diameters in the 390–460 nm range, but with broad particle size distribution. Furthermore, chain extension with styrene was performed under similar conditions after 80% conversion of BA leading, thanks to a high reinitiation efficiency, to a poly(*n*-butyl acrylate)-*b*-polystyrene (PBA-*b*-PS) diblock copolymer of narrow molar mass distribution ($M_w/M_n = 1.27$), the purity of which depended on the proportion of the BA monomer remaining after the synthesis of the first block (Fig. 6).

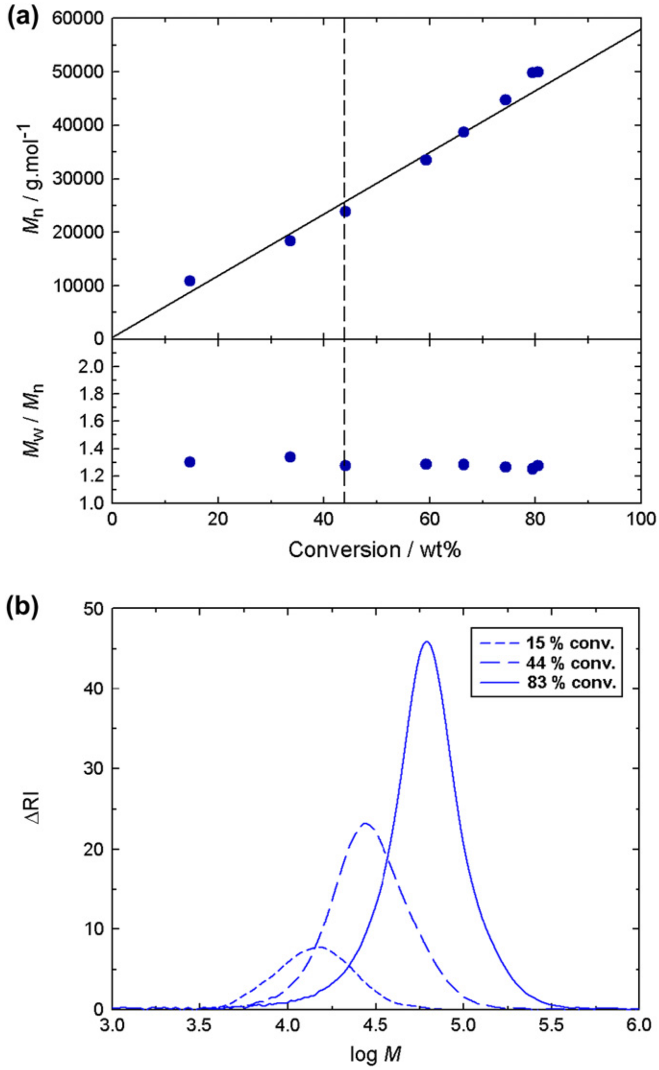


Fig. 6. Synthesis of a PBA-*b*-PS diblock copolymer by SG1-mediated miniemulsion polymerization at 120 °C initiated by the MONAMS alkoxyamine with $[SG1]_0/[MONAMS]_0 = 0.025$. Evolution of M_n and M_w/M_n with overall monomer conversion (the vertical dotted line marks the addition of styrene) (a) and size exclusion chromatograms recorded at various conversions (b).

In agreement with the above-mentioned theoretical study for large particles, it was shown that the miniemulsion process did not differ from the bulk counterpart: the molar masses and kinetics were governed by the addition of chosen initial concentrations of alkoxyamine and free nitroxide, respectively [56,57]. In 20 wt% solid latexes obtained at 112 °C, polymer chains exhibited molar masses ranging from 12 000 to 42 000 g mol^{-1} depending on the initial concentration of MONAMS. The initially added free nitroxide (from 0 to 10 mol.% with respect to the alkoxyamine) indeed acted as a rate moderator, which also allowed molar mass distribution to be finely tuned (Fig. 7); the higher the added free SG1, the lower the polydispersity index [56]. Similar trends were also witnessed when *n*-butyl acrylate and styrene were copolymerized in miniemulsion, forming well-defined gradient copolymers with both narrow molar mass and composition distributions in stable 32 wt% solid latexes [57].

However, one feature often encountered in the reported miniemulsion polymerizations performed with the MONAMS initiator at 112 °C was that initiation efficiency was below 100% (typically 80%); in other words, the experimental molar masses were usually larger than the expected ones. We disregarded the effect of extensive self-termination of primary radicals because the 20% loss in polymer chains did not match the calculated 3.5 mol.% of released SG1 and no strong effect on the polymerization rate was evidenced. The relevant experiment, which helped us to strongly improve the initiation efficiency, was to increase the dissociation rate constant (k_d) of the starting initiator. This was achieved by two main techniques: (i) an increase in the reaction temperature to 125 °C

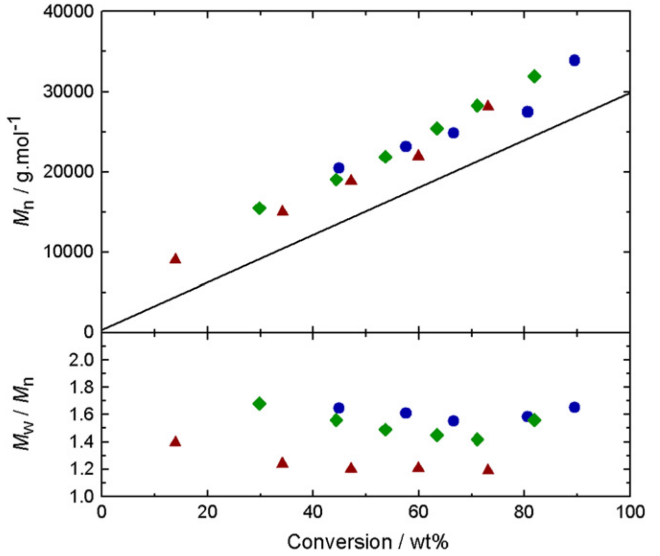


Fig. 7. Evolution of M_n and M_w/M_n with monomer conversion for the miniemulsion polymerization of *n*-butyl acrylate at 112 °C initiated by the MONAMS alkoxyamine with various initial concentration of free SG1. (●): $r = [SG1]_0/[MONAMS]_0 = 0$; (◆): $r = 0.013$; (▲): $r = 0.026$.

with the MONAMS alkoxyamine (Fig. 8) and (ii) the use of a preformed SG1-terminated poly(*n*-butyl acrylate) (PBA-SG1) macro-alkoxyamine ($M_n = 9550$ g mol^{-1}; $M_w/M_n = 1.76$) at 112 °C. Both of these approaches raised the initiation efficiencies to almost 100%. The first method was a way of enhancing the dissociation rate constant of the MONAMS and therefore the rate of initiation, which was particularly important in the present case because this alkoxyamine is composed of two diastereoisomers of different k_d values [58]. The second method had the same effect because the PBA-SG1 macroinitiator exhibits a higher k_d than MONAMS [59]. There is also an additional benefit derived from the use of a macroinitiator in aqueous dispersed media; it would prevent the exit of the initiating radical from the monomer droplets toward the aqueous phase, as opposed to the unimolecular MONAMS, for which the initiator moiety (1-(methoxycarbonyl)eth-1-yl) is known to be quite hydrophilic. Nevertheless, the excellent agreement between the theoretical molar masses and the experimental ones with the MONAMS at 125 °C demonstrated that, even if exit of primary radical in the aqueous phase might occur, its influence on the control of the polymerization was negligible [56,60]. Considering the colloidal characteristics of the latexes, large average diameters (390−460 nm) and broad particle size distributions were commonly observed whatever the experimental conditions. We also changed the stabilizing system and used Dowfax 8390 surfactant (a mixture of mono- and dihexadecyl disulfonated diphenyloxide disodium salts; cmc = 0.05 wt% at 25 °C, approximately 0.5−1 mM) to avoid partial hydrolysis of SDS at such high temperature, leading to dodecanol.

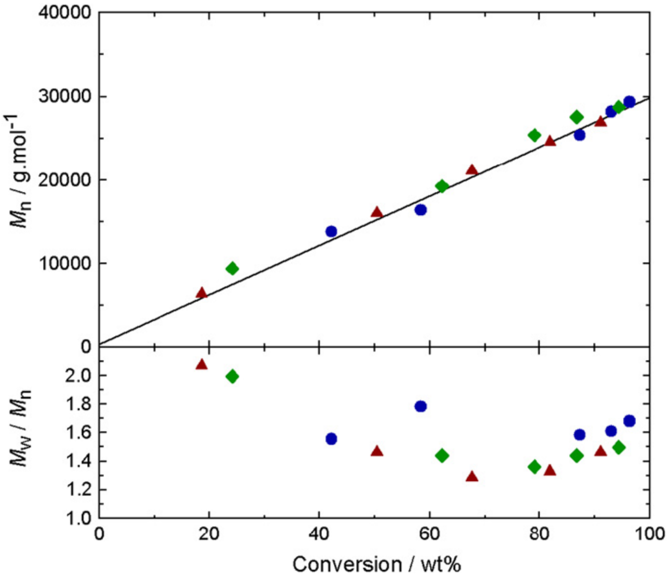
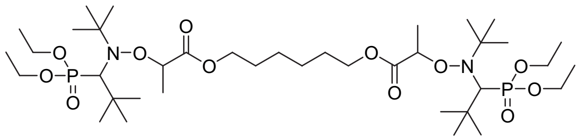


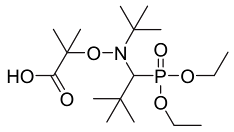
Fig. 8. Evolution of M_n and M_w/M_n with monomer conversion for the miniemulsion polymerization at 125 °C of *n*-butyl acrylate initiated by the MONAMS alkoxyamine with various initial concentration of free SG1. (●): $r = [SG1]_0/[MONAMS]_0 = 0.026$; (◆): $r = 0.051$; (▲): $r = 0.101$.

