Surfactant-free synthesis of amphiphilic diblock copolymer nanoparticles *via* nitroxide-mediated emulsion polymerization†

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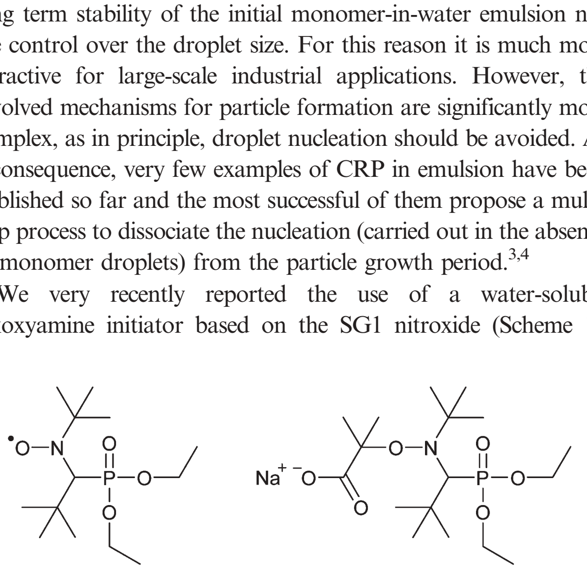
Amphiphilic hairy nanoparticles are prepared in a one step, batch, heterogeneous polymerization of styrene or *n*-butyl acrylate, using a water-soluble poly(sodium acrylate) alkoxyamine macroinitiator based on the SG1 nitroxide.

Controlled/living free-radical polymerization (CRP) is a powerful tool to synthesize tailor-made macromolecules without the drawbacks of the ionic polymerization methods.[1] In particular, it can be applied to complex processes such as aqueous dispersed systems, which are of high academic and industrial interest. In this domain, miniemulsion and emulsion polymerizations are the techniques of choice to produce submicron latex particles. Although studied for more than five years now, those processes were not applied very easily to CRP, whatever the selected system.[2] The general conclusion drawn so far is that the colloidal characteristics were usually poor (large particles, broad particle size distribution), whereas the control over the molar mass, molar mass distribution and (co)polymer architecture could be as good as in the corresponding homogeneous systems. In all cases, however, the latex stability was much better controlled in miniemulsion than in emulsion polymerization. The latter is much simpler than the former from the process viewpoint, since it requires neither the long term stability of the initial monomer-in-water emulsion nor the control over the droplet size. For this reason it is much more attractive for large-scale industrial applications. However, the involved mechanisms for particle formation are significantly more complex, as in principle, droplet nucleation should be avoided. As a consequence, very few examples of CRP in emulsion have been published so far and the most successful of them propose a multi-step process to dissociate the nucleation (carried out in the absence of monomer droplets) from the particle growth period.[3,4]

We very recently reported the use of a water-soluble alkoxyamine initiator based on the SG1 nitroxide (Scheme 1), allowing to produce stable, high solids content latexes, in a two-step emulsion polymerization process.[4] Such a small alkoxyamine with a simple sodium carboxylate group however did not prevent droplet nucleation and therefore the *ab initio* batch polymerizations did not lead to stable latexes. At this stage we thought the system might be improved by increasing the water-solubility of the alkoxyamine initiator.



Scheme 1 Structure of the SG1 nitroxide (left) and the water-soluble alkoxyamine initiator (right).

On this basis, we report here a new and very simple way to perform nitroxide-mediated emulsion polymerization of styrene (S) and *n*-butyl acrylate (BA) in a single batch step. The selected initiator is a SG1-terminated poly(sodium acrylate). Besides a better control over the initiation locus (*i.e.* the water phase), the method is also a one-step strategy to prepare, *in situ*, poly(acrylic acid)-based hairy nanoparticles, analogous to block copolymer crew-cut micelles,[5] without the need of an organic co-solvent to induce the self-association in water.

