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Nitroxide-Mediated Copolymerization of Methacrylic Acid and Styrene To Form Amphiphilic Diblock Copolymers

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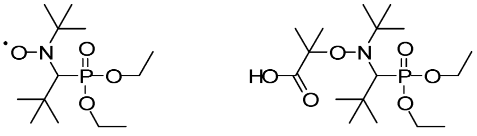
ABSTRACT: The controlled free-radical polymerization of methacrylic acid was performed at 73 and 83 °C using a methacrylic acid-based alkoxyamine and the nitroxide SG1 as a mediator in the presence of a small concentration of styrene, without protection of the carboxylic acid groups. The solvent was 1,4-dioxane or ethanol, and no chain transfer to the solvent could be detected. Because of the presence of styrene, the polymerization exhibited the characteristics of a living one. In particular, the polymers could be chain-extended and were used as efficient macroinitiators in the polymerization of styrene, allowing well-defined, amphiphilic diblock copolymers to be synthesized.

Introduction

Among the possible techniques that allow the synthesis of well-defined homopolymers and copolymers by a controlled free-radical polymerization (CRP) process, nitroxide-mediated polymerization (NMP)[1,2] is one of the oldest. It was originally restricted to styrenic monomers, especially with the use of TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) as a mediator. However, a more recent class of acyclic nitroxides has demonstrated their ability to control the polymerization of a much broader range of monomers.[3−5] Indeed, acrylates, acrylamides, styrene, and maleic anhydride (co)polymerizations exhibited the features of living/controlled systems. One of those nitroxides is the *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, also called SG1[3,4] (Scheme 1).

Quite recently, our group showed that, in addition to the monomers listed above, methyl methacrylate (MMA) could also be polymerized in a living way using an SG1-based alkoxyamine with a high dissociation rate constant as an initiator.[6,7] It represented an important challenge since in nitroxide-mediated polymerization, the monomers with a very high activation−deactivation equilibrium constant, *K*, such as the methacrylic esters, do not lead to controlled homopolymerization in the presence of nitroxides like SG1. This is the consequence of a too high concentration of propagating radicals, favoring irreversible self-termination reactions instead of reversible termination with SG1. For the purpose of reducing this concentration efficiently, a small fraction of a comonomer was added. From the average activation−deactivation equilibrium constant, $\langle K \rangle$, determined for copolymerization on a theoretical basis,[6] it was indeed shown that the addition of a small fraction of an appropriate comonomer to a monomer with a very large activation−deactivation equilibrium constant, *K*, might lead to a strong reduction of $\langle K \rangle$, providing the added comonomer exhibits a low *K*. This method was indeed successfully applied to the NMP of MMA at 90 °C initiated with the SG1-based alkoxyamine depicted in Scheme 1: by adding a small amount of styrene, polymerizations reached high conversions and exhibited all the features of a controlled system.[6] In addition, it was later demonstrated that the polymerization temperature could be decreased below 90 °C.[7] This was explained by the nature of the chain end, namely the methacrylate−styrene−SG1 sequence, and the effect of the methacrylate group in the penultimate position on the alkoxyamine dissociation.

Scheme 1. Structure of the Nitroxide SG1 and of the SG1-Based Alkoxyamine (BlocBuilder) Used in This Work



SG1 BlocBuilder$^{\text{TM}}$ alkoxyamine initiator

The purpose of this article is to demonstrate, in the same way, that it is possible to achieve a controlled polymerization of another methacrylate, namely methacrylic acid, with SG1 as a mediator by adding only a few mol % of styrene. If really controlled, the polymerization, initiated by an alkoxyamine, should lead to macromolecules exhibiting all the same structure with the initiating radical of the alkoxyamine at the α-end and the nitroxide attached at the ω-end. ^{31}P NMR spectroscopy of the isolated copolymer was carried out to fully confirm the presence of the nitroxide at the ω-end. Then, chain extension with styrene was applied to assess livingness and create amphiphilic diblock copolymers.

Experimental Part

1. Materials. Methacrylic acid (MAA, purest grade, Acros, stabilized with 250 ppm of methylethylhydroquinone) was used without further purification. Styrene (S, Aldrich, 99%) was 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%) were kindly supplied by Arkema. The solvents, 1,4-dioxane (from SDS, synthesis grade) and ethanol (from VWR Prolabo, synthesis grade), trimethylsilyldiazomethane (Aldrich, 2 M solution in hexane), 1,3,5-trioxane (Aldrich, 99+%), and diethyl phosphite (Aldrich, 98%) were used as received.

