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Nitroxide-Mediated Controlled/Living Free-Radical Surfactant-Free Emulsion Polymerization of Methyl Methacrylate Using a Poly(methacrylic acid)-Based Macroalkoxyamine Initiator

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ABSTRACT: Water-soluble, SG1 nitroxide-capped poly(methacrylic acid-*co*-styrene) macroalkoxyamines with ~10 mol % of styrene subunits were used as initiators in the surfactant-free, ab initio, batch, emulsion homopolymerization of methyl methacrylate and its copolymerization with a low percentage of styrene, in alkaline conditions at temperatures below 90 °C. The polymerizations were well-controlled, with a very high initiating efficiency, due to the high dissociation rate constant of the macroalkoxyamines. It led to the in situ formation of amphiphilic block copolymers that self-assembled into small particles with diameter below 100 nm, according to a polymerization-induced micellization process. The polymerization kinetics, the control over molar mass and molar distribution, and the colloidal characteristics of the so-formed block copolymer micelles were studied in detail. This work represents a breakthrough in controlled/living radical polymerization in aqueous emulsion with the development of new, very efficient macroinitiators used as the sole additive for initiation, stabilization, and chain-growth control. It is also the first development of nitroxide-mediated emulsion polymerization of methyl methacrylate performed at low temperature.

Introduction

The use of a water-soluble alkoxyamine macroinitiator in emulsion polymerization[1−5] is a way to achieve batch process at high solids content, in conditions where the reactive polymer plays the role of the initiator, of the stabilizer and of the control agent.[6,7] The concept is based on self-assembly of amphiphilic block copolymers formed in situ by chain extension via a controlled/living free-radical polymerization mechanism (i.e., nitroxide-mediated polymerization, NMP[8,9]). The micellization is then induced by polymerization, and both processes are closely interconnected to directly form amphiphilic block copolymer micelles, the type of which depends on the block lengths (star micelles[10−16] with short hydrophobic block and long hydrophilic one or crew-cut micelles[17−19] for the reverse structure). It therefore corresponds to an advance in block copolymer micelle formation (in the absence of added cosolvent as far as crew-cut micelles are regarded) along with a breakthrough in (controlled/living) emulsion polymerization[1−5] with a reduction of the number of reagents (only two, i.e., the monomer and the macroalkoxyamine) and the formation of self-stabilized polymer particles. The system requires neither the addition of a classical initiator nor that of a surfactant.

Our previous works were devoted to the application of living poly(acrylic acid) functionalized by an alkoxyamine end group based on the nitroxide SG1, PAA-SG1 (Scheme 1).[20,21] Such a polyelectrolyte in alkaline conditions was used for the emulsion polymerization of styrene and *n*-butyl acrylate[6,7] and for the dispersion polymerization of *N*,*N*-diethylacrylamide.[22] In the latter case, the polymer exhibits a LCST (lower critical solution temperature), and self-stabilized, thermally responsive nanogels were obtained when polymerization was performed in the presence of a cross-linking agent (i.e., a difunctional comonomer). The difficulty with PAA-SG1 was however a low initiating efficiency, partly due to the low dissociation rate constant at 120 °C.

The purpose of this work is to propose a new, water-soluble, macroalkoxyamine based on SG1 with higher dissociation rate constant, to initiate the polymerization with improved efficiency. In this context, an ideal macroalkoxyamine structure would be based on poly(methacrylic acid) with SG1 as a capping agent (PMAA-SG1). The chain-end structure would then mimick that of the BlocBuilder alkoxyamine (Scheme 1), which demonstrated a high initiating efficiency[23,24] due to the high dissociation rate constant.[25,26] However, the main drawback to target such a PMAA-SG1 living homopolymer is the lack of control of NMP over methacrylates. This is mainly due to the poor stability of the polymeric alkoxyamine and to side reactions occurring during the polymerization.[27−29]

Nevertheless, we previously showed that the addition of a small percentage of styrene to the SG1-mediated polymerization of methacrylic esters allowed the formation of living polymers with a stable methacrylate−styrene−SG1 terminal sequence, able to dissociate at low temperature (70−90 °C) due to the penultimate unit effect of the methacrylate attached to the terminal styrene.[30,31] In this work, we applied that concept to the formation of poly(methacrylic acid)-based macroinitiators with an SG1-based alkoxyamine end group.[32] The very good crossover efficiency was previously shown in the solution polymerization of styrene, allowing well-defined, amphiphilic diblock copolymers to be synthesized.[32] The purpose is then to apply those macroinitiators to the surfactant-free, batch emulsion polymerization of methyl methacrylate either in the absence or in the presence of a small proportion of styrene, at low temperature. The polymerization kinetics, the control over molar mass and molar distribution, and the colloidal characteristics of the so-formed block copolymer micelles are studied in detail.

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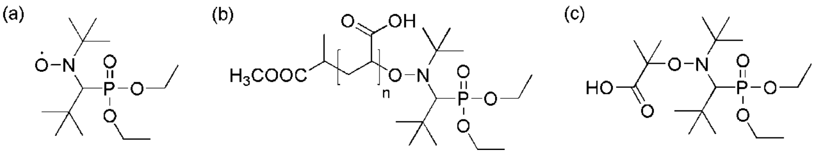
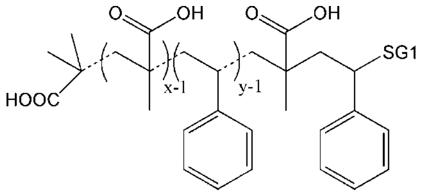
Scheme 1. Structure of the Nitroxide SG1 (a), of the SG1-Terminated Poly(acrylic acid) (PAA-SG1, b), and of the SG1-Based Alkoxyamine, BlocBuilder (c)



Scheme 2. Structure of the Poly(methacrylic acid-*co*-styrene) Macroinitiators, P(MAA$_x$-*co*-S$_y$)-SG1, Used in This Work



Experimental Part

1. Materials. Methacrylic acid (MAA, purest grade, Acros, stabilized with 250 ppm of methyl ether hydroquinone) was used without further purification. Methyl methacrylate (MMA, Aldrich, 99%) and styrene (S, Aldrich, 99%) were distilled under reduced pressure before use. The *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxylprop-2-yl)hydroxylamine initiator (the so-called BlocBuilder, 99%) and the *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, 88.4%) (see Scheme 1) were kindly supplied by Arkema. 1,4-Dioxane (from SDS, synthesis grade), trimethylsilyldiazomethane (Aldrich, 2 M solution in hexane), sodium carbonate (Na_2CO_3, Prolabo, pure), and NaOH (SDS, 1 M solution in water) were used as received. For the emulsion polymerizations, deionized water was used (USF Regeneration).

2. SG1-Mediated Copolymerization of Methacrylic Acid (MAA) with a Low Percentage of Styrene (S). The copolymerization reaction was carried out in 1,4-dioxane solution at 75 °C, according to a protocol described elsewhere.[32] The typical procedure is as follows: a mixture of MAA (62.5 g, 4.38 mol L^{-1}) and S (7.3 g, 0.42 mol L^{-1}, initial molar fraction of S in the comonomer mixture: $f_{S,0} = 0.088$) with free SG1 (0.46 g, 9.5×10^{-3} mol L^{-1}, 10.2 mol % based on the initiatior) and 1,4-dioxane (99.5 g, 96.2 mL) was deoxygenated with a nitrogen stream for 20 min at room temperature. The BlocBuilder initiator (5.9 g, 9.3×10^{-2} mol L^{-1}) was then added, and nitrogen bubbling was carried out for an additional 10 min. The so-formed solution was then introduced into a 500 mL three-neck round-bottom flask, immersed in a thermostated oil bath, and fitted with a reflux condenser, a nitrogen inlet, and a thermometer. The polymerization reaction was performed for 110 min at 75 °C. The overall monomer conversion (x) was determined by ^{1}H NMR.[32] Before using the copolymers as macroinitiators (see structure in Scheme 2), the polymerization medium was precipitated in diethyl ether, and the polymer was filtered and dried under vacuum at room temperature for 3 days to eliminate monomers and solvent. The purified copolymers appear as fine, bright, white powder. A complete description of the synthesis and characterization of the various copolymers used in this work is given in the Supporting Information. The general characteristics are summarized in Table 1.