The structure of the PBA chains with $M_{n,th} = 30\,000$ g mol^{-1} obtained by miniemulsion polymerization at 112 °C was examined to study the influence of chain transfer to polymer, and was further compared to that obtained by SG1-mediated bulk polymerization [61]. On the basis of size exclusion chromatography, NMR and MALDI-TOF mass spectrometry analyses, the majority of the poly(*n*-butyl acrylate) polymer chains exhibited the ideal structure, even at high conversion, with one initiator moiety (1-(methoxycarbonyl)eth-1-yl derived from the MONAMS alkoxyamine) and one SG1 end-group at the α and ω positions, respectively. This confirmed that well-defined PBA-based macromolecular architectures such as block copolymers could be prepared by SG1-mediated CRP in bulk, and more importantly, in miniemulsion. Although the existence of a small proportion of branches was highlighted (1−2 mol.%), the mechanism by which they were produced seemed to be mainly an intramolecular transfer reaction (presumably by the so-called backbiting mechanism) leading to short chain branches. However, even though intermolecular chain transfer to polymer, which would produce long chain branches, could not be ruled out especially at high conversions, its occurrence remained comparatively low under such experimental conditions.

The agreement between the experimental macromolecular structure and the theoretical one was then investigated with the use of a difunctional SG1-based alkoxyamine (DIAMS, Scheme 4) in miniemulsion at 112 °C where high molar mass PBA homopolymers were targeted ($M_{n,th} = 121\,000$ g mol^{-1}) [62]. Molar masses increased linearly with monomer conversion and followed the theoretical line up to values as large as 70 000 g mol^{-1} (e.g. 60−70% conversion) with polydispersity indices as small as 1.3−1.4 (Fig. 9). Increasing monomer conversion above 70% resulted in a slight downward deviation of the M_n *vs* conversion data points, together with a strong increase of the polydispersity indices (larger than 2). This feature was mainly assigned to the aforementioned transfer to polymer leading to branched structures with lower hydrodynamic diameter than the linear counterparts; irreversible terminations by combination could also be responsible for the molar



Scheme 4. Structure of the oil-soluble SG1-based dialkoxyamine, DIAMS.



Scheme 5. Structure of the water-soluble SG1-based alkoxyamine, MAMA (BlocBuilder™).

mass distribution broadening as they lead to still living difunctional polymers with double M_n. Nevertheless, we took benefit of the divergent chain-growth provided by the DIAMS dialkoxyamine to prepare a PS-*b*-PBA-*b*-PS triblock copolymer by sequential monomer addition [53]. Stable latexes up to 32 wt% solids were obtained without any coagulum neither destabilization over time. As a proof of a high livingness, a complete reinitiation of the PBA middle block was shown by liquid adsorption chromatography (LAC, which performs separation according to the chemical composition only) in good agreement with previous structural characterizations.

As a conclusion, the use of oil-soluble alkoxyamines allowed us to successfully transfer nitroxide-mediated polymerization from bulk system to aqueous miniemulsion and to overcome the classical drawbacks encountered with bicomponent systems [54]. Very stable latexes with solids content up to 32 wt% were prepared and thanks to the unique characteristics of SG1, the polymerization of *n*-butyl acrylate and styrene were efficiently controlled, which opened the door to more complex macromolecular architectures such as gradient, diblock and triblock copolymers.

6. Low molar mass water-soluble alkoxyamines

To perform nitroxide-mediated polymerization in emulsion, we were aware that using a water-soluble initiator was an essential condition, as shown very early by Marestin et al. when they applied a TEMPO-based alkoxyamine with a sulfate ionic group attached to the initiating radical [63]. However, using a water-soluble alkoxyamine in aqueous dispersed media totally differs, from the mechanistic viewpoint, from using an oil-soluble one because the dissociation and initiation steps take place in the water phase, where monomer and nitroxide concentrations are significantly different from those in the droplets. This can have a dramatic influence on the mass transfer from water to oil phase and hence on the nucleation step. To favour water-phase propagation together with a fast and quantitative entry of the chains into the latex particles (as propagating radicals or as dormant alkoxyamines), the aqueous concentration of nitroxide has to be reduced and an alkoxyamine initiator exhibiting a high dissociation rate constant should be used [60].

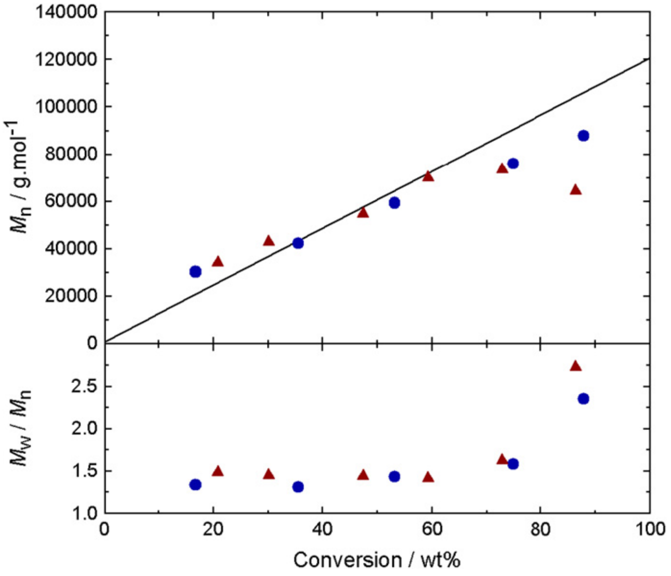


Fig. 9. Evolution of M_n and M_w/M_n with monomer conversion for the miniemulsion polymerization of *n*-butyl acrylate at 112 °C initiated by the DIAMS dialkoxyamine for various initial concentration of free SG1. (●): $r = [SG1]_0/2\times[DIAMS]_0 = 0.024$; (▲): $r = 0.040$.

The novel SG1-based alkoxyamine *N*-(*tert*-butyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxylprop-2-yl)hydroxylamine (MAMA, Scheme 5), originally synthesized by Tordo's research group and developed by Arkema under the trademark of BlocBuilder™, represented a breakthrough in NMP in homogeneous and aqueous dispersed media.

Indeed, the MAMA alkoxyamine presents important benefits as compared to other alkoxyamines used so far. Concerning our research, the most important feature was undoubtedly its water solubility due to the presence of the carboxylic acid function which allows the alkoxyamine to be readily turned into the corresponding salt (termed MAMA–Na) in alkaline solution. Moreover, due to the hydrophobicity of the SG1 group, the MAMA–Na exhibits surface activity in aqueous solution. For instance, the surface tension was $\gamma = 37.2$ mN m^{-1} at 0.05 mol L^{-1} and a critical micelle concentration (cmc) of ~0.065 mol L^{-1} was found, which is far above the typical initial concentration we used for our polymerizations [64,65]. The other important specificity concerns its steric hindrance which has been strongly increased as compared to MONAMS, owing to the tertiary carbon radical attached to the nitroxide. The direct consequence is a very high dissociation rate constant (0.3 s^{-1} at 120 °C) [66], which is expressed by a fast and quantitative initiation step. Thus, it is possible, for instance, to efficiently control the bulk polymerizations of styrene and even *n*-butyl acrylate without any initially introduced free SG1 [64].

6.1. Miniemulsion polymerization

Before directly moving toward emulsion polymerization, we firstly used this novel water-soluble alkoxyamine in aqueous miniemulsion polymerization [64]. The aim of this preliminary step was obviously to lay the foundations of work in true emulsion polymerization systems by investigating the ability of the MAMA–Na alkoxyamine to efficiently initiate and control the polymerization of *n*-butyl acrylate and styrene in a simplified system. Due to the water solubility of this alkoxyamine, special attention was given to mass transfer from the aqueous phase (locus of dissociation/initiation) to the oil phase (locus of polymerization) as well as to the colloidal characteristics of the latexes. Concerning *n*-butyl acrylate, very satisfying results were obtained. Polymerizations were fast (typically 90% conversion in 8 h) while exhibiting all the features of a controlled system; M_n increased linearly with monomer conversion following the theoretical line as a result of a high initiator efficiency and molar mass distributions were narrow (Fig. 10a). An increase of the polydispersity indices was, however, observed above 80% conversion which was not surprising with an acrylate at very high conversion due to side reactions such as chain transfer to polymer. Nevertheless, as expected from the high dissociation rate constant of the MAMA–Na alkoxyamine and the pronounced persistent radical effect, there was no difference in the polymerization rate whatever the initial concentration of added free SG1 (0 or 2.7 mol.%). Thus, there was no need to add free nitroxide at the onset of the polymerization to regulate the kinetics and to enhance the control, as had been the case with the MONAMS [56].

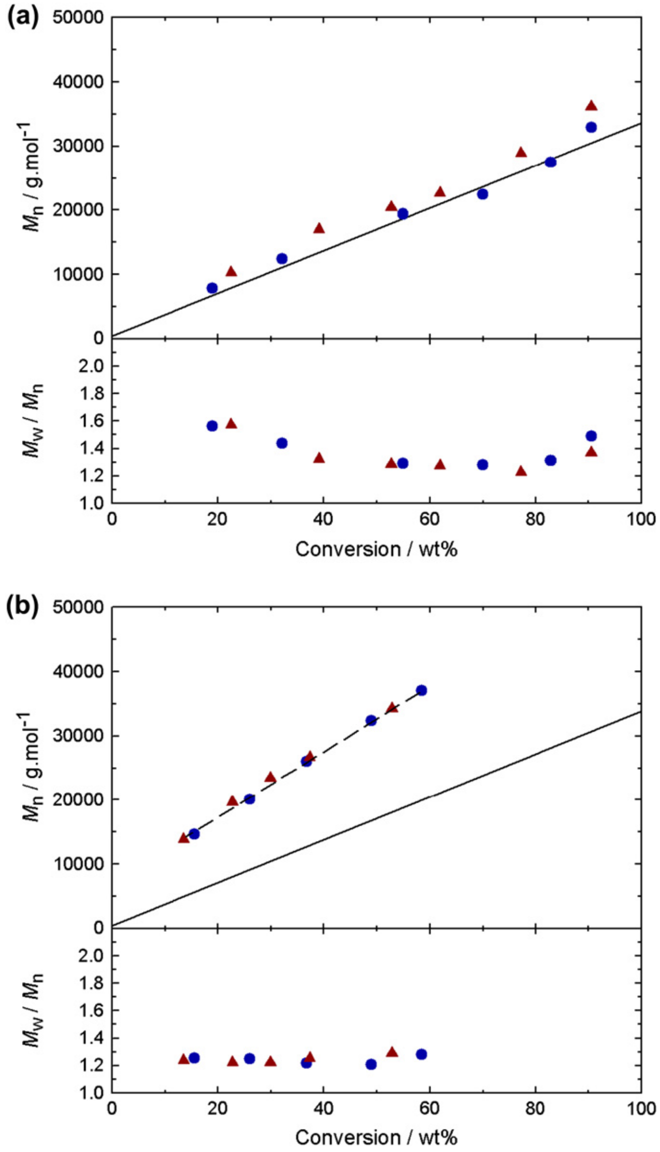


Fig. 10. Evolution of M_n and M_w/M_n with monomer conversion for the miniemulsion polymerization of *n*-butyl acrylate at 112 °C (a) and styrene at 120 °C (b), initiated by the MAMA–Na water-soluble alkoxyamine. (●): $r = [SG1]_0/[MONAMS]_0 = 0.027$; (▲): $r = 0$.