2. SG1-Mediated Copolymerization of Methacrylic Acid and Styrene in Solution. All copolymerizations of methacrylic acid

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Table 1. Experimental Conditions for the SG1-Mediated Copolymerizations of Methacrylic Acid (MAA) with a Low Proportion of Styrene (S)

expt	symbol	$[MAA]_0$ (mol L^{-1})	$[S]_0$ (mol L^{-1})	$f_{S,0}$[a]	solvent	$[initiator]_0$ (mol L^{-1})	r[b] (%)	target M_n[c] at 100% conv (g mol^{-1})	T (°C)	overall time (min)
1	▲	10.4	1.01	0.089		1.18×10^{-1}	10.1	8900	83	*d*
2	■	3.27	0.316	0.088	1,4-dioxane	3.70×10^{-2}	9.8	8870	83	100
3	●	4.31	0.424	0.090	1,4-dioxane	4.89×10^{-2}	9.7	8880	84	40[e]
4	◆	3.27	0.316	0.088	1,4-dioxane	3.82×10^{-2}	9.6	8630	73	300
5	□	4.31	0.421	0.089	1,4-dioxane	4.77×10^{-2}	10.1	9080	73	150
6	○	4.38	0.421	0.088	1,4-dioxane	9.42×10^{-2}	10.2	4840	73	110
7	×	4.30	0.383	0.082	ethanol	4.74×10^{-2}	10.3	9020	73	235
8	▽▼	4.31	0.180	0.040	ethanol	4.45×10^{-2}	10.6	9150	73	175

[a] Initial molar fraction of styrene. [b] $r = 100 \times [SG1]_0/[initiator]_0$; the initiator is BlocBuilder displayed in Scheme 1. [c] Theoretical number-average molar mass, calculated according to $M_n = MM_{initiator} +$ conversion $\times$ initial weight of monomers/initial mol number of initiator, with conversion $= 1$ and $MM_{initiator}$ $=$ the molar mass of the initiator (381 g mol^{-1}). [d] Thermal autoacceleration after 5 min at 83 °C. [e] Thermal autoacceleration after 50 min at 84 °C.

Table 2. Synthesis of Poly(methacrylic acid-*co*-styrene)-*b*-polystyrene Block Copolymers in 1,4-Dioxane Solution at 120 °C

expt	$[macroinitiator]_0$[a] (mol L^{-1})	$[styrene]_0$ (mol L^{-1})	target overall M_n[b] at 100% conv (g mol^{-1})	target DP_n[b] of the polystyrene block at 100% conv	polymerization time (h)
9	1.5×10^{-2}	4.39	36840	300	2.25
10	9.9×10^{-3}	0.165	7370	17	6.5

[a] The macroinitiator is copolymer **5** (see Table 1) purified by one precipitation in diethyl ether; $M_n = 5640$ g mol^{-1}; P(MAA_{54}-*co*-S_6)-SG1. [b] M_n is the number-average molar mass; DP_n is the number-average degree of polymerization.

Table 3. Kinetic Parameters for the SG1-Mediated Copolymerization of Styrene (S) and Methacrylic Acid (MAA) at 80 °C

	kinetic or thermodynamic parameter	value	ref
$k_{p,S}$ (L mol^{-1} s^{-1})	propagation rate constant of styrene	628	12
$k_{p,MAA}$ (L mol^{-1} s^{-1})	propagation rate constant of methacrylic acid (at 4.55 mol L^{-1} in water)	4003	13
r_S	reactivity ratio for styrene	0.14	14
r_{MAA}	reactivity ratio for methacrylic acid	0.61	14
K_S (mol L^{-1})	activation−deactivation equilibrium constant for the SG1-mediated polymerization of styrene	1.3×10^{-10}	15
K_{MMA}[a] (mol L^{-1})	activation−deactivation equilibrium constant for the SG1-mediated polymerization of methyl methacrylate[a]	1×10^{-6}	16, 17

[a] We made the assumption that methacrylic acid behaves similarly to methyl methacrylate, i.e., $K_{MAA} = K_{MMA}$.