3. Surfactant-Free, ab Initio, Batch Emulsion Homopolymerization of Methyl Methacrylate Initiated by a Living P(MAA-*co*-S)-SG1 Macroinitiator. In experiment **H1**, a mixture of water (64.78 g), the P(MAA$_{23}$-*co*-S$_3$)-SG1 macroinitiator (1.246 g, 5.84×10^{-3} mol L^{-1}), NaOH 1 M (15.17 g, 1.90×10^{-1} mol L^{-1}, i.e., 1 equiv of NaOH based on the carboxylic acid groups) and Na_2CO_3 (0.301 g, 3.5×10^{-2} mol L^{-1}) was introduced into a 250 mL round-bottom flask and stirred at room temperature until the P(MAA$_{23}$-*co*-S$_3$)-SG1 macroinitiator was well dissolved. Methyl methacrylate (20.39 g, 2.04×10^{-1} mol, 19.9 wt % based on water) was then added to this homogeneous mixture, and the obtained unstable biphasic system was heated at 40 °C for 54 h after nitrogen bubbling for 20 min at room temperature. Time zero of the polymerization was arbitrarily taken at the beginning of the heating period. Samples were periodically withdrawn to follow monomer conversion by gravimetry and to analyze the copolymers and the particles by methods described below. Experimental conditions of experiment **H1** are reported in Table 1.

4. Surfactant-Free, ab Initio, Batch Emulsion Copolymerization of Methyl Methacrylate and Styrene Initiated by a Living P(MAA-*co*-S)-SG1 Macroinitiator. The copolymerizations **C1**, **C2**, and **C3** were carried out in a 100 mL round-bottom flask at atmospheric pressure whereas the other copolymerizations (**C4**−**C11**) were carried out in a 300 mL thermostated glass reactor (PARR/Equilabo) under 3 bar pressure of nitrogen. The same typical polymerization procedure was applied, and experiment **C2** (Table 1) is described in detail below. A mixture of water (34.6 g), the P(MAA$_{27}$-*co*-S$_3$)-SG1 macroinitiator (0.729 g, 5.94×10^{-3} mol L^{-1}), NaOH 1 M (6.59 g, 1.55×10^{-1} mol L^{-1}, i.e. 1 equiv of NaOH based on the carboxylic acid groups) and Na_2CO_3 (0.154 g, 3.5×10^{-2} mol L^{-1}) was introduced in a 100 mL round-bottom flask and stirred at room temperature until the P(MAA$_{27}$-*co*-S$_3$)-SG1 macroinitiator was well dissolved. The comonomer mixture (MMA (9.8 g, 9.8×10^{-2} mol) and S (0.43 g, 4.1×10^{-3} mol, initial molar fraction of S in the comonomer mixture: $f_{S,0} = 0.04$), 19.5 wt % based on water) was then added to the aqueous solution, and the obtained unstable biphasic system was heated at 70 °C for 23 h after nitrogen bubbling for 20 min at room temperature. Time zero of the polymerization was arbitrarily taken at the beginning of the heating period. Samples were periodically withdrawn to follow the overall monomer conversion by gravimetry and to analyze the copolymers and the particles by methods described below. The various experimental conditions are reported in Table 1.

5. Analytical Techniques. Size exclusion chromatography (SEC) was used to determine the number-average molar mass (M_n) and the polydispersity index (PDI = M_w/M_n, with M_w, the weight-average molar mass) of the polymers. Before injecting the polymer samples containing methacrylic acid units, a reaction of methylation was performed, to turn the acid groups into methyl esters, using trimethylsilyldiazomethane.[20] The samples were injected (using a Viscotek VE 5200 injector) in two PSS linear M columns (separation limits: 400−2 × 10^6 g mol^{-1}), thermostated at 40 °C, with THF as an eluent (flow rate at 1 mL/min). Detection was made with a refractometer Refracto Monitor IV (LDC analytical). The Viscotek OmniSEC software was used for data analysis; calculation was made with a calibration curve based on poly(methyl methacrylate) standards (from Polymer Laboratories). In all figures displaying M_n as a function of monomer conversion, the M_n values correspond to those of the methylated copolymers. (Only the M_n values of the macroinitiators given in the Supporting Information were recalculated for the corresponding methacrylic acid units.)

Composition of the precipitated P(MAA-*co*-S) copolymers was determined by ^{13}C NMR spectroscopy in DMSO-d_6 solution from integration of the quaternary aromatic carbon peak of the styrene subunits (broad peak in the 146.5−147.8 ppm region) and integration of the carbonyl peak of the MAA units (δ = 178−180 ppm). Analyses were performed in 10 mm diameter tubes at room temperature using a Bruker Avance 300 spectrometer operating at a frequency of 75 MHz. Spectra were recorded using the following conditions, allowing quantitative analysis: spectral width 222 ppm

Table 1. Experimental Conditions for the Surfactant-Free, ab Initio, Batch Emulsion Homopolymerization of Methyl Methacrylate and Copolymerizations with a Low Percentage of Styrene Initiated by a Living P(MAA-*co*-S)-SG1 Macroinitiator[a]

expt	macroinitiator (PDI)	monomer content (wt %)	target M_n at 100% conversion (g mol^{-1})	[macroinitiator]$_0$ (mmol L^{-1}$_{\text{water}}$)	$f_{S,0}$[b]	T (°C)
H1	P(MAA$_{23}$-*co*-S$_3$)-SG1 (1.44)	19.9	46 400	5.8	0	40
C1	P(MAA$_{23}$-*co*-S$_3$)-SG1 (1.44)	19.7	45 300	5.9	0.030	60
C2	P(MAA$_{27}$-*co*-S$_3$)-SG1 (1.40)	19.5	45 100	5.9	0.040	70
C3	P(MAA$_{27}$-*co*-S$_3$)-SG1 (1.40)	19.5	44 200	6.0	0.088	80
C4	P(MAA$_{32}$-*co*-S$_4$)-SG1 (1.36)	19.5	43 500	6.3	0.088	85
C5	P(MAA$_{30}$-*co*-S$_3$)-SG1 (1.47)	21.1	49 100	6.0	0.088	90
C6	P(MAA$_{30}$-*co*-S$_3$)-SG1 (1.47)	20.6	26 200	11.9	0.088	90
C7	P(MAA$_{30}$-*co*-S$_3$)-SG1 (1.47)	21.3	96 100	3.0	0.088	90
C8	P(MAA$_{32}$-*co*-S$_4$)-SG1 (1.36)	28.9	43 000	10.8	0.088	90
C9	P(MAA$_{32}$-*co*-S$_4$)-SG1 (1.36)	29.4	71 100	6.4	0.088	90
C10	P(MAA$_{17}$-*co*-S$_2$)-SG1 (1.41)	21.3	48 700	5.9	0.088	90
C11	P(MAA$_{40}$-*co*-S$_4$)-SG1 (1.40)	19.5	44 900	6.2	0.088	90

[a] [Na$_2$CO$_3$]$_0$ = 35 mmol L^{-1}$_{\text{water}}$; 1 equiv of NaOH based on the COOH groups; pH = 8; atmospheric pressure for the experiments **H1** and **C1**-**C3** and P = 3 bar for all other polymerizations. Detailed information on the macroinitiators can be found in the Supporting Information. [b] Initial molar fraction of styrene in the MMA/S mixture.

with 65K data points, flip angle of 35°, relaxation delay of 30 s, suppression of the NOE, and digital resolution of 0.25 Hz pt^{-1}. The chemical shift scale was calibrated on the basis of the solvent peak (DMSO-d_6 at 39.52 ppm).