With styrene under similar conditions, the results were quite different. Even though a linear increase of M_n with monomer conversion together with low polydispersity indices supported the living character of the reaction, polymerization rate was slow (<60% conversion in 8 h) with an induction period of about 1 h and led to a poor initiator efficiency as low as 50% (Fig. 10b). This phenomenon was assumed to arise from the large activation–deactivation equilibrium constant, K, for polystyrene [9] leading to high concentration of propagating oligoradicals, promoting self-termination, mainly in the water phase. Such extensive termination resulted in low initiator efficiency together with a large concentration of nitroxide deactivator, which had the effect of strongly reducing the polymerization rate.

To support our explanation, miniemulsion polymerizations of styrene were performed under similar conditions but with small amounts of a suitable comonomer to enhance the rate of propagation in the water phase, to reduce the overall activation–deactivation equilibrium constant and thus to induce an efficient entry of living oligoradicals into monomer droplets. To fit the above-mentioned criteria, the comonomer should exhibit the following properties as compared with styrene: (i) a larger water solubility, (ii) a larger propagation rate constant and (iii) a lower activation–deactivation rate constant. Our first choice was acrylic acid but significant degradation of the nitroxide under such acidic conditions, leading to a complete loss of control, led us to choose methyl acrylate (MA) as an appropriate comonomer. Miniemulsion polymerizations of styrene were carried out with increasing amounts of methyl acrylate (0, 2.5, 5.1 and 10 molar equivalents based on the MAMA–Na) and results were in perfect agreement with what was expected. When increasing the initial concentration of methyl acrylate, polymerization rates were larger with no induction period (Fig. 11a). In parallel, the apparent initiator efficiency increased with the initial concentration of MA and an almost perfect match between experimental and predicted molar masses for $[MA]_0/[MAMA{-}Na]_0 = 10.0$ was reached, again with low polydispersity indices (Fig. 11b).

Latexes were synthesized at 20 wt% solids and stabilized by Dowfax 8390 surfactant at low concentration (2.2 wt% with respect to the monomer) in the presence of hexadecane. Their stability was assessed and neither coagulum nor destabilization over time was detected. An additional benefit derived from the use of the MAMA–Na as a water-soluble initiator was a strong improvement of the colloidal characteristics of the final latexes. Compared with latexes synthesized with MONAMS under the same conditions, the particle size distribution narrowed and the average diameters shifted toward

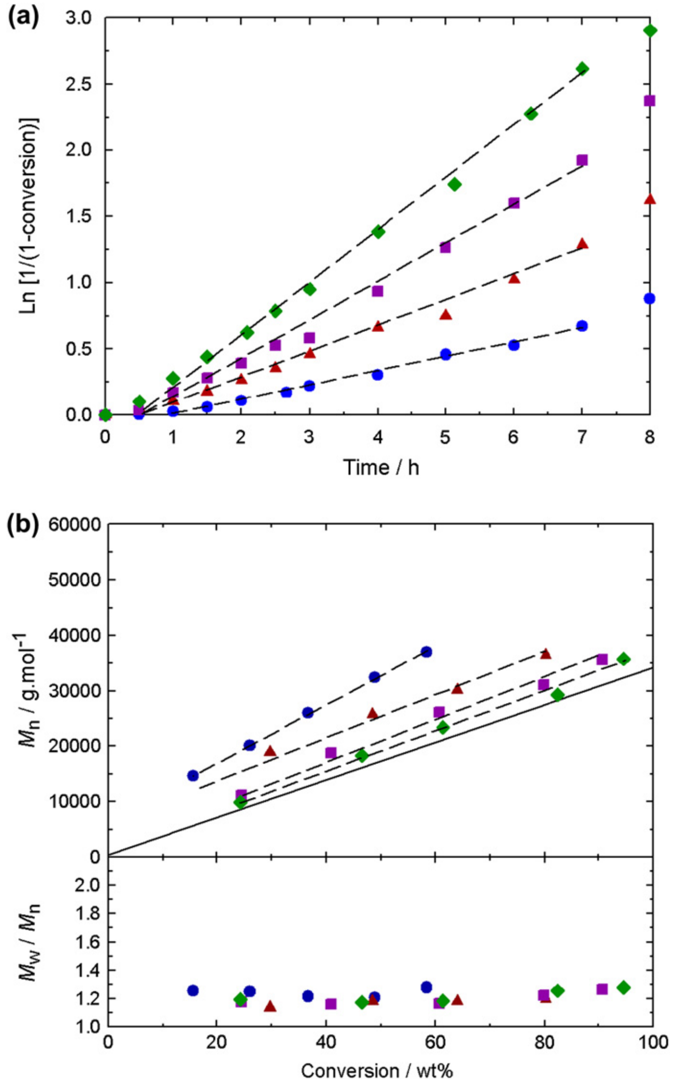


Fig. 11. Miniemulsion polymerization of styrene at 120 °C initiated by the alkoxyamine MAMA–Na as a function of the concentration of methyl acrylate (MA) as a comonomer. Evolution of the logarithmic conversion with time (a) and evolution of M_n and M_w/M_n with monomer conversion (b). (●): $[MA]_0/[MAMA{-}Na]_0 = 0$; (▲): $[MA]_0/[MAMA{-}Na]_0 = 2.5$; (■): $[MA]_0/[MAMA{-}Na]_0 = 5.1$; (◆): $[MA]_0/[MAMA{-}Na]_0 = 10.0$.

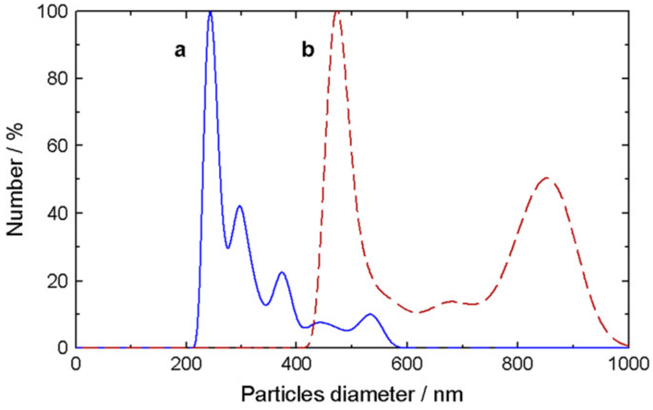


Fig. 12. Number distribution of particle diameter from capillary hydrodynamic fractionation (CHDF) analysis of the final latexes obtained by miniemulsion polymerizations of *n*-butyl acrylate at 112 °C initiated by the MAMA–Na (a) or by the MONAMS (b) alkoxyamines under identical experimental conditions.

lower values (Fig. 12). This trend was directly assigned to the negative charge of the MAMA–Na, a significant proportion of which may remain located at the water/polymer interface, increasing the surface charge density of the particles.

6.2. Emulsion polymerization

The first set of experiments we performed in emulsion polymerization was using a simple batch process. A typical *ab initio* batch emulsion polymerization starts with water, hydrophobic monomer(s), surfactant and water-soluble initiator, all ingredients being poured into the reaction vessel at the beginning of the reaction. Neither the addition of a hydrophobic compound nor the application of high shear is necessary for the polymerization process, which makes it more industrially viable. Due to the encouraging results obtained in miniemulsion polymerization with the water-soluble alkoxyamine MAMA–Na, the same initiator was also selected for the polymerizations of *n*-butyl acrylate and styrene at 20 wt% solids with various surfactants [67]. The polymerizations were well controlled whatever the monomer, with a linear increase of M_n with monomer conversion and low polydispersity indices (BA: $M_n = 21\,400{-}28\,200\ \text{g mol}^{-1}$, $M_w/M_n = 1.21{-}1.22$; S: $M_n = 31\,400\ \text{g mol}^{-1}$, $M_w/M_n = 1.26$). Interestingly with styrene, a poor initiation efficiency was also noticed (∼50%), identical to what was previously observed in miniemulsion. Unfortunately, in all cases, a substantial amount of coagulum was detected in the course of the polymerization, similarly to what is usually obtained in *ab initio* batch emulsion NMP [68]. Besides, no beneficial influence of the surfactant or other experimental parameters was detected [67,65]. The recurrent colloidal instability was ascribed to the partition of the initially formed oligomeric alkoxyamines between the water phase and the oil phase due to a slow chain-growth process contrary to conventional free-radical polymerization, leading to unwanted droplet nucleation. Thus, the remaining issue to address in order to successfully perform nitroxide-mediated emulsion polymerization was the improvement of the colloidal characteristics of the latexes.