with a low amount of styrene were carried out using the BlocBuilder initiator (Scheme 1) and ~10 mol % of free SG1 based on the initiator to obey the experimental protocol previously established for the copolymerization of methyl methacrylate with styrene.[6,7] The typical procedure is as follows (see experiment 2 in Table 1): a mixture of MAA (40.3 g, 3.27 mol L^{-1}), S (4.7 g, 0.316 mol L^{-1}; initial molar fraction, $f_{S,0} = 0.088$) and free SG1 (0.153 g, 3.6 $\times$ 10^{-3} mol L^{-1}) in the solvent (1,4-dioxane, 101.8 g, 98.5 mL) was deoxygenated with a nitrogen stream for 20 min at room temperature. The BlocBuilder initiator was then added (2.00 g, 3.70 $\times$ 10^{-2} mol L^{-1}), and nitrogen bubbling was carried out for an additional 10 min. The so-formed solution was then introduced into a 250 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 reactions were carried out at either 73 or 83 °C. Time zero of the polymerization was chosen when the temperature of the mixture reached 70 °C (i.e., approximately 7−8 min after immersion of the flask in the bath). Samples were periodically withdrawn and cooled in an ice−water bath to stop the reaction. The overall monomer conversion (x) was determined by gravimetry after drying the polymer samples for 4 days at room temperature. For some samples, it was also checked by ^{1}H NMR spectroscopy. Before determining the proportion of living chains by ^{31}P NMR or using the copolymers as macroinitiators, the polymerization medium was precipitated in diethyl ether and the polymer was filtered off and dried under vacuum at room temperature for 3 days to eliminate monomers and solvent. All purified copolymers appear as a fine, bright, white powder.

3. Synthesis of the Poly(methacrylic acid-*co*-styrene)-*b*-polystyrene Diblock Copolymers (P(MAA-*co*-S)-*b*-PS). A typical experiment is as follows (experiment 10, Table 2): 1.63 g (9.9 $\times$ 10^{-3} mol L^{-1}) of the purified poly(methacrylic acid-*co*-styrene) copolymer **5** (P(MAA_{54}-*co*-S_6)-SG1, $M_n = 5640$ g mol^{-1}, $M_w/M_n = 1.37$) was introduced into a 100 mL round-bottom flask with an appropriate amount of styrene (0.498 g, 0.165 mol L^{-1}) and 1,4-dioxane (30 g, 29 mL). After complete solubilization, the mixture was deoxygenated by nitrogen bubbling. The flask was further immersed for 6.5 h in an oil bath, thermostated at 120 °C. After stopping the polymerization by cooling in an ice−water bath, the final monomer conversion was determined by ^{1}H NMR in DMSO-d_6 solution. The resulting copolymer was purified by precipitation in diethyl ether, and after filtration, it was dried under vacuum at room temperature for 3 days. Like the macronitiator, the resulting purified block copolymers appear as a fine, bright, white powder.

4. 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, as described before.[8,9] The samples were injected (using a Viscotek VE 5200 injector) in two PSS linear M columns (PSS SDV, linear MU, 8 mm $\times$ 300 mm; bead diameter, 5 μm; separation limits, 400−2 $\times$ 10^6 g mol^{-1}) thermostated at 40 °C, with THF as an eluent (flow rate of 1 mL/min). Detection was made with a refractometer Refracto Monitor IV (LDC analytical). The Viscotek TriSEC software was used for data analysis; calculation was made with a calibration curve based on poly(methyl methacrylate) standards (from Polymer Laboratories) for the poly(methyl methacrylate-*co*-styrene) copolymers and on polystyrene ones (from Polymer Standards Service) for the poly(methyl methacrylate-*co*-styrene)-*b*-polystyrene block copolymers. All experimental M_n values based on methyl methacrylate subunits have been recalculated for methacrylic acid units.