The *Z*-average particle diameter (D_z) for the monomodal particle size distribution of latex **H1**, the intensity-average diameter (D_i) for the multimodal particle size distibution of the other latexes, and the polydispersity factor σ (the particle size distribution is considered as narrow when $\sigma < 0.1$) were measured by dynamic light scattering (DLS) at a temperature of 25 °C and an angle of 90° using a Zetasizer Nano Series (S90) from Malvern Instrument and the multimodal calculation mode. Before measurements, the latex samples were diluted in deionized water. The particles were also visualized by transmission electron microscopy (TEM) using a JEOL 100 Cx II at 100 keV equipped with a high-resolution CCD camera Keen View from SIS.

Viscosity of the very fluid latexes ($\eta < 100$ cP) was measured using a Contraves Low-Shear 30 viscometer equipped with stainless steel coaxial cylinders (inner conical cylinder: 11 mm, outer diameter: 12 mm, length: 8 mm), and the shear rate was varied from 0.02 to 100 s^{-1}. The viscosity of the more viscous latex was measured using a strain-controlled rheometric fluid spectrometer (RFSII) equipped with cone and plate geometry (diameter: 50 mm, angle: 0.04 rad; gap: 45 μm) composed of titanium and stainless steel, and the shear rate was varied from 0.02 to 30 s^{-1}.

Results and Discussion

It was shown earlier that the SG1-mediated copolymerization of methyl methacrylate with a low proportion of styrene exhibited the features of a controlled system,[30] leading to formation of well-defined polymer with an alkoxyamine chain end.[31] The polymerization was efficiently initiated by the BlocBuilder alkoxyamine at temperatures ranging from 70 to 90 °C. In this work, we were interested in the formation of block copolymer self-assembly induced by chain extension of a living polyelectrolyte by a hydrophobic monomer in a batch, aqueous, emulsion polymerization system. To optimize the initiation step, P(MAA-*co*-S)-SG1 macroalkoxyamines were purposely designed, and the hydrophobic monomer was either pure MMA or a mixture of MMA and S. This work is then a new step in both the design of new alkoxyamine macroinitiators and the application to SG1-mediated polymerization of methyl methacrylate in emulsion. In a first approach, we had to determine the best polymerization conditions, i.e., temperature and proportion of styrene, and we then studied the effect of macroinitiator concentration and chain length as well as the monomer/water ratio in the system.

1. Synthesis of Appropriate P(MAA-*co*-S)-SG1 Macroinitiators. On the basis of our previous works performed with PAA-SG1 macroinitiators and with PAA-*b*-PS amphiphilic block copolymers used as nonreactive stabilizers in emulsion polymerization,[16,33,34] the number of MAA units in the P(MAA-*co*-S)-SG1 macroalkoxyamines was targeted in the 17−40 range (Table 1 and Supporting Information). With an ideal proportion of styrene below 10 mol %, the average number of styrene subunits was 2−4, one of them being the terminal one. With such a low proportion of hydrophobic comonomer, all macroinitiators were highly water-soluble in alkaline conditions, whatever the temperature. The polydispersity indexes were not very low, close to 1.4, owing to low target molar mass. Unlike those derived from acrylic acid, the polymeric propagating radicals of such a system are less prone to chain transfer reactions to the polymer or to the solvent and highly linear chains with high chain-end functionality were expected and were actually observed, whatever the target molar mass.[32] Another interesting feature is the low polymerization temperature, which makes the process very easily accessible.

2. Surfactant-Free, ab Initio, Batch Emulsion Homopolymerization of Methyl Methacrylate Initiated by a Living P(MAA-*co*-S)-SG1 Macroinitiator. Methyl methacrylate was first homopolymerized at low temperature, namely 40 °C. The idea was to reduce the activation−deactivation equilibrium constant in order to reduce the concentration of propagating radicals and hence avoid the need for adding styrene as a comonomer. Such homopolymerization was previously studied at 45 °C, in bulk, using the BlocBuilder alkoxyamine as an initiator,[29] and the results showed relatively high conversions, with however poor livingness. The conversion versus time and variation of the number-average molar mass, M_n, with monomer conversion are shown in Figure 1. Not surprisingly, the polymerization was very slow, but high conversion, around 75%, was eventually reached after 27 h. The low dissociation rate constant of the macroalkoxyamine P(MAA$_{23}$-*co*-S$_3$)-SG1 at 40 °C is illustrated in Figure 1b,c by the slow initiation process: the macroinitiator was only slowly consumed, and no very significant shift in the SEC block copolymer peaks could be observed; moreover, the number-average molar mass of those block copolymers slightly decreased with monomer conversion, and the polydispersity indexes increased due to a continuous increase in the number of block copolymer chains.

Despite the lack of control of the homopolymerization of MMA at 40 °C,[29] the colloidal characteristics of the resulting latex were particularly satisfactory, as shown in Figure 2. The average particle diameter increased with monomer conversion and was 123 nm at the end of the polymerization. Moreover, the particle size distribution was monomodal and narrow (low polydispersity factor from DLS: $\sigma < 0.06$), and the transmission electron microscopy image in Figure 3 confirms this result.

The polymerization conditions can be of interest for the design of diblock copolymer particles with a pure poly(methyl meth-