The main problem being the entry of dormant oligomers in the large monomer droplets, successful NMP in emulsion was achieved by using a simple two-step process [67,69], in which this unwanted nucleation was avoided (Fig. 13). The first step was the preparation of a living poly(*n*-butyl acrylate) seed latex with low solids content (∼1 wt%), containing macro-alkoxyamine chains of low number-average degree of polymerization ($DP_n \sim 10$). Such a seed was prepared *via* an *ab initio* batch emulsion polymerization initiated by the MAMA–Na alkoxyamine and stabilized by the Dowfax 8390 surfactant in concentrations above its cmc. In this first step, due to the large surfactant over monomer molar ratio, the system mimics a microemulsion recipe preventing the existence of large droplets of monomer. Thus, the majority of the *n*-butyl acrylate monomer

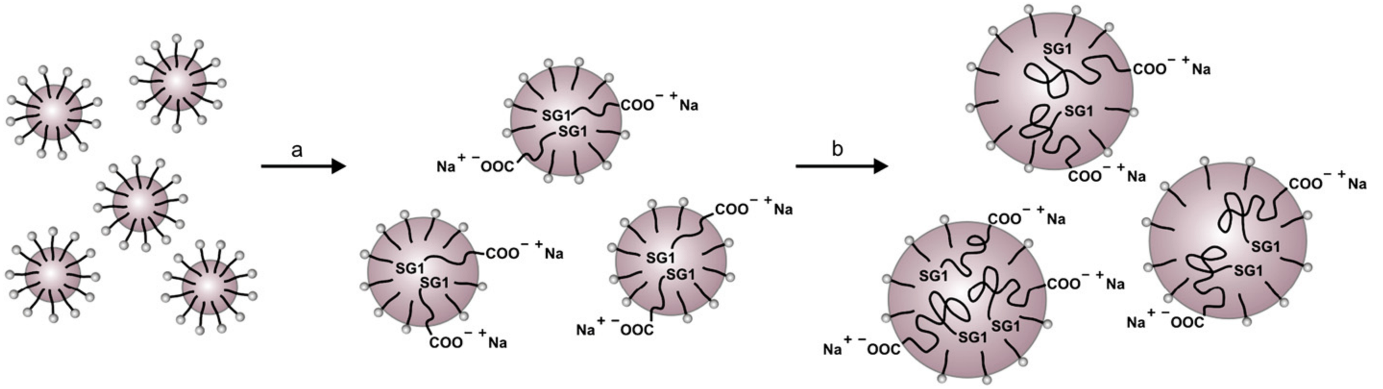


Fig. 13. Two-step SG1-mediated emulsion polymerization of *n*-butyl acrylate or styrene initiated with the water-soluble SG1-based alkoxyamine MAMA–Na. Synthesis of the living seed latex initiated by the MAMA–Na alkoxyamine (a) and extension of the living seed latex after "one shot" addition of monomer (b).

was either located in the water solution or in the swollen micelles. After 8 h of polymerization at 112 °C, perfectly stable living seed latexes were obtained with average diameters ($D_z = 160–210$ nm) varying in agreement with the initial surfactant concentration. Moreover, PBA oligomers exhibited very satisfying macromolecular characteristics ($M_n = 1000–1100\ \mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.14–1.20$), matching the predicted values. The second step consisted in a "one shot" addition of either *n*-butyl acrylate or styrene to target higher solids content and higher molar mass (for instance 16 wt% and theoretical $M_n \sim 35\,000\ \mathrm{g\,mol^{-1}}$ at full conversion), followed by the resumption of the polymerization simply by heating for another 8 h.

All polymerizations exhibited fast kinetics with almost complete conversion (85–95% conversion within 8 h) together with controlled molar masses and narrow molar mass distributions. The experimental M_ns were very close to the theoretical values, indicating high reinitiation efficiency, which was a proof of the high degree of livingness of the PBA oligo-alkoxyamines in the seed (Fig. 14). However, the most important result was undoubtedly that all recovered latexes were very stable with neither coagulum nor destabilization over time for at least one year [65]. However, particle size distributions were broad with rather large average diameters, in the 260–660 nm range, depending on the initial concentration of surfactant (corresponding, to final concentrations in Dowfax 8390 as small as 2.2 or 5.1 wt% based on the monomer). The flexibility of our process was also illustrated by a three-step synthesis of a poly(*n*-butyl acrylate)-*b*-polystyrene diblock copolymer simply by adding styrene after the synthesis of the PBA block [67]. All the features of a controlled system were maintained with the linear increase of the number-average molar mass with monomer conversion up to 80%, obtained within 8 h. In an example, the diblock copolymer had $M_n = 61\,000\ \mathrm{g\,mol^{-1}}$ and $M_w/M_n = 1.4$ and again, a stable latex with solids as high as 26 wt% was recovered ($D_z = 330$ nm).

Following this discovery, we wanted to move forward by increasing the complexity of the macromolecular architectures and by improving the colloidal characteristics of the latexes. Ideally, the synthesis of well-defined triblock copolymers, a perfect control of the average diameter as well as the production of latexes with narrow particle size distribution were our next challenges. Basically, all requirements were met by using a novel SG1-based water-soluble difunctional alkoxyamine, DIAMA (Scheme 6). This new alkoxyamine was readily prepared by intermolecular radical 1,2-addition of the MAMA monofunctional alkoxyamine onto tri(ethylene glycol) diacrylate at 100 °C for 1 h in *tert*-butanol with good yield [70]. This simple synthetic route is quite versatile and can be applied to the preparation of a variety of mono- and multifunctional alkoxyamines [71,72]. Mechanistically speaking, due to the low cleavage temperature of the starting MAMA alkoxyamine ($T_c < 50$ °C), intermolecular radical 1,2-addition can be performed onto activated olefins leading to new alkoxyamines with lower dissociation rate constants and hence higher stability at the reaction temperature. Again, the DIAMA–Na dialkoxyamine is fully water-soluble in alkaline solution with surface activity ($\gamma = 38.7\ \mathrm{mN\,m^{-1}}$ at $0.02\ \mathrm{mol\,L^{-1}}$), but with no well-identified cmc.

As with the MAMA–Na initiator, all our attempts to produce stable latexes by *ab inito* batch emulsion polymerization failed. As a consequence, the DIAMA dialkoxyamine was employed to initiate the polymerization of *n*-butyl acrylate or styrene in the same two-step emulsion polymerization protocol as previously used. In the synthesis of living difunctional PBA seed latexes, the chains exhibited good macromolecular characteristics: $M_n = 1400–1450\ \mathrm{g\,mol^{-1}}$ and $M_w/M_n = 1.33–1.36$. More interestingly, a dramatic decrease of the average particle diameter, compared to those formed in the presence of MAMA–Na under identical experimental conditions, was noticed. For instance, with the same surfactant concentration, [Dowfax 8390] $= 6.9 \times 10^{-3}\ \mathrm{mol\,L^{-1}}$, dynamic light scattering (DLS) measurement gave $D_z = 60$ nm with DIAMA–Na, whereas it was 210 nm with MAMA–Na. This important decrease of the average diameter of the PBA living seed particles may be ascribed to the double negative charge provided by the DIAMA–Na, improving the colloidal stabilization. Moreover, as long as only one of the two alkoxyamine groups of DIAMA–Na dissociates at the same time (which is highly probable), the initiator can keep its surface-activity during the initiation/nucleation step and thus contributes to the stabilization, contrary to the monofunctional MAMA–Na, for which

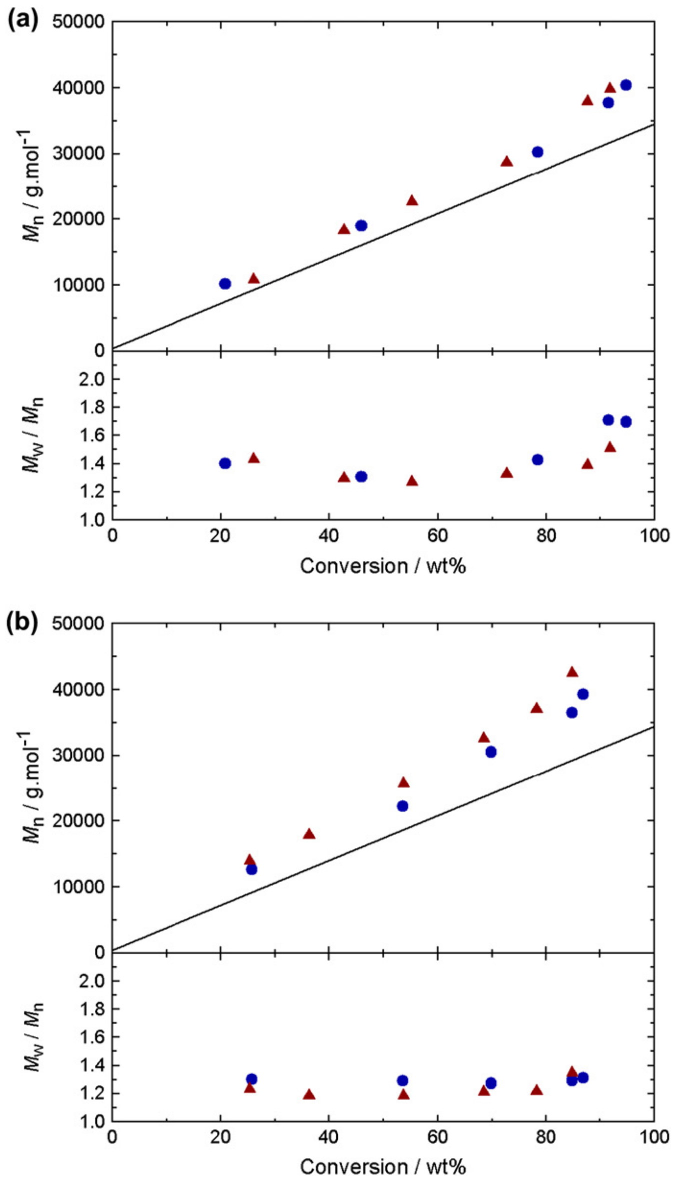
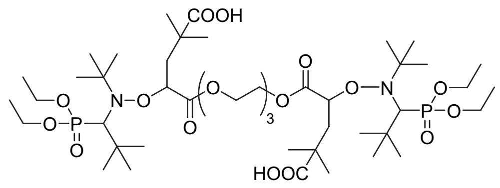


Fig. 14. Two-step SG1-mediated emulsion polymerization of *n*-butyl acrylate at 112 °C (a) or styrene at 120 °C (b) initiated by the MAMA–Na alkoxyamine as a function of the initial surfactant concentration. (●): [Dowfax 8390] = 6.89 × 10^{-3} mol L^{-1}; (▲): [Dowfax 8390] = 1.54 × 10^{-2} mol L^{-1}.

the initiating moiety (sodium methacrylate-based radical) is fully water-soluble. Finally, the favourable impact of the short poly(ethylene glycol) spacer of the DIAMA–Na over the stabilization mechanism, even if not investigated, cannot be ruled out.