For one copolymerization of methacrylic acid and styrene (experiment 8, Table 1), the raw polymerization media with added DMSO-d_6 were analyzed by proton NMR spectroscopy at regular time intervals. Analyses were performed in 5 mm diameter tubes at room temperature using a Bruker AC250 apparatus, operating

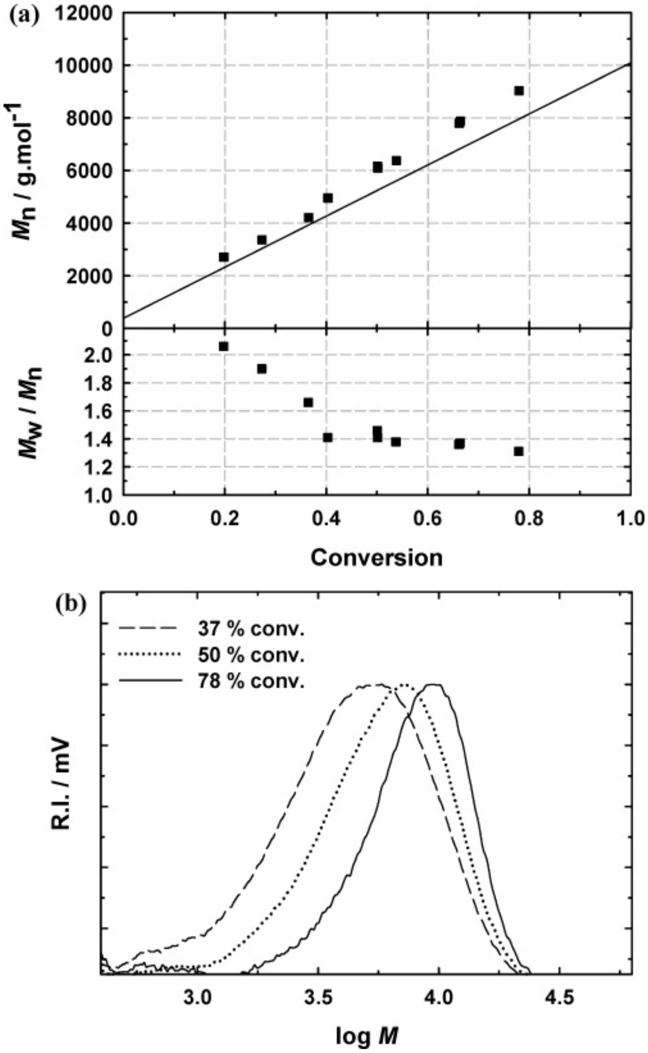

Figure 1. Copolymerization of methacrylic acid (MAA) and 8.8 mol % of styrene at 83 °C in 1,4-dioxane, with $[\mathrm{MAA}]_0 = 3.27$ mol L^{-1}, in the presence of 3.70×10^{-2} mol L^{-1} of alkoxyamine initiator and 9.8 mol % of free SG1 based on the initiator (experiment 2, Table 1): (a) number-average molar mass, M_n, and polydispersity index, PDI, vs conversion; the full line represents the theoretical M_n; (b) size exclusion chromatograms as a function of monomers conversion.

at a frequency of 250 MHz. The chemical shift scale was calibrated on the basis of the solvent peak (DMSO-d_6 at 2.54 ppm). The individual conversions (x_{MAA} for methacrylic acid and x_{S} for styrene) were determined by integrating the peaks corresponding to the vinyl protons of the considered monomer, using the broad peak between 6.5 and 7.5 ppm as an internal reference (five aromatic H for styrene and polystyrene). The overall weight conversion (x) was calculated from the individual conversions and the initial weight fraction of each monomer ($w_{\mathrm{MAA},0}$ and $w_{\mathrm{S},0}$) according to $x = x_{\mathrm{MAA}}w_{\mathrm{MAA},0} + x_{\mathrm{S}}w_{\mathrm{S},0}$. The obtained values showed that determination of the conversions by gravimetry generated an overestimation, which could reach ~15% above 50% conversion, because of an incomplete evaporation of methacrylic acid and solvent from the raw samples, even after long drying times (a similar behavior was previously observed for the copolymerization of styrene and acrylic acid).[9] For synthesis of the poly(methacrylic acid-*co*-styrene)-*b*-polystyrene diblock copolymers, the styrene conversion was determined by integrating the peaks corresponding respectively to one vinylic proton of styrene ($\delta = 5.3$ ppm) and to the six protons of 1,3,5-trioxane ($\delta = 5.1$ ppm), which was added in the polymerization medium as an internal reference.