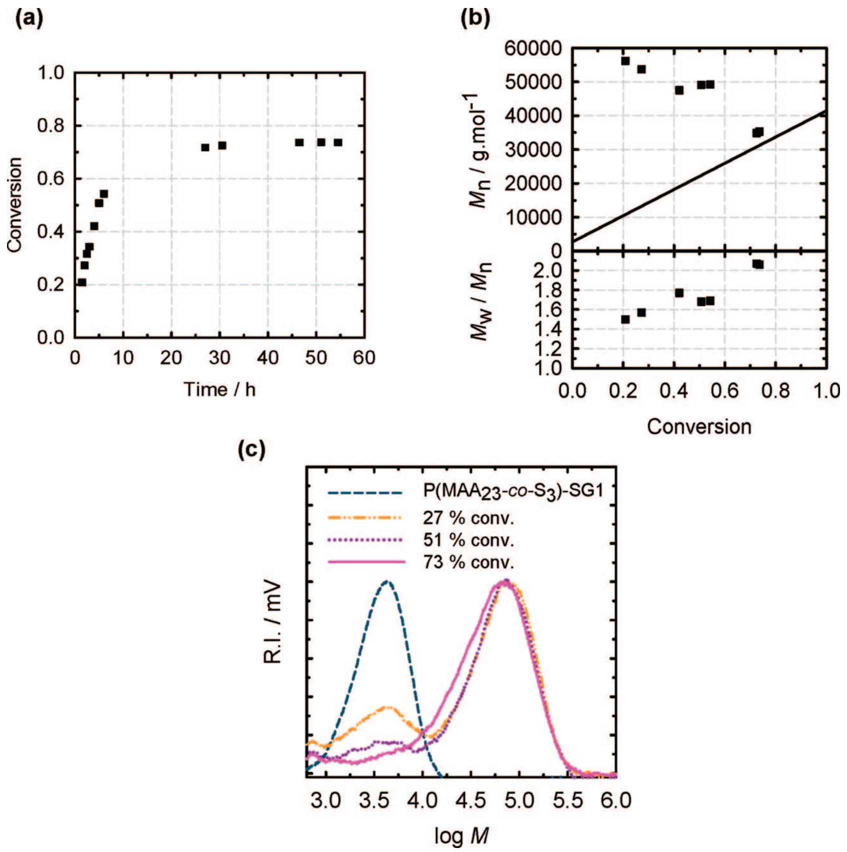


Figure 1. Overall conversion vs time (a), number-average molar mass, M_n, of the diblock copolymer (the remaining macroinitiator was not considered here for calculation) and polydispersity index, PDI = M_w/M_n, vs conversion (the full line represents the theoretical M_n) (b), and SEC chromatograms at various conversions (c) for the SG1-mediated surfactant-free, ab initio, batch emulsion homopolymerization of methyl methacrylate, **H1**, at 40 °C and 20 wt % solids, initiated by the macroalkoxyamine P(MAA$_{23}$-*co*-S$_3$)-SG1 (see Tables 1 and 2).

Table 2. Experimental Results for the Surfactant-Free, ab Initio, Batch Emulsion Homopolymerization of Methyl Methacrylate and Copolymerizations with a Low Percentage of Styrene Initiated by a Living P(MAA-*co*-S)-SG1 Macroinitiator

expt	time (h)	conv (%)	overall solids content (wt %)	core polymer content (wt %)	$M_{n,th}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	PDI	D_i (σ) from DLS (nm)	η (cP)
H1	54	73.6	15.9	14.7	31 200	35 300	2.06	D_z = 123 (0.02)	
C1	26.7	77.9	16.5	15.3	34 700	36 600	1.26	47 (0.21)	
C2	23	64.1	13.9	12.5	30 300	34 400	1.21	40 (0.22)	
C3	22	70.3	15.1	13.7	32 400	39 300	1.17	33/250[a] (0.34)	
C4	5.3	82.0	17.7	16.0	36 800	38 800	1.28	25/100[a] (0.17)	
C5	5.6	87.5	20.0	18.5	43 800	50 700	1.27	34/300[a] (0.31)	17[b]
C6	5.9	84.7	20.4	17.4	23 000	28 300	1.26	30/200[a] (0.35)	76[b]
C7	5	75.4	16.8	16.0	73 700	77 600	1.33	50 (0.13)	4[b]
C8	3	74.9	24.2	21.6	33 500	38 600	1.31	42 (0.22)	12 000[c]
C9	6	78.2	24.5	23.0	56 800	66 400	1.29	37/200[a] (0.26)	
C10	7.3	68.5	15.5	14.6	34 200	39 600	1.43	35 (0.19)	
C11	6.5	74.5	16.6	14.5	39 400	49 200	1.34	27/150[a] (0.33)	

[a] The second population, with higher diameter, was present in the intensity distribution only. [b] Measured with the Contraves Low-Shear 30 viscometer: all latexes are Newtonian fluids, the values of viscosity being constant whithin the shear rate range of 0.02–100 s^{-1}. [c] Measured with the RFSII viscometer: value of the viscosity was determined at a shear rate of 0.02 s^{-1} (shear-thinning fluid).

acrylate) core and a polyelectrolyte stabilizing layer. However, due to the very slow polymerization at 40 °C together with the poor control, the system was not further investigated, and the method of introducing a low percentage of styrene at higher temperature was then considered.

3. Surfactant-Free, ab Initio, Batch Emulsion Copolymerization of Methyl Methacrylate and Styrene Initiated by a Living P(MAA-*co*-S)-SG1 Macroinitiator. *Influence of $f_{S,0}$ and of the Temperature (Experiments* **C1–C5***).* For the first series of emulsion polymerizations of MMA with a low percentage of styrene (experiments **C1–C5**, Table 1), the styrene molar fraction ($f_{S,0}$) and the polymerization temperature were varied simultaneoulsy; i.e., $f_{S,0}$ was increased when the temperature was increased, to concomitantly adapt the polymerization rate by varying the overall kinetic parameter k_pK (k_p is the apparent rate constant of propagation for the copolymerization and K is the apparent activation–deactivation equilibrium constant)[30] and find the best conditions for a well-controlled polymerization. In this way, $f_{S,0}$ was varied from 0.030 (experiment **C1**) to 0.088 (experiments **C3–C5**) when the temperature was increased from 60 to 90 °C, respectively. The conversion versus time plots and variation of the number-average molar masses, M_n, with monomer conversion are shown in Figure 4. It appears that the temperature had a much stronger effect on the polymerization kinetics than the proportion of styrene. Indeed, more than 20 h was needed to reach high conversions when temperature was in the 60–80 °C range, whereas only a few hours was sufficient at 85–90 °C. The

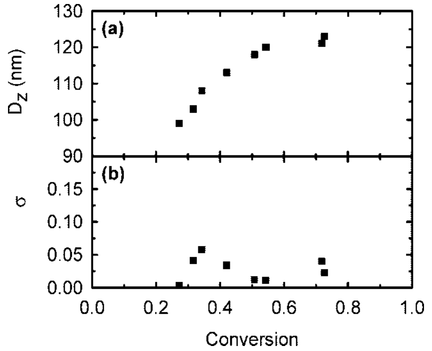


Figure 2. Average particle diameter, D_z from DLS, vs conversion (a) and polydispersity factor, σ, vs conversion (b) for the SG1-mediated surfactant-free, ab initio, batch emulsion homopolymerization of methyl methacrylate, **H1**, at 40 °C and 20 wt % solids, initiated by the macroalkoxyamine P(MAA_{23}-*co*-S_3)-SG1 (see Tables 1 and 2).

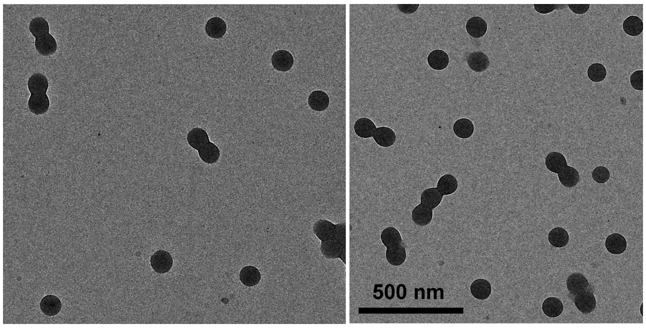


Figure 3. Transmission electron microscopy (TEM) images of the P(MAA_{23}-*co*-S_3)-*b*-PMMA particles formed by SG1-mediated surfactant-free, ab initio, batch emulsion homopolymerization of methyl methacrylate, **H1**, at 40 °C and 20 wt % solids, initiated by the macroalkoxyamine P(MAA_{23}-*co*-S_3)-SG1 (see Tables 1 and 2).

conversion versus time plot usually reached a final plateau at ~90%, which can be explained by side reactions (in particular, hydrogen transfer from PMMA propagating radical to SG1—which may essentially take place after complete conversion of styrene—and irreversible homotermination), as shown and studied in previous publications, which tend to reduce the overall concentration of active species.[27,28,30] Irrespective of the temperature and styrene content, the molar masses were well controlled. The number-average molar masses increased linearly with monomer conversion and were close to the theoretical line. This was actually a fully expected result as M_n was calculated from the whole SEC peak. However, no trace of residual macroinitiator could be seen on the chromatograms (Figure 5), indicating a very high crossover efficiency. The complete shift of the SEC peaks with conversion along with decreasing polydispersity indexes toward values as low as 1.2 (Figure 4) are good indications of the simultaneous growth of all polymer chains and confirm the very efficient reinitiation. At low temperature, however, the initiation step was rather slow as consumption of the macroinitiator was not complete before ca. 20 % conversion. Such a situation was not observed at 80 or 90 °C, and fast initiation indeed occurred as shown by the complete shift of the macroinitiator SEC peak at low conversions. With those results, the most appropriate polymerization conditions were selected, i.e., 90 °C and $f_{S,0} = 0.088$, and were applied in all other experiments.