Various difunctional poly(*n*-butyl acrylate) living seeds containing different initial surfactant concentrations were then extended by a ‘‘one shot’’ addition of monomer (either *n*-butyl acrylate or styrene) to reach higher solids content latexes [70]. In all cases, fast polymerizations were observed (typically 90% conversion after 8 h) and molar masses increased linearly with monomer conversion closely to the theoretical values with low polydispersity indices (Figs. 15 and 16).

Perfectly stable 16 wt% latexes with small amounts of surfactant were again recovered and, as anticipated from the previous results concerning the living seeds, all final latexes exhibited smaller diameters than those initiated with the



Scheme 6. Structure of the water-soluble SG1-based dialkoxyamine DIAMA (DIAMA–Na in the sodium salt form).

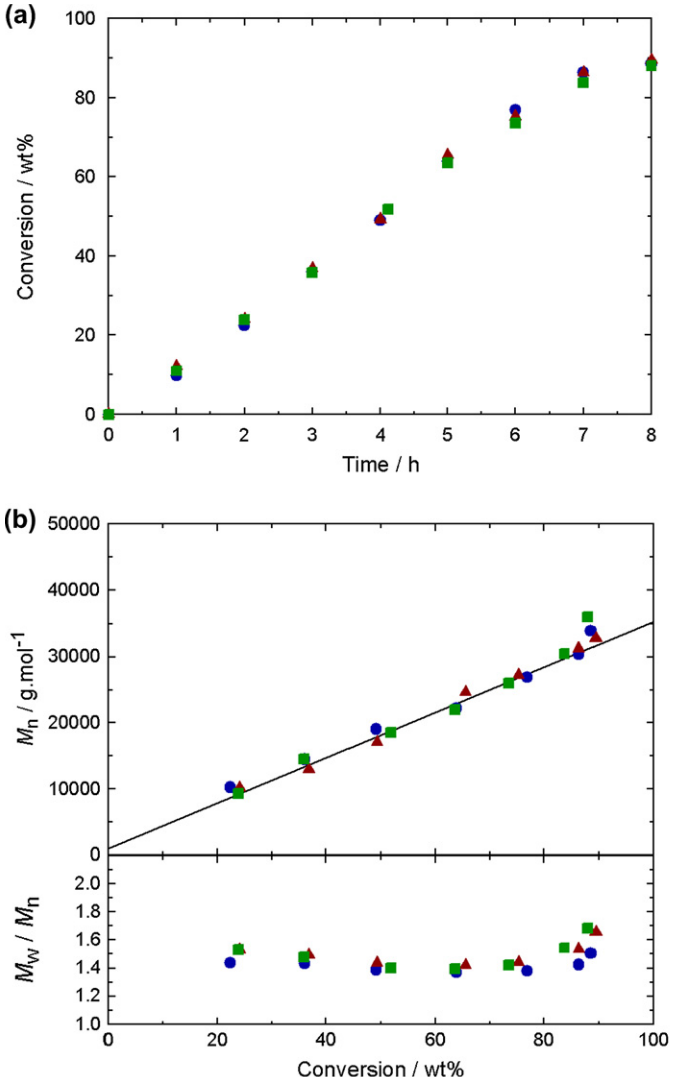


Fig. 15. Two-step SG1-mediated emulsion polymerization of *n*-butyl acrylate at 112 °C initiated by the DIAMA–Na alkoxyamine as a function of the initial surfactant concentration. Evolution of monomer conversion with time (a) and evolution of M_n and M_w/M_n with monomer conversion (b). (●): [Dowfax 8390] = 6.88 × 10^{-3} mol L^{-1}; (▲): [Dowfax 8390] = 3.02 × 10^{-3} mol L^{-1}; (■): [Dowfax 8390] = 1.52 × 10^{-3} mol L^{-1}.

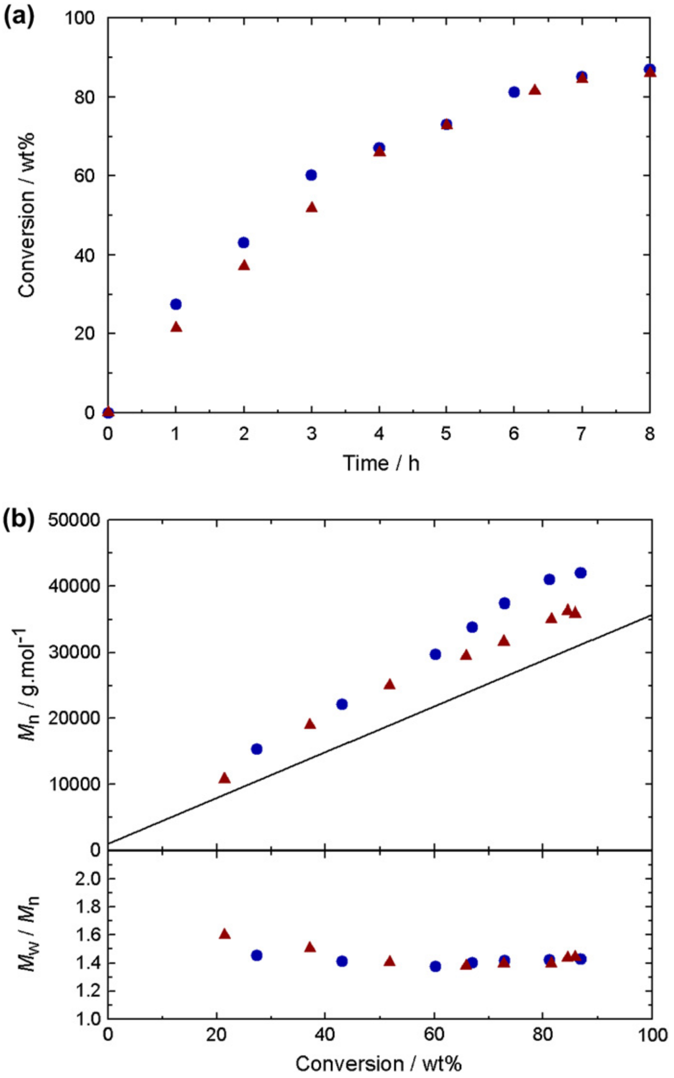


Fig. 16. Two-step SG1-mediated emulsion polymerization of styrene at 112 °C initiated by the DIAMA–Na alkoxyamine as a function of the initial surfactant concentration. Evolution of monomer conversion with time (a) and evolution of M_n and M_w/M_n with monomer conversion (b). (●): [Dowfax 8390] = 1.50×10^{-2} mol L^{-1}; (▲): [Dowfax 8390] = 6.70×10^{-3} mol L^{-1}.

MAMA–Na alkoxyamine, other experimental conditions being identical. For instance, DLS gave $D_z = 660$ nm for a final PBA latex at 2.2 wt% surfactant based on the monomer when the MAMA–Na was used, whereas $D_z = 170$ nm with the DIAMA–Na. Moreover, the most important improvement was a strong narrowing of the particle size distribution as shown by DLS measurements and TEM images (Fig. 17). In addition, according to particle numbers, no secondary nucleation seemed to occur in this two-step emulsion polymerization process. Starting from a PBA living seed, we also took benefit of the divergent chain-growth induced by the difunctional alkoxyamine to synthesize a polystyrene-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene triblock copolymer (1:1 mol:mol of S and BA) by sequential monomer additions [70]. Addition of styrene was performed at 71% conversion of BA in the second step, in order to minimize termination and/or transfer reactions and polymerization was resumed for 8 h. Molar masses continued to follow the predicted values and reached 51 000 g mol^{-1} for a final $M_w/M_n = 1.64$, which was satisfying for such a complex architecture in aqueous dispersed media. The formation of a block copolymer was also demonstrated by LAC, where the sharp peak accounted for a narrow composition distribution.

It is now well accepted that the industrial application of all CRP methods might depend on the development of suitable waterborne processes, in direct relation with ever increasing environmental constraints. We therefore aimed at improving our two-step process and moved forward a semibatch NMP process [73]. From an industrial viewpoint, a semibatch process offers important flexibility in latex production because, contrary to the batch counterpart, it allows additional experimental parameters such as the flow rate and the moment of component introduction (monomer, surfactant, initiator, etc.) to be precisely monitored, which favours better control over the latex properties. Basically, the living seeds were polymerized during variable, short periods of time, typically from 0.5 to 2 h, just to allow particles to be formed. Then, during the course of the polymerization, a continuous addition of the required monomer was performed over a period of ~3 h; polymer chains were extended under controlled/living conditions

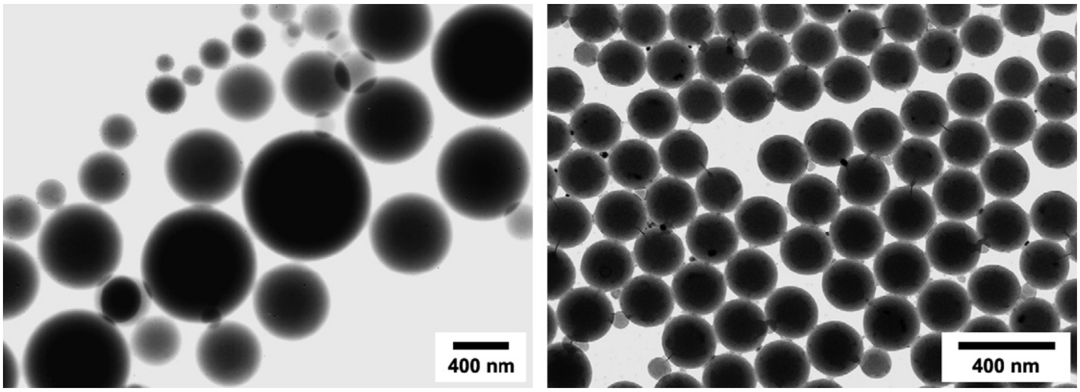


Fig. 17. Final transmission electron micrographs of the PS latexes synthesized by the two-step SG1-mediated emulsion polymerization process, initiated with the MAMA–Na (left) or with the DIAMA–Na (right). [Dowfax 8390] = 6.9×10^{-3} mol L^{-1}.