The ^{31}P NMR analyses of the precipitated P(MAA-*co*-S) polymers in DMSO-d_6 solution were performed in 10 mm diameter tubes at 25 °C, using a Bruker Avance 300 spectrometer operating at the frequency of 121.44 MHz. Spectra were recorded applying conditions for quantitative analysis: spectral width of 75 ppm, flip angle of 10°, relaxation delay of 90 s, digital resolution of 0.27 Hz pt^{-1}, and suppression of the NOE. To allow quantitative analysis of the end group, the polymers were weighed (and further corrected from the amount of residual solvent and monomer determined by thermogravimetric analysis; the corrected mass was 300.4 mg (5.33×10^{-5} mol) for copolymer **5** and 239.0 mg (7.45×10^{-5} mol) for copolymer **6**), and a known amount of diethyl phosphite was added as an internal reference (7.8 mg, 5.68×10^{-5} mol for copolymer **5** and 15.7 mg, 1.14×10^{-4} mol for copolymer **6**). The chemical shift scale was calibrated on the basis of the added diethyl phosphite at 7.1 ppm.

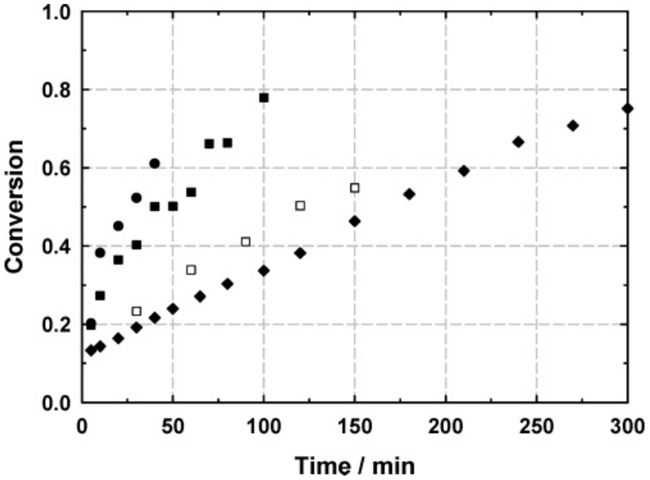

Figure 2. Effect of the concentration of methacrylic acid (MAA) and of the temperature on the copolymerization kinetics in 1,4-dioxane, in the presence of 8.8 mol % of styrene based on the monomers and 10 mol % of free SG1 based on the initiator. Overall conversion vs time for experiments 2 (■; $[\mathrm{MAA}]_0 = 3.27$ mol L^{-1}, $[\mathrm{initiator}]_0 = 3.70 \times 10^{-2}$ mol L^{-1}, $T = 83$ °C), 3 (●; $[\mathrm{MAA}]_0 = 4.31$ mol L^{-1}, $[\mathrm{initiator}]_0 = 4.89 \times 10^{-2}$ mol L^{-1}, $T = 84$ °C), 4 (◆; $[\mathrm{MAA}]_0 = 3.27$ mol L^{-1}, $[\mathrm{initiator}]_0 = 3.82 \times 10^{-2}$ mol L^{-1}, $T = 73$ °C), and 5 (□; $[\mathrm{MAA}]_0 = 4.31$ mol L^{-1}, $[\mathrm{initiator}]_0 = 4.77 \times 10^{-2}$ mol L^{-1}, $T = 73$ °C).

Composition of the 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 ($\delta = 178{-}180$ 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 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).

Results and Discussion

1. Selection of Appropriate Experimental Conditions for the Copolymerization of Methacrylic Acid with a Small Proportion of Styrene. *General Background.* The nitroxide-mediated controlled free-radical polymerization of monomers bearing a carboxylic acid function has hardly been reported in the literature.[5,8−11] Our group described the homopolymerization of acrylic acid (AA)[8] and its copolymerization with styrene[9] using SG1 as a nitroxide mediator. The polymerizations were conducted in 1,4-dioxane solution, but the system suffered from chain transfer to the solvent, leading to molar mass limitation of the target living polymers.[8] Concerning methacrylic acid, the main difficulty is related to its very high activation−deactivation equilibrium constant, *K*, which prevents the use of SG1-mediated polymerization to achieve the synthesis of living homopolymers.