Influence of the Macroinitiator Concentration (Experiments **C5**−**C7***).* At a given monomer/water ratio, the macroinitiator aqueous concentration is an important parameter to fine-tune the molar mass of the hydrophobic block and change the particle size. This was done by varying it from 3.0 to 11.9 mmol $L^{-1}{}_{water}$ at a monomer content close to 20 wt % (experiments **C7**, **C5**, and **C6**). Figure 6 shows the kinetic and molar mass evolutions, which confirm the controlled character of the polymerizations. The polymerization rate was not significantly influenced by the macroinitiator concentration as already observed for the emulsion polymerization of styrene initiated by the PAA-SG1 macroinitiator.[35]

At a given monomer conversion, the number-average molar mass of the block copolymers formed in our emulsion polymerization process directly depends on the macroinitiator concentration and can thus be predicted with high accuracy, as confirmed by the good agreement between the experimental and calculated values (Figure 6b). The technique allows relatively high molar mass polymers to be obtained, close to 10^5 g mol^{-1}, with still a low polydispersity index. As shown in Table 2, the final latex viscosity was that of a Newtonian fluid (constant value in the 0.02−100 s^{-1} shear rate range) and increased when the macroinitiator concentration was increased in correlation with the decrease in particle size (and hence the increase in particle number per unit volume).[36] Dynamic light scattering showed relatively high polydispersity factors for all three latexes (σ was above 0.1 for experiment **C7** and above 0.3 for experiments **C5** and **C6**). For the latter two latexes, a second population with larger diameter was clearly identified by the DLS analysis above 87% conversion for experiment **C5** and at all conversions for experiment **C6**: it was visible in the intensity distributions only but not in the number distributions (Table 2 and Figure 7). In contrast to DLS, transmission electron microscopy showed a rather narrow particle size distribution (Figure 8). The combined results may then support the existence of a large number fraction of small particles along with a few aggregates rather than broad particle size distribution (Figures 7 and 8). If one considers the population of small particles (Table 2), the intensity-average particle diameter, D_i, given by DLS decreased from 50 to 30 nm when the macroinitiator concentration was increased. This result is similar to that already observed in the emulsion polymerization of styrene initiated by the PAA-SG1 macroinitiator.[7] In parallel, the latexes became more translucent, indicating only little influence of the aggregates on the scattered intensity (Figure 9). The particle size is very small for surfactant-free emulsion polymerizations carried out at 20 wt % solids in batch conditions. This correlates well with the formation of amphiphilic diblock copolymer particles, which are self-stabilized by the poly(sodium methacrylate)-based water-soluble block. For the latex **C5** with 6.0 × 10^{-3} mol $L^{-1}{}_{water}$ of macroinitiator, D_i was 37 nm (σ ~ 0.23) at pH = 11.2 and slightly decreased to D_i ~ 34 nm (σ ~ 0.25) at pH ranging from 8.3 to 5.7. At pH between 5.1 and 4.7, a large proportion of aggregates formed (D_i ~ 200 nm), but the latex remained stable, whereas complete destabilization was observed at pH below 4. When particle size was measured as a function of pH after filtration of the samples through 0.2 μm membrane (to eliminate the aggregates), the *z*-average diameter was D_z = 42 nm (σ = 0.07) at pH = 12 and it was 34 nm (σ = 0.05) at pH = 6. In contrast to poly(sodium acrylate),[7] the poly(sodium methacrylate-*co*-styrene) stabilizing layer was not fully extended at high pH and exhibited a rather hydrophobic behavior at low pH. Both results are most likely the consequence of the more hydrophobic character of poly(methacrylic acid) together with the presence of styrene subunits in the chains, which may induce hydrophobic interactions.

Influence of the Monomer Content (Experiments **C5***,* **C6***,* **C8***, and* **C9***).* To change the target chain length, the monomer/macroinitiator ratio can also be changed by varying the monomer content in the aqueous dispersion, while keeping the macroinitiator concentration constant (Figures 10 and 11). This was done by varying the target solids content from approximately 20 to 30 wt % with two different macroinitiator concentrations. The

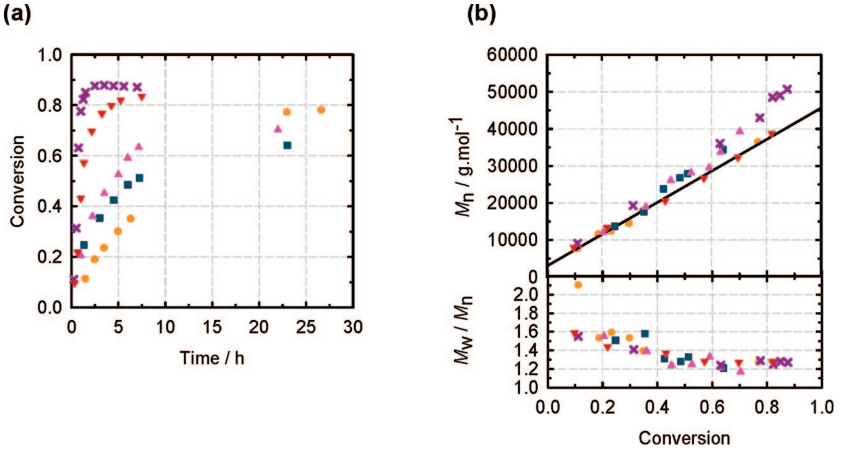


Figure 4. Influence of the molar proportion of styrene, $f_{S,0}$, and of the temperature on the kinetics and on the copolymer characteristics, for the SG1-mediated surfactant-free, ab initio, batch emulsion copolymerizations of methyl methacrylate (MMA) and styrene (S) at 20 wt % solids, initiated by the P(MAA$_{23-32}$-*co*-S$_{3-4}$)-SG1 macroalkoxyamines. Experiment **C1** (●, $f_{S,0}$ = 0.030, T = 60 °C), experiment **C2** (■, $f_{S,0}$ = 0.040, T = 70 °C), experiment **C3** (▲, $f_{S,0}$ = 0.088, T = 80 °C), experiment **C4** (▼, $f_{S,0}$ = 0.088, T = 85 °C), and experiment **C5** (×, $f_{S,0}$ = 0.088, T = 90 °C). (a) Overall conversion vs time; (b) number-average molar mass, M_n, (calculation based on the whole peak) and polydispersity index, PDI, vs conversion (the full line represents the theoretical M_n) (see Tables 1 and 2).