The strategy, however, might not be achievable without the availability of SG1-terminated poly(acrylic acid)-based macroinitiators. Actually, their synthesis has been reported quite recently, when we demonstrated that acrylic acid could be directly polymerized in a living way, using SG1-mediated polymerization in 1,4-dioxane solution at 120 °C.[6] When the experimental conditions were properly selected so as to target low molar mass poly(acrylic acid)s, a living polymer was recovered with approximately 95% alkoxyamine end-functionality.[6b] It is this type of SG1-terminated, pH-sensitive homopolymer we propose to use as a water-soluble macroinitiator under alkaline conditions: M_n = 1900 g mol^{-1} in the acidic form, after precipitation (DP$_n$ = 21), M_w/M_n = 1.17 (macroinitiator identified as PNaA$_{21}$-SG1).

The heterogeneous polymerizations were carried out in batch, at 120 °C, under 3 bar pressure of nitrogen, in a 300 mL thermostated glass reactor stirred at 300 rpm. In a typical recipe, 38 g of the monomer (S or BA, 20 wt% based on water) was added at room temperature to an aqueous NaOH solution (150 mL, 0.12 mol L^{-1} = 1 equiv. NaOH based on the acrylic acid groups; 36 mM K_2CO_3) containing the required amount of macroinitiator (2.12 g, 0.006 mol L$_{aq}$$^{-1}$; 5 wt% based on the hydrophobic monomer). The obtained unstable biphasic system (note that no surfactant was added) was introduced into the preheated and stirred reactor, after nitrogen bubbling for 20 min at room temperature. The polymerizations were allowed to proceed for 8 h. During the polymerization course, 10 mL samples were taken at regular time intervals to follow the monomer conversion by gravimetry and to analyze the polymer and the particles according to the methods described in the ESI.† After complete polymerization, the products were stable latexes.

From the conversion *vs.* time plot displayed in Fig. 1 (left), it can be seen that both monomers polymerized quite rapidly as S

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† Electronic supplementary information (ESI) available: Experimental procedure; polymer and particle characterization techniques. See http://www.rsc.org/suppdata/cc/b4/b415959d/
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conversion reached 95% within 8 h and BA conversion was 91%. This confirms the ability of the $PNaA_{21}$-SG1 macroinitiator to start the polymerization in the water-phase. Fig. 1 (right) shows that the polystyrene (PS) and poly(*n*-butyl acrylate) (PBA) produced in such an aqueous dispersed system followed the trend one expects from a controlled polymerization. Indeed the number average molar masses (M_n) increased with monomer conversion and a shift toward the higher molar masses was simultaneously observed for the size exclusion chromatograms (ESI†).

In both cases, the hydrophobic block was much longer than the hydrophilic one, as block copolymers with the following structure: $PNaA_{21}$–PS_{920} and $PNaA_{21}$–PBA_{400} were indeed synthesized. The polydispersity indexes were below 1.5 until about 80% conversion. They however increased for larger conversions, up to 2 for PS at 95% conversion and to 3 at 91% conversion for PBA. Such a result is not unexpected for controlled radical polymerization as dead chains accumulate when very large monomer conversions are reached. In addition, the radical polymerization of *n*-butyl acrylate is subjected to transfer to polymer, which inevitably broadens the molar mass distribution.[7] From the evolution of M_n *vs.* conversion it can also be seen that the experimental molar masses were above the theoretical ones, as a result of low initiator efficiency: approximately 60% for BA and 35% for S. Such low efficiency is an indication of radical–radical termination taking place in the aqueous phase, in the early polymerization stage. This side-reaction is particularly significant for styrene owing to the large activation-deactivation equilibrium constant in SG1-mediated controlled polymerization. The same results were indeed reported when the water-soluble low molar mass alkoxyamine shown in Scheme 1 was used in miniemulsion polymerization.[8] In this way, water-soluble or amphiphilic dead chains are thus produced, with either no or short hydrophobic block, and do not participate in particle core formation, but might enhance their stabilization.