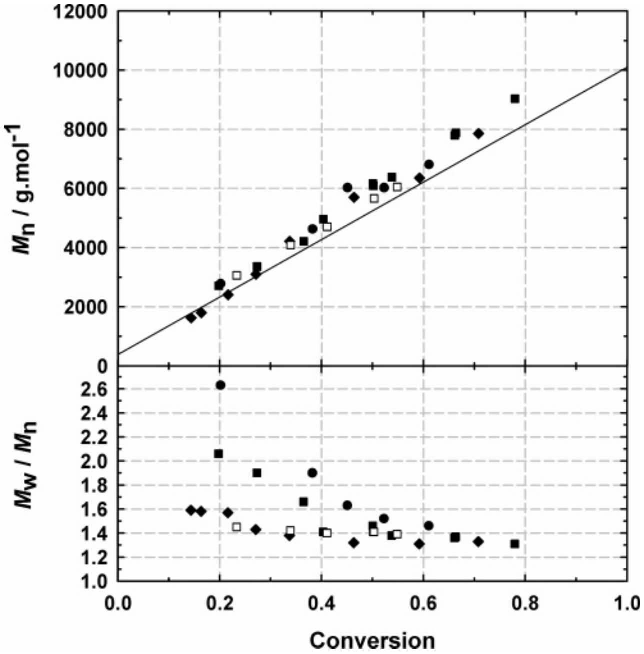

Figure 3. Effect of the concentration of methacrylic acid (MAA) and of the temperature on the copolymerization kinetics in 1,4-dioxane, in the presence of 8.8 mol % of styrene based on the monomers and 10 mol % of free SG1 based on the initiator. Number-average molar mass, M_n, and polydispersity index, PDI, vs conversion (the full line represents the theoretical M_n) for experiments 2 (■; $[MAA]_0 = 3.27$ mol L^{-1}, $[initiator]_0 = 3.70 \times 10^{-2}$ mol L^{-1}, $T = 83$ °C), 3 (●; $[MAA]_0 = 4.31$ mol L^{-1}, $[initiator]_0 = 4.89 \times 10^{-2}$ mol L^{-1}, $T = 84$ °C), 4 (◆; $[MAA]_0 = 3.27$ mol L^{-1}, $[initiator]_0 = 3.82 \times 10^{-2}$ mol L^{-1}, $T = 73$ °C), and 5 (□; $[MAA]_0 = 4.31$ mol L^{-1}, $[initiator]_0 = 4.77 \times 10^{-2}$ mol L^{-1}, $T = 73$ °C).

However, with our recent results showing that the copolymerization of methyl methacrylate with a low amount of styrene allowed a living polymer to be formed, the difficulty was overcome.[6,7] It is then the aim of this paper to show that the work performed with methyl methacrylate can be extended to methacrylic acid, with the purpose of generating amphiphilic poly(methacrylic acid-*co*-styrene)-*b*-polystyrene diblock copolymers.

On the basis of the equation giving the average activation–deactivation equilibrium constant $\langle K\rangle$ of a nitroxide-mediated copolymerization system (eq 1),[6] using the terminal model in a first approach, it can be anticipated that methacrylic acid should behave very similarly to methyl methacrylate, regarding the SG1-mediated copolymerization with styrene. In particular, with a high $k_{p,MAA}$ and a high K_{MAA}, the average activation–deactivation equilibrium constant should be very close to that of styrene, even for low proportions of this comonomer.

$$\langle K\rangle = \frac{\dfrac{r_{MAA}f_{MAA}}{k_{p,MAA}} + \dfrac{r_S f_S}{k_{p,S}}}{\dfrac{r_{MAA}f_{MAA}}{k_{p,MAA}K_{MAA}} + \dfrac{r_S f_S}{k_{p,S}K_S}} \quad (1)$$

In eq 1, the r_is are the reactivity ratios (i = MAA or S for methacrylic acid and styrene, respectively), the f_is are the comonomer molar fractions, the $k_{p,i}$s are the homopropagation rate constants, and the K_is are the activation–deactivation equilibrium constants for the SG1-mediated free-radical respective homopolymerizations. The experimental values are given in Table 3 for a copolymerization carried out at low temperature. At 80 °C, when the initial proportion of styrene is $f_{S,0} = 0.088$, the calculated value of $\langle K\rangle$ is 1.03×10^{-9} mol L^{-1}, and for $f_{S,0} = 0.040$ $\langle K\rangle = 2.22 \times 10^{-9}$ mol L^{-1}, small enough in both cases to enable a well-controlled polymerization.