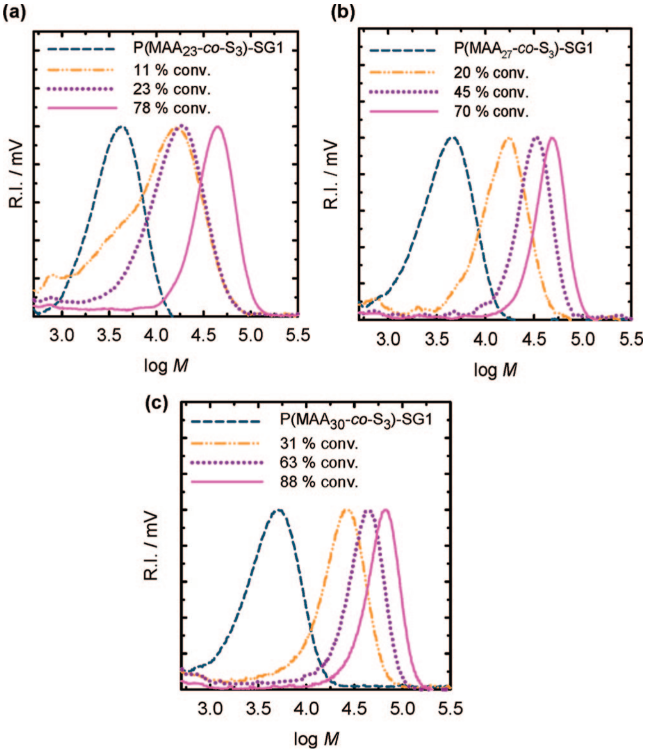


Figure 5. Evolution of the size exclusion chromatograms with conversion for the SG1-mediated surfactant-free, ab initio, batch emulsion copolymerizations of methyl methacrylate and styrene: experiment **C1** (a, $f_{S,0}$ = 0.030, T = 60 °C), experiment **C3** (b, $f_{S,0}$ = 0.088, T = 80 °C), and experiment **C5** (c, $f_{S,0}$ = 0.088, T = 90 °C).

conversion vs time plots and the evolution of M_n with monomer conversion show the very little influence of the monomer/water ratio on the polymerization kinetics and control over molar mass, as already explained and discussed previously for the PAA-SG1/styrene system.[35] The slight apparent decrease in monomer conversion at long times for the experiment **C9** is due to partial latex destabilization (gravimetric analysis does not take into account the flocculated polymer).

When the macroinitiator concentration was close to 6 × 10^{-3} mol L^{-1}$_{\text{water}}$ (experiments **C5** and **C9**), the monomer/water ratio had no significant effect on the average particle size and particle size distribution. Like previously, the presence of aggregates

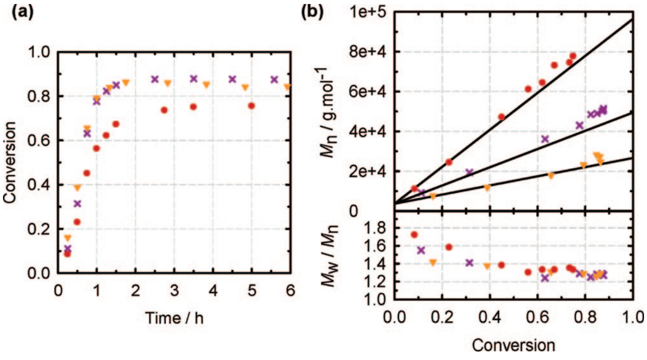


Figure 6. Influence of the P(MAA$_{30}$-*co*-S$_3$)-SG1 macroinitiator concentration on the kinetics and on the copolymer characteristics, for the SG1-mediated surfactant-free, ab initio, batch emulsion copolymerizations of methyl methacrylate and styrene ($f_{S,0}$ = 0.088) at 90 °C and 20 wt % solids. Experiment **C7** (●, 3.0 × 10^{-3} mol L^{-1}$_{\text{water}}$), experiment **C5** (×, 6.0 × 10^{-3} mol L^{-1}$_{\text{water}}$), and experiment **C6** (▼, 1.19 × 10^{-2} mol L^{-1}$_{\text{water}}$). (a) Overall conversion vs time; (b) number-average molar mass, M_n, and polydispersity index, PDI, vs conversion (the full lines represent the theoretical M_n) (see Tables 1 and 2).

was confirmed by the DLS analysis (two populations), while the TEM pictures displayed a rather narrow particle size distribution (no particle with diameter in the 200−300 nm range could be seen) (Figure 12). For the experiments with the macroinitiator concentration close to 10^{-2} mol L^{-1}$_{\text{water}}$ (experiments **C6** and **C8**), a slight increase of the average particle diameter with the increase in solids content could be detected. Quite interesting is the observation that the final latex **C8** was significantly more viscous and formed a white gel, however still able to flow (see Figure 13).

Influence of the Macroinitiator Chain Length (Experiments **C10***,* **C5***, and* **C11***).* Finally, the macroinitiator chain length was increased from 17 MAA units to 40 MAA units (experiments **C10**, **C5**, and **C11** in Table 1), all other experimental parameters being kept constant. It appears in Figure 14 that the initial polymerization rate was the same for all three polymerizations but that the final conversion value at the plateau changed, for reasons that remain unclear at the moment. Control over the hydrophobic block growth was the same for all three macroinitiators. The diameter results reported in Table 2 show that the macroinitiator chain length had a very little effect on the average particle diameter (population of small particles determined by DLS): it decreased from 35 to 27 nm when the