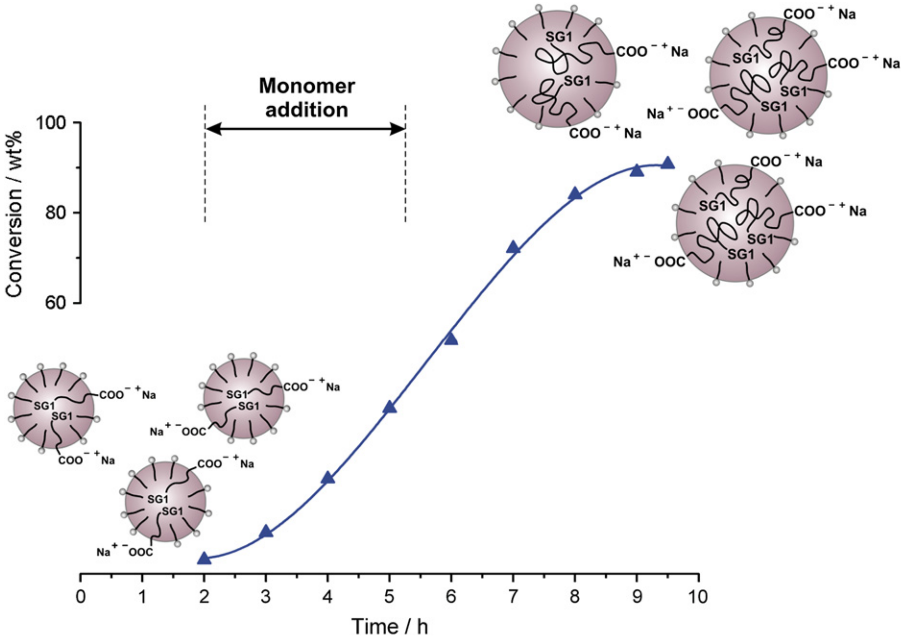


Fig. 18. Typical semibatch SG1-mediated emulsion polymerization using the MAMA–Na alkoxyamine as a water-soluble initiator.

and the latexes simultaneously reached higher solids content in a reduced period of time (Fig. 18). It is worth mentioning that the addition was fast enough with respect to the polymerization rate to avoid starved conditions, which would increase the impact of side reactions.

This process was successfully applied to the polymerization of *n*-butyl acrylate, initiated either by MAMA–Na or by DIAMA–Na. With the monofunctional alkoxyamine, high conversions were reached in less than a working day and the polymerization rate during the second step (monomer addition) was strongly reduced when duration of the first step (creation of the seed latex) was longer, as a result of larger concentration of free SG1 released by irreversible terminations (Fig. 19). Polymerizations exhibited all the features normally expected for a controlled system, i.e. a linear evolution of the molar masses with BA conversion, very close to the calculated values together with low polydispersity indices throughout the polymerization, even at high conversion. Average diameters were in direct relation with the initial concentration of Dowfax 8390 and, not surprisingly, a broad particle size distribution was noticed. The same quality of control was witnessed with the DIAMA–Na dialkoxyamine as well as its ability to narrow the particle size distribution.

Very recently, we also investigated the ability of the block copolymers to self-assemble and spontaneously produce nanostructured latex particles [74]. AFM (atomic force microscopy) and TEM images of latex films obtained from 27% solid suspensions of PBA-*b*-PS or PMMA-*b*-PBA-*b*-PMMA (with PMMA: poly(methyl methacrylate)) block copolymers synthesized by the multistep emulsion polymerization process (the PMMA outer blocks of the latter being obtained in an uncontrolled fashion) revealed the occurrence of ''onion-like'' lamellar microphases inside the latex particles, providing the purity of the second/outer block(s) and the copolymer molar mass was high enough (Fig. 20). It was also shown that this particular organization was not affected by the molar mass distribution and evolved toward more classical block copolymer lamellar morphologies upon re-dissolution and/or annealing of the latex films (Fig. 20b and c).

7. Water-soluble macro-alkoxyamine

After the use of water-soluble low molar mass alkoxyamines, we decided to apply water-soluble macro-alkoxyamine initiators for the polymerization of hydrophobic monomers such as styrene and *n*-butyl acrylate. In those conditions, we chose to avoid the addition of surface-active material and to work in surfactant-free, batch emulsion polymerization. *In situ* formation of amphiphilic diblock copolymer nanoparticles was thus targeted in a single polymerization step. The macro-alkoxyamine initiator was poly(acrylic acid) (PAA), which was used in alkaline conditions. The first challenge was actually to produce a SG1-terminated PAA, with high chain-end functionality. Usually, well-defined PAA is afforded by the living polymerization of *tert*-butyl acrylate or other acrylic ester, followed by deprotection *via* either acidolysis or thermolysis, depending on the protecting ester group. The method was, however, not considered as fully satisfying for preserving the living end-functionality. In our group, we studied the direct SG1-mediated homopolymerization of acrylic acid at 120 °C in an organic solvent, typically 1,4-dioxane [35]. All conditions were carefully chosen in order to synthesize low molar mass PAA–SG1 with more than 90% alkoxyamine end-group: it was for instance important to use a large concentration of the alkoxyamine initiator (MONAMS) and to stop the polymerization at incomplete conversions, to avoid the influence of chain transfer to the solvent (this side reaction, as well as transfer to polymer, had to be considered

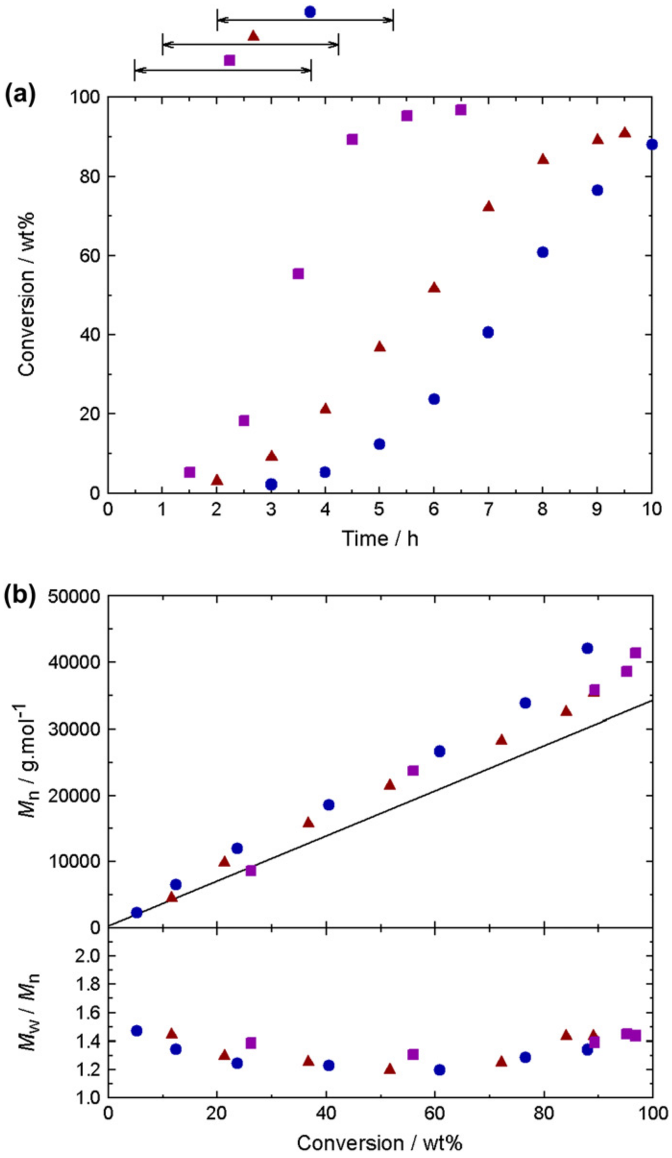


Fig. 19. Semibatch SG1-mediated emulsion polymerization of *n*-butyl acrylate at 112 °C initiated by the MAMA–Na alkoxyamine as a function of the seed polymerization time (t_{seed}). Evolution of monomer conversion with time (a) and evolution of M_n and M_w/M_n with monomer conversion (b). (●): $t_{seed} = 2$ h; (▲): $t_{seed} = 1$ h; (■): $t_{seed} = 0.5$. The horizontal arrows define the periods of *n*-butyl acrylate addition.

owing to the high reactivity of the propagating radicals derived from acrylic monomers). A thorough chain-end characterization allowed us to demonstrate the high quality of the PAA-based macroinitiators [36].

The living homopolymers shown in Scheme 7 were used as macroinitiators for the polymerization of styrene and *n*-butyl acrylate in alkaline water at 120 °C [75]. The polymerization mixture was composed of a very limited number of reagents: macroinitiator in the sodium salt form, monomer and water. Additionally, free SG1 and an electrolyte were introduced for some experiments to test their effect on the polymerization kinetics and particle size, respectively. In the absence of surfactant, the initial monomer/water (20:80, w/w) mixture was an unstable emulsion but, upon polymerization, a stable latex formed with high conversion rate (typically 90% conversion within 8 h, independent of the monomer). Unlike the previous experiments with a low molar mass alkoxyamine initiator, no flocculation was observed provided that the degree of polymerization of the macroinitiator was large enough (20 or 38). Spherical particles were recovered with a diameter generally below 100 nm and very narrow particle size distribution; the average particle diameter was systematically larger for poly(*n*-butyl acrylate) than for polystyrene (Fig. 21).