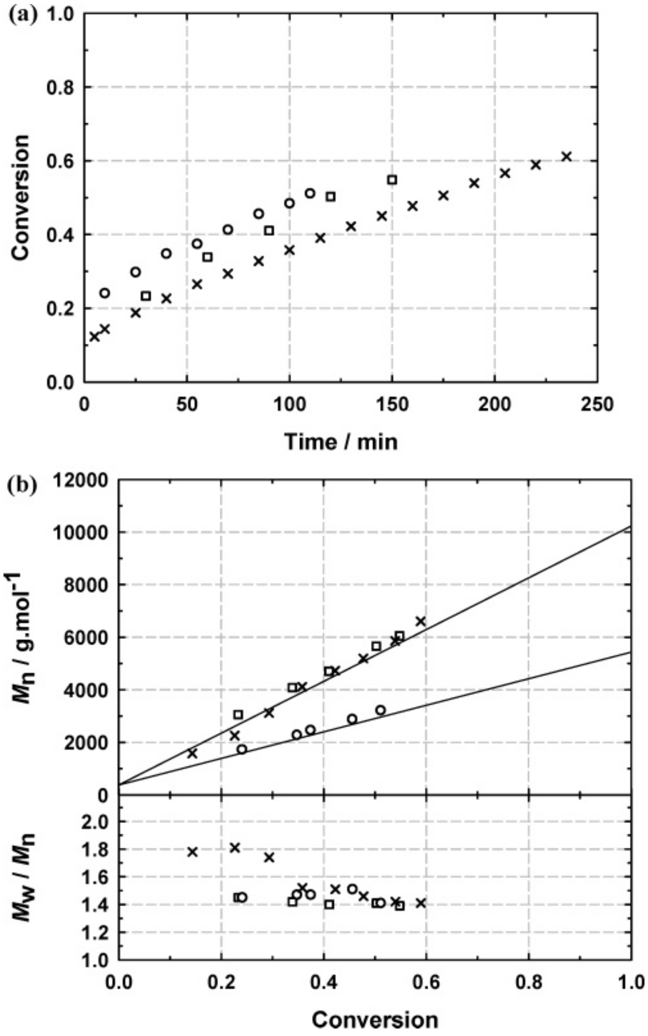

Figure 4. Effect of the initiator concentration and of the solvent on the kinetics and on the copolymer characteristics, for copolymerizations of methacrylic acid (MAA) carried out at 73 °C in the presence of 8.8 mol % of styrene based on the monomers and 10 mol % of free SG1 based on the initiator. Experiment 5 (□; $[MAA]_0 = 4.31$ mol L^{-1} and $[initiator]_0 = 4.77 \times 10^{-2}$ mol L^{-1} in 1,4-dioxane), experiment 6 (○; $[MAA]_0 = 4.38$ mol L^{-1} and $[initiator]_0 = 9.42 \times 10^{-2}$ mol L^{-1} in 1,4-dioxane), and experiment 7 (×; $[MAA]_0 = 4.30$ mol L^{-1} and $[initiator]_0 = 4.74 \times 10^{-2}$ mol L^{-1} in ethanol). (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).

Effect of the Concentration of MAA and of the Temperature. The copolymerization of methacrylic acid with styrene ($f_{S,0} = 0.088$) was first performed in bulk at 83 °C (see the experiment 1 in Table 1). The polymerization, however, was too fast and suffered from an uncontrolled exothermicity. Consequently, all subsequent polymerizations were performed in solution, and the solvent (1,4-dioxane or ethanol) was selected to allow a good solubilization of the monomers, the initiator, the nitroxide, and the copolymer. In contrast to acrylates, the methacrylate-based radicals are much less reactive toward hydrogen abstraction, and consequently the polymer molar mass should not be significantly affected by chain transfer reaction to the solvent (for instance, the chain transfer constant to ethanol is $C_{tr} = 0.429 \times 10^{-4}$ for methacrylic acid at 80 °C, whereas it is 10 times larger for acrylic acid, i.e., $C_{tr} = 4.38 \times 10^{-4}$; in 1,4-dioxane, the chain transfer constant is $C_{tr} = 3.9 \times 10^{-4}$ for acrylic acid