From the colloidal viewpoint, the use of a polyelectrolyte macroinitiator really improved the system, as the aqueous suspensions of polymer particles were very stable, with small particles and narrow particle size distribution. Dynamic light scattering (DLS) gave a final number average hydrodynamic diameter of 65 nm for the PS particles and of 90 nm for those based on PBA, when measured in distilled water at pH 7, with a charged hydrophilic shell (pH was above the $pK_A = 6.15$ of the poly(acrylic acid)). When analyzed in an aqueous acidic solution at pH = 4, the particles were still stable but the average diameters decreased: 55 nm for PS and 76 nm for PBA. The hard PS particles could be visualized by transmission electron microscopy (TEM): they appeared to be spherical with a rather narrow particle size distribution (see Fig. 2). TEM allowed to determine a number average diameter of 56 nm and a weight average diameter of 61 nm.

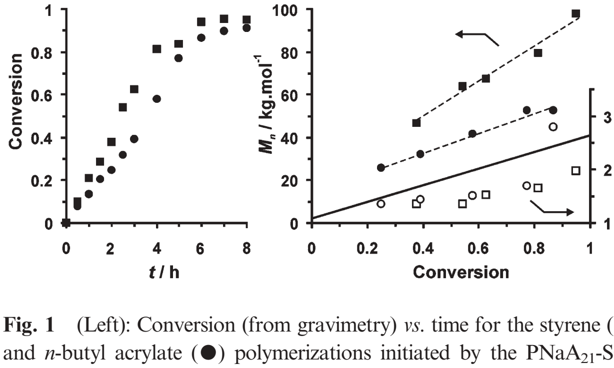

Fig. 1 (Left): Conversion (from gravimetry) *vs.* time for the styrene (■) and *n*-butyl acrylate (●) polymerizations initiated by the $PNaA_{21}$-SG1 macroinitiator in water at 120 °C. (Right): Experimental number average molar masses (M_n, calculated from the copolymer peak, without considering the residual macroinitiator) and polydispersity indexes (M_w/M_n) *vs.* conversion for the methylated copolymers, from size exclusion chromatography in THF solution (black straight line: theoretical M_n).

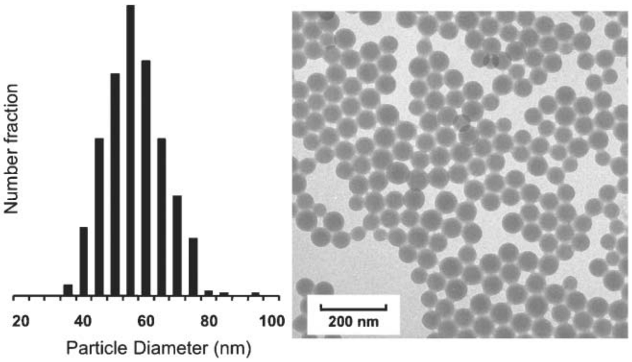

Fig. 2 Transmission electron microscope image of the polystyrene particles.

The colloidal characteristics of the produced latexes were all consistent with the formation of 'hairy' spherical particles, with a hydrophobic polymer core (hard for PS and soft for PBA) stabilized by a hydrophilic poly(acrylic acid)-based shell. The latter exhibited a pH sensitive thickness: at pH 7, it was a stretched polyelectrolyte brush, whereas at pH 4 the chains collapsed onto the particle surface. In alkaline conditions the shell thickness was 5–7 nm, based on the DLS measurements.

This article is the first report describing the use of a poly(sodium acrylate) water-soluble macroinitiator for the nitroxide-mediated free-radical heterogeneous polymerization of hydrophobic monomers in water. This very simple batch system leads to the formation of amphiphilic diblock copolymers, which grow and simultaneously associate *in situ* to form stable suspensions of hairy, spherical nanoparticles. As far as the colloidal characteristics are considered this is the best result obtained in nitroxide-mediated polymerization. Future work will focus on a better understanding of the experimental parameters that govern the particle size, the polymerization kinetics, and the control over molar mass and molar mass distribution with the improvement of the macroinitiator efficiency. The system might also be extended to various hydrophilic and hydrophobic monomers, to induce more complex particle morphologies.

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