Based on the size exclusion chromatography analyses, asymmetrical poly(sodium acrylate)-*b*-polystyrene and poly(sodium acrylate)-*b*-poly(*n*-butyl acrylate) amphiphilic diblock copolymers with short hydrophilic block and long hydrophobic block were generated during the heterophase polymerization. The macroinitiator efficiency was below 1, indicating an important effect of the irreversible termination reactions, most probably in the aqueous phase, but a linear increase of M_n *vs* monomer conversion was witnessed in all cases along with satisfying polydispersity indices. The diblock copolymers self-assembled into nanoparticles analogous to crew-cut micelles and exhibited a pH sensitive diameter, corroborating the location of the poly(sodium acrylate) block at the particle surface (Fig. 22). The particle size was a function of the macroinitiator concentration and chain length: it increased when the concentration was decreased and when the length was increased. In contrast, the salt concentration had no particular effect [76].

The method was further extended to a water-soluble monomer, i.e. *N*,*N*-diethylacrylamide (DEAAm), the homopolymer of which exhibits a LCST (lower critical solution temperature) at 32 °C in aqueous solution. In such conditions, the polymerization system can be considered as a dispersion polymerization since the initial mixture was a solution but the polymer, being insoluble at the polymerization temperature, phase-separated. Submicronic polymer particles with a thermally responsive core of poly(*N*,*N*-diethylacrylamide) (PDEAAm) and pH responsive shell of poly(sodium acrylate) (PNaA) were then prepared *in situ* [77]. At room temperature and alkaline pH, the particles dissociated to form a solution of double hydrophilic diblock copolymers; when the temperature was increased above the LCST, the copolymer chains self-assembled again, but the particles exhibited a larger size than the original ones; at low temperature and low pH, they formed ‘‘inverse’’ particles, whereas precipitation occurred at low pH and high temperature. When *N*,*N*′-methylenebisacrylamide (MBAAm) was used as a cross-linker from the onset of the dispersion polymerization reaction, cross-linked particles formed when the concentration of the difunctional monomer was maintained rather low (typically below 3 mol.% based on the DEAAm monomer) (Fig. 23), whereas macrogelation was observed at larger concentration. To overcome this insufficient control over particle size, the introduction of the cross-linker was performed after the nucleation step. In such conditions (from 3 to 10 mol.% MBAAm), macrogels were not observed anymore, but thermo-responsive hydrogel particles which exhibit a diameter close to 100 nm or below, with a cross-linked, thermally

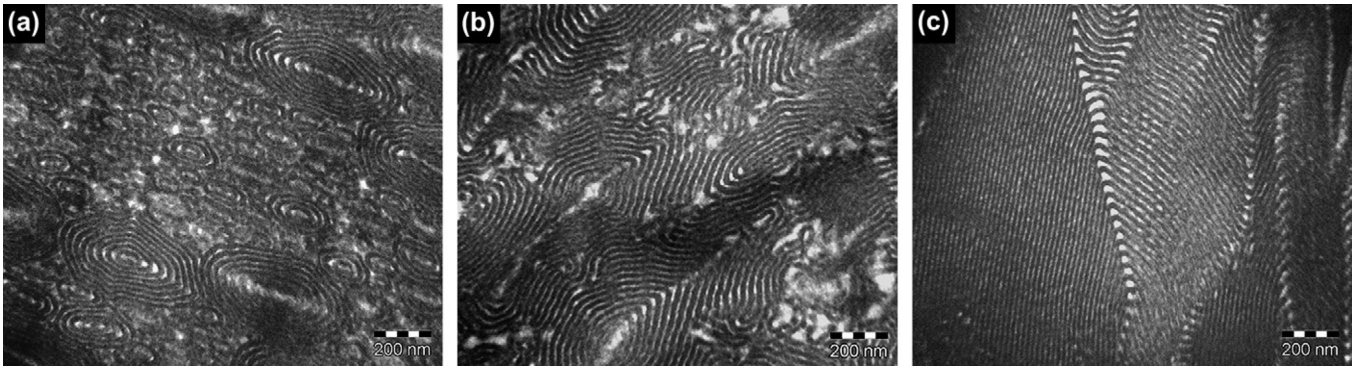
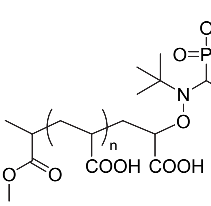


Fig. 20. Transmission electron micrographs of latex films obtained from a 27 wt% solids PBA-*b*-PS diblock copolymer suspension following different thermal treatments. Drying of the latex at room temperature during 4 days (a); annealing of the latex film at 150 °C under vacuum for 48 h (b) and re-dissolution of the latex film in dichloromethane and annealing under vacuum at 150 °C for 48 h (c).



Scheme 7. Structure of the poly(acrylic acid) SG1-based macro-alkoxyamine (PAA–SG1). $n+1 = 14$, 20–21 or 38.

responsive core stabilized by covalently attached PNaA chains.

As a conclusion, the use of a polyelectrolyte macro-alkoxyamine initiator offers the possibility to achieve *ab initio* batch emulsion and dispersion polymerizations. Moreover, the method combines many advantages over classical self-assembly of preformed diblock copolymers. In particular, particles can be synthesized with a limited number of steps, directly in the water phase. A cross-linking reaction can be performed simultaneously to the growth step and, thanks to the living character of the polymerization, the cross-linker addition can be triggered at any time, while preserving the possibility of covalently binding all growing chains.

8. Brief comparison with the other CRP methods

Preformed alkoxyamine initiators are particularly advantageous in nitroxide-mediated controlled free-radical polymerization as they allow the polymerization kinetics and polymer molar mass to be finely tuned in a very simple and efficient manner, using thermal activation. Consequently, the system requires neither the use of an additional initiator like the RAFT method (reversible addition–fragmentation chain transfer) nor that of an activator like in ATRP (atom transfer radical polymerization). This is a real advantage in heterophase systems like emulsion polymerization, for which the initiation and propagation processes do not take place in the same phase. It is the reason why RAFT and ATRP were mainly applied in miniemulsion polymerization systems [78,79]. Nevertheless, with RAFT, the use of an asymmetrical trithiocarbonate chain transfer agent allowed an emulsion polymerization system to be set with success provided that a short poly(sodium acrylate) first block was created *in situ*, followed by slow and continuous addition of the hydrophobic monomer(s) [80]. In batch conditions where a water-soluble macro(RAFT agent) was used, it was shown to play the role of a stabilizer as an amphiphilic diblock copolymer was created *in situ*, but

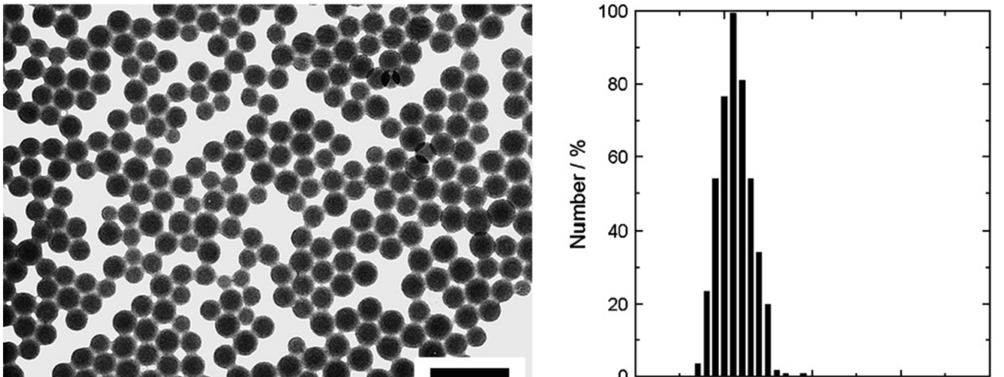


Fig. 21. Transmission electron microscopy (TEM) image and associate particle size distribution of 20 wt% surfactant-free polystyrene nanoparticles obtained by NMP in *ab initio* emulsion polymerization initiated by the $PNaA_{20}$–SG1 water-soluble macro-alkoxyamine.