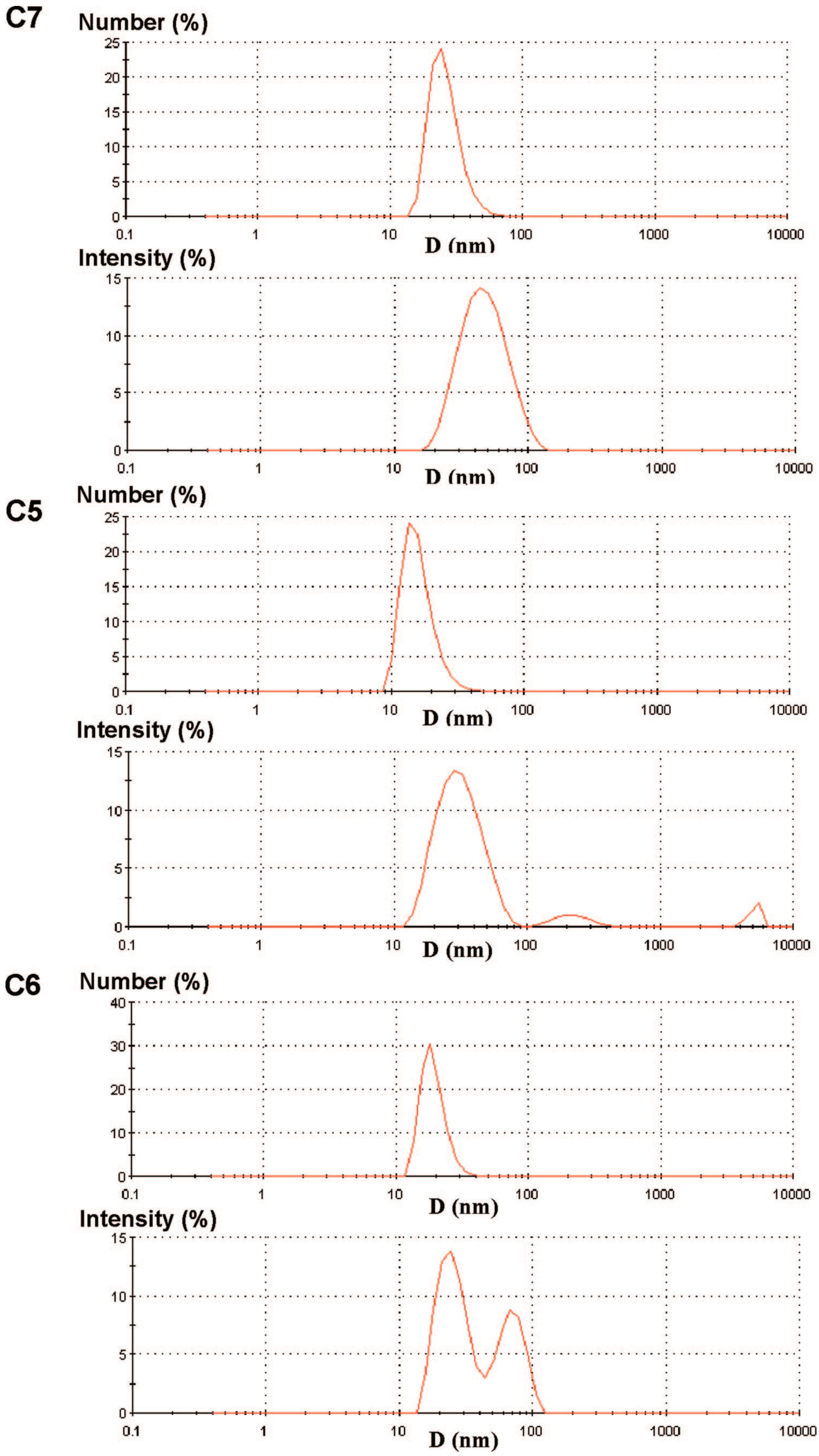


Figure 7. Number and intensity distributions of particle diameter from DLS for the final P(MAA$_{30}$-*co*-S$_3$)-*b*-P(MMA-*co*-S) particles from experiment **C7** (t = 5 h, x = 75.4%, [P(MAA$_{30}$-*co*-S$_3$)-SG1]$_0$ = 3.0 × 10^{-3} mol L^{-1}$_{\text{water}}$), experiment **C5** (t = 5.6 h, x = 87.5%, [P(MAA$_{30}$-*co*-S$_3$)-SG1]$_0$ = 6.0 × 10^{-3} mol L^{-1}$_{\text{water}}$) and experiment **C6** (t = 5.9 h, x = 84.7%, [P(MAA$_{30}$-*co*-S$_3$)-SG1]$_0$ = 1.19 × 10^{-2} mol L^{-1}$_{\text{water}}$) (see Tables 1 and 2).

macroinitiator chain length was increased. The opposite result was found for the PAA-SG1/styrene system.[7] In parallel, however, the DLS polydispersity factor increased, showing an increased proportion of aggregates in the latex, possibly favored

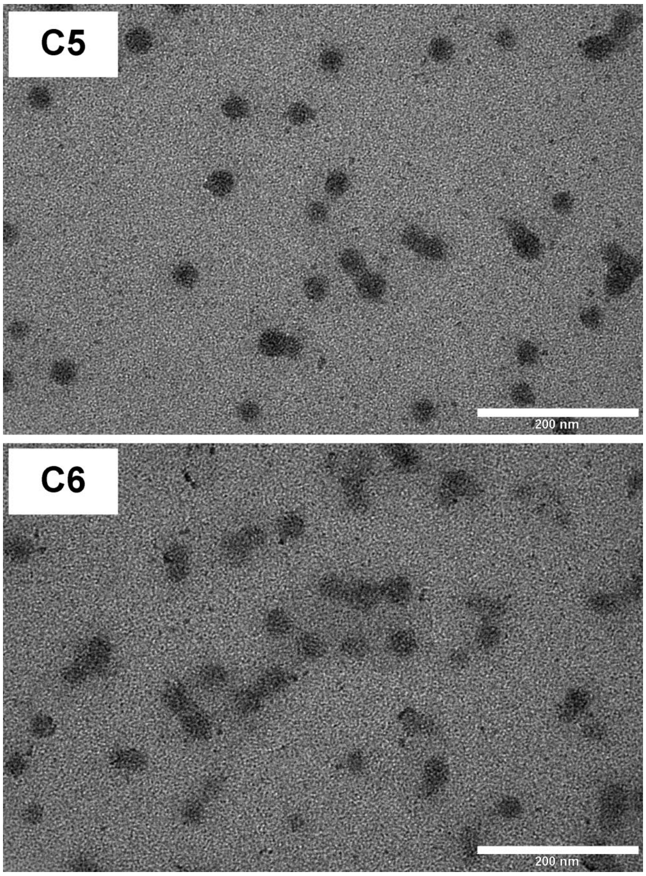


Figure 8. Transmission electron microscopy (TEM) images of the final P(MAA$_{30}$-*co*-S$_3$)-*b*-P(MMA-*co*-S) particles from experiment **C5** (t = 5.6 h, x = 87.5%, [P(MAA$_{30}$-*co*-S$_3$)-SG1]$_0$ = 6.0 × 10^{-3} mol L$^{-1}{}_{\text{water}}$) and experiment **C6** (t = 5.9 h, x = 84.7%, [P(MAA$_{30}$-*co*-S$_3$)-SG1]$_0$ = 1.19 × 10^{-2} mol L$^{-1}{}_{\text{water}}$); the white bar stands for 200 nm (see Tables 1 and 2).

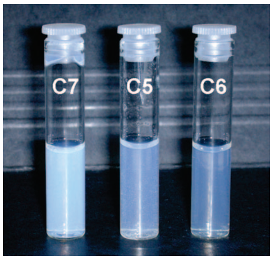


Figure 9. Pictures of the final latex obtained from experiment **C7** (t = 5 h, x = 75.4%, [P(MAA$_{30}$-*co*-S$_3$)-SG1]$_0$ = 3.0 × 10^{-3} mol L$^{-1}{}_{\text{water}}$), from experiment **C5** (t = 5.6 h, x = 87.5%, [P(MAA$_{30}$-*co*-S$_3$)-SG1]$_0$ = 6.0 × 10^{-3} mol L$^{-1}{}_{\text{water}}$) and from experiment **C6** (t = 5.9 h, x = 84.7%, [P(MAA$_{30}$-*co*-S$_3$)-SG1]$_0$ = 1.19 × 10^{-2} mol L$^{-1}{}_{\text{water}}$) (see Tables 1 and 2).

by the increased content of styrene subunits in the stabilizing layer.

Conclusion

Water-soluble, SG1 nitroxide-capped poly(methacrylic acid-*co*-styrene) macroalkoxyamines with ~10 mol % of styrene subunits were purposely designed and used as initiators in the surfactant-free, ab initio, batch, emulsion homopolymerization of methyl methacrylate and its copolymerization with a low percentage of styrene, in alkaline conditions at temperatures below 90 °C. The best polymerization conditions were selected, and in particular the introduction of 8.8 mol % of styrene and a temperature of 90 °C led to very fast reactions with high conversions reached in less than 3 h. The polymerizations were well-controlled, with a very high initiating efficiency, due to the high dissociation rate constant of the macroalkoxyamines. They led to low-polydispersity, amphiphilic diblock copolymers that self-assembled into small particles with diameter below 100 nm. Whereas the initiating efficiency was much higher than that observed with the analogous SG1-capped poly(acrylic acid) macroalkoxyamines, the colloidal characteristics of the particles were slightly less satisfactory, since a small fraction of aggregates formed during the polymerization, possibly explained by the presence of styrene subunits in the hydrophilic corona. Improvement may further come from the use of sodium styrenesulfonate instead of styrene in the poly(methacrylic acid) chains, a work which is in progress. Those results represent a breakthrough in living radical polymerization in aqueous emulsion with the development of new, very efficient macroinitiators used as the sole additive for initiation, stabilization, and chain-growth control. It is also the first development of nitroxide-mediated emulsion

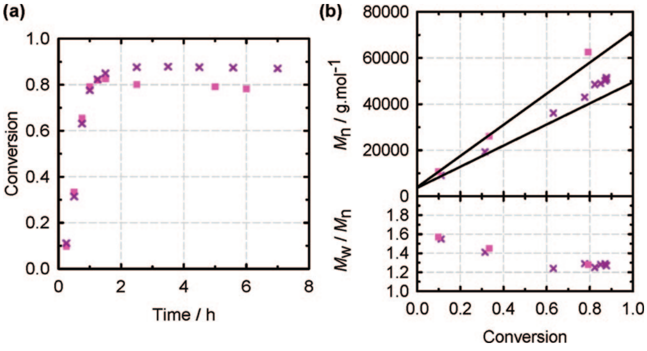


Figure 10. Influence of the solids content on the kinetics and on the copolymer characteristics, for the SG1-mediated surfactant-free, ab initio, batch emulsion copolymerizations of methyl methacrylate and styrene ($f_{S,0}$ = 0.088) at 90 °C. Experiment **C5** (×, 21.1 wt % monomer content, [P(MAA$_{30}$-*co*-S$_3$)-SG1]$_0$ = 6.0 × 10^{-3} mol L$^{-1}{}_{\text{water}}$) and experiment **C9** (■, 29.4 wt % monomer content, [P(MAA$_{32}$-*co*-S$_4$)-SG1]$_0$ = 6.4 × 10^{-3} mol L$^{-1}{}_{\text{water}}$). (a) Overall conversion vs time; (b) number-average molar mass, M_n, and polydispersity index, PDI, vs conversion (the full lines represent the theoretical M_n) (see Tables 1 and 2).

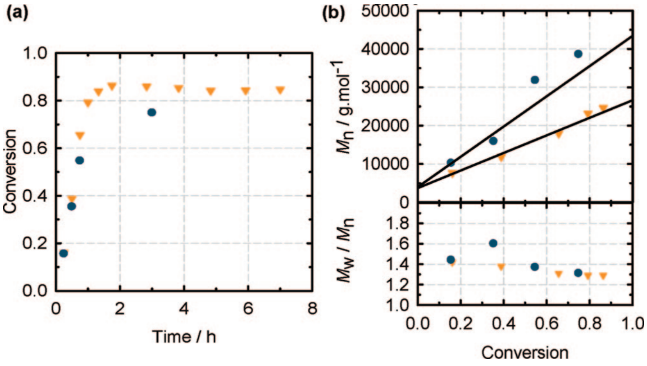


Figure 11. Influence of the solids content on the kinetics and on the copolymer characteristics, for the SG1-mediated surfactant-free, ab initio, batch emulsion copolymerizations of methyl methacrylate and styrene ($f_{S,0}$ = 0.088) at 90 °C. Experiment **C6** (▼, 20.6 wt % monomer content, [P(MAA$_{30}$-*co*-S$_3$)-SG1]$_0$ = 1.19 × 10^{-2} mol L$^{-1}{}_{\text{water}}$) and experiment **C8** (●, 28.9 wt % monomer content, [P(MAA$_{32}$-*co*-S$_4$)-SG1]$_0$ = 1.08 × 10^{-2} mol L$^{-1}{}_{\text{water}}$). (a) Overall conversion vs time; (b) number-average molar mass, M_n, and polydispersity index, PDI, vs conversion (the full lines represent the theoretical M_n) (see Tables 1 and 2).

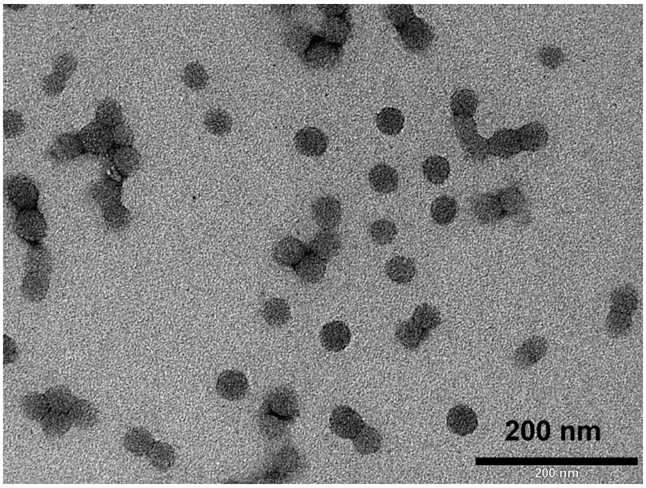


Figure 12. Transmission electron microscopy (TEM) image of the P(MAA$_{32}$-*co*-S$_4$)-*b*-P(MMA-*co*-S) particles from experiment **C9** (t = 5 h, x = 78.2%, 29.4 wt % solids content, [P(MAA$_{32}$-*co*-S$_4$)-SG1]$_0$ = 6.4×10^{-3} mol L$^{-1}{}_{\text{water}}$) (see Tables 1 and 2).

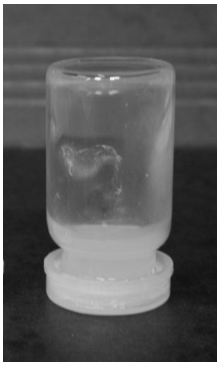


Figure 13. Picture of the final latex obtained from experiment **C8** (t = 3 h, x = 75%, 28.9 wt % monomer content, [P(MAA$_{32}$-*co*-S$_4$)-SG1]$_0$ = 1.08×10^{-2} mol L$^{-1}{}_{\text{water}}$) (see Tables 1 and 2).

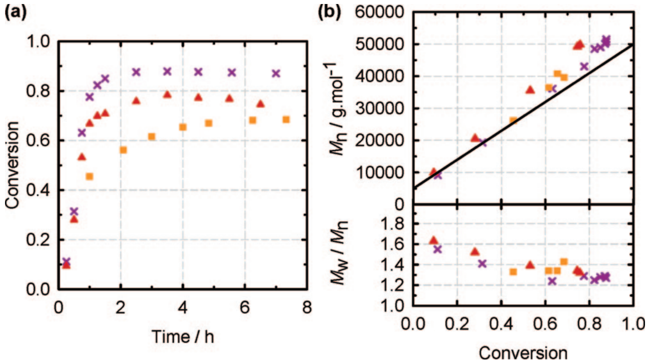


Figure 14. Influence of the length of the hydrophilic block on the kinetics and on the copolymer characteristics, for the SG1-mediated surfactant-free, ab initio, batch emulsion copolymerizations of methyl methacrylate and styrene ($f_{S,0}$ = 0.088) at 90 °C and 20 wt % solids. Experiment **C10** (■, P(MAA$_{17}$-*co*-S$_2$)-SG1), experiment **C5** (×, P(MAA$_{30}$-*co*-S$_3$)-SG1), and experiment **C11** (▲, P(MAA$_{40}$-*co*-S$_4$)-SG1). (a) Overall conversion vs time; (b) number-average molar mass, M_n, and polydispersity index, PDI, vs conversion (the full line represents the theoretical M_n) (see Tables 1 and 2).

polymerization of methyl methacrylate, performed at low temperature.

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Supporting Information Available: Detailed information on the synthesis and characterization of the macroinitiators. This material is available free of charge via the Internet at http://pubs.acs.org.

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