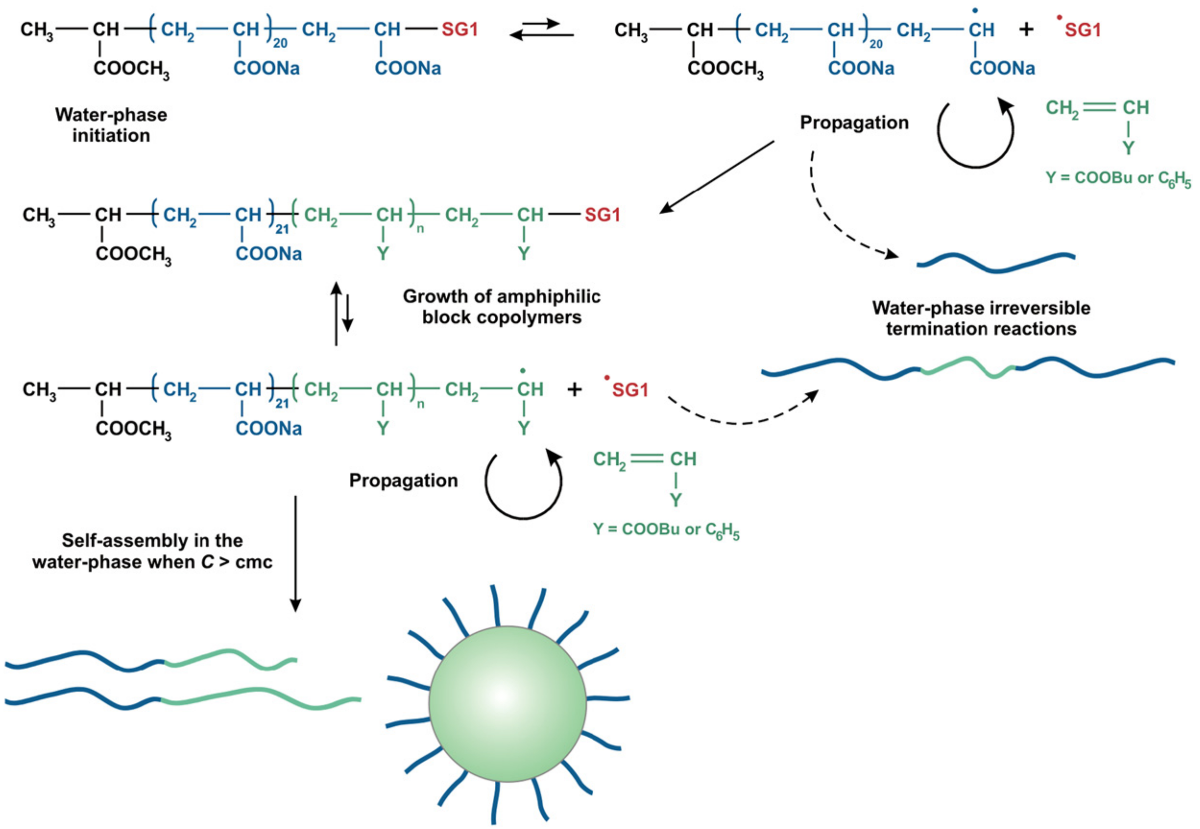


Fig. 22. Proposed particles' formation mechanism in surfactant-free emulsion polymerization initiated by a poly(sodium acrylate) SG1-based macro-alkoxyamine (PNaA−SG1).

control of the polymerization was not effective [81,82]. With ATRP, the activator (Cu(I) complex for instance) and deactivator (Cu(II) complex for instance) have to be located in the polymerization locus (miniemulsion or microemulsion droplets) together with the oil-soluble alkyl halide initiator, so that all reactions occur in the organic phase of the system. Only reverse ATRP was successful in emulsion polymerization, using a classical water-soluble radical initiator and Cu(II) complex deactivator. Well controlled polymerizations were usually achieved, exhibiting a linear increase of molar mass with monomer conversion and low polydispersity index, but the initiator efficiency remained invariably low, as the consequence of extensive termination reactions in the water phase [83−85]. Water-soluble alkyl halide initiators (low molar mass or polymeric) have never been reported so far; nevertheless, a two-step emulsion polymerization recipe, very similar to ours, was successfully applied, using a microemulsion polymerization in the first stage, along with the AGET (activator generated by electron transfer) initiation method [86].

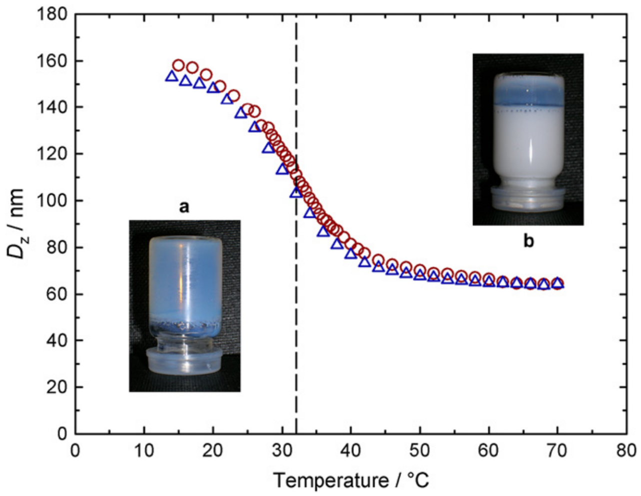
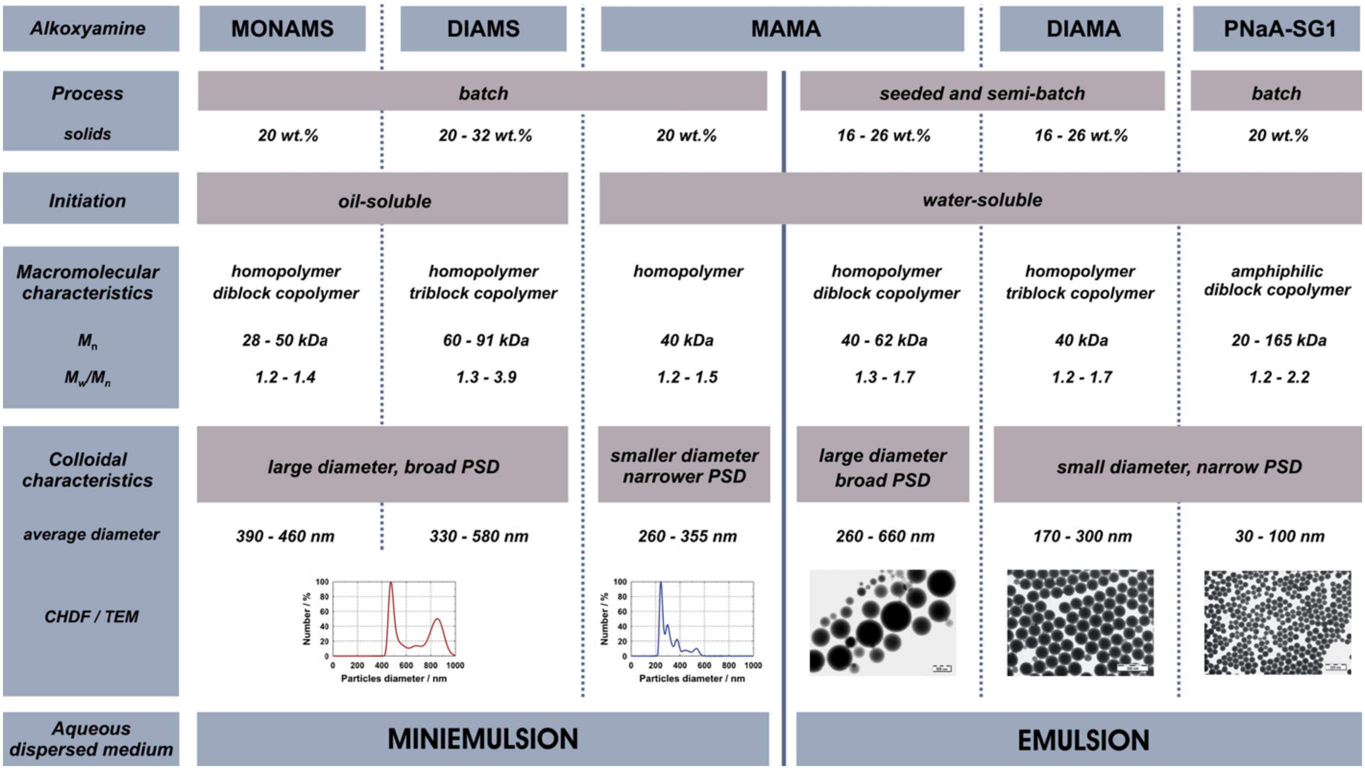


Fig. 23. Effect of the temperature ((○): heating; (△) cooling) on the hydrodynamic diameter (DLS measurement at pH = 8) of the PNaA shell-PDEAAm microgel core nanoparticles with 1.0 mol.% MBAAm based on monomers. Inset: pictures of the final polymerization medium below (a) and above (b) the LCST of PDEAAm.

9. Conclusion

The successful application of nitroxide-mediated polymerization: (i) to up-scalable emulsion polymerization recipes with formation of well-defined homopolymers as well as gradient, diblock and triblock copolymers, (ii) to latexes exhibiting well controlled colloidal properties in terms of average diameter and particle size distribution, (iii) to the design of surfactant-free amphiphilic block copolymer core−shell nanoparticles by an *in situ* synthesis and (iv) to spontaneously nanostructured particles and materials, was the result of an intensive work based on the nitroxide SG1 (Fig. 24). At the



Alkoxyamine	MONAMS	DIAMS	MAMA		DIAMA	PNaA-SG1
Process	batch			seeded and semi-batch		batch
solids	20 wt.%	20 - 32 wt.%	20 wt.%	16 - 26 wt.%	16 - 26 wt.%	20 wt.%
Initiation	oil-soluble		water-soluble			
Macromolecular characteristics	homopolymer diblock copolymer	homopolymer triblock copolymer	homopolymer	homopolymer diblock copolymer	homopolymer triblock copolymer	amphiphilic diblock copolymer
M_n	28 - 50 kDa	60 - 91 kDa	40 kDa	40 - 62 kDa	40 kDa	20 - 165 kDa
M_w/M_n	1.2 - 1.4	1.3 - 3.9	1.2 - 1.5	1.3 - 1.7	1.2 - 1.7	1.2 - 2.2
Colloidal characteristics	large diameter, broad PSD		smaller diameter narrower PSD	large diameter broad PSD	small diameter, narrow PSD	
average diameter	390 - 460 nm	330 - 580 nm	260 - 355 nm	260 - 660 nm	170 - 300 nm	30 - 100 nm
CHDF / TEM						
Aqueous dispersed medium	MINIEMULSION			EMULSION		

Fig. 24. Global overview of waterborne NMP systems using SG1-based oil- and water-soluble alkoxyamines, with typical macromolecular and colloidal characteristics of *n*-butyl acrylate and styrene (co)polymers and associated latexes.

beginning, it started with the understanding of the miniemulsion polymerization process as a simplified model of emulsion polymerization. All the experimental conditions and parameters were carefully investigated to check the viability of the SG1-mediated miniemulsion polymerization technique. Then, its transfer to emulsion polymerization processes, such as *ab initio* batch, seeded and semibatch, was successfully performed thanks to the development of appropriate water-soluble SG1-based (macro)alkoxyamines. In the end, all the features of a controlled/living system together with tunable colloidal characteristics were shown to be easily achieved in emulsion polymerization, which was unprecedented in this field. NMP remains a very convenient and environmentally friendly way to carry out such heterophase polymerizations since a single molecule is responsible for both the initiation and control *via* a thermal activation process and no post-polymerization purification step is required.

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