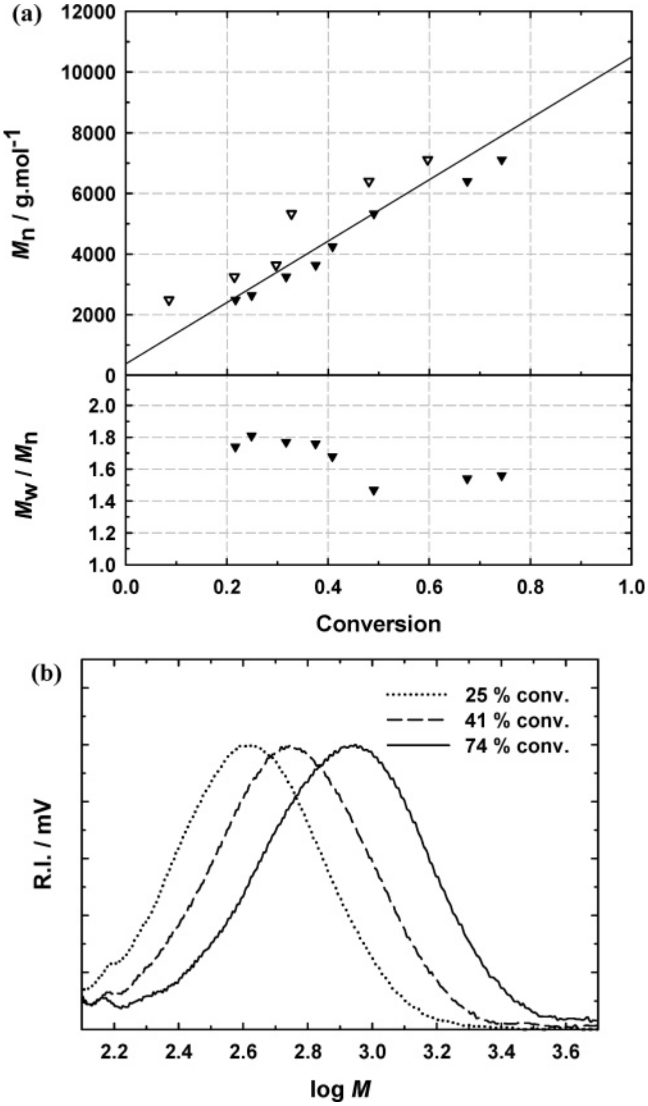

Figure 5. Copolymerization of methacrylic acid (MAA) with 4.0 mol % of styrene in ethanol at 73 °C, in the presence of 10 mol % of free SG1 based on the initiator (experiment 8: $[\mathrm{MAA}]_0 = 4.31$ mol L^{-1} and $[\mathrm{initiator}]_0 = 4.45 \times 10^{-2}$ mol L^{-1}; empty triangles = conversion measured by ^{1}H NMR; black triangles = conversion measured by gravimetry). (a) Number-average molar mass, M_n, and polydispersity index, PDI, vs conversion; the full line represents the theoretical M_n; (b) evolution of the size exclusion chromatograms with conversion.

at 80 °C; the corresponding value for methacrylic acid was not found in the literature, but according to the previous values it is reasonable to assume that the transfer constant is not very different from that in ethanol).[18] A model copolymerization was then carried out in 1,4-dioxane at 83 °C, with a MAA concentration of 3.27 mol L^{-1} (experiment 2, Table 1). The polymerization was quite fast, and the characteristics of the recovered copolymers were in good agreement with those expected for a living/controlled system (Figure 1): (i) Linear evolution of M_n with monomer conversion and good correlation between the experimental values and the theoretical ones. At this stage, it is nevertheless important to bear in mind that determination of conversions by gravimetry led to an overestimation on the order of 10−15% from low to high conversions. As a consequence, initiator efficiency, which is apparently close to 1 according to Figure 1a, should rather be close to 0.80 as already observed for the copolymerization of methyl methacrylate and styrene.[6,7] (ii) Continuous decrease of the polydispersity indices with monomer conversion, from 2.1 to 1.3. (iii) Continuous and complete shift of the size exclusion chromatograms toward the high molar mass region throughout the copolymerization reaction. All those results support the controlled character of the SG1-mediated free-radical polymerization of methacrylic acid performed in the presence of a low amount of styrene ($f_{\mathrm{S},0} = 0.088$) and free SG1 ($r = [\mathrm{SG1}]_0/[\mathrm{initiator}]_0 = 0.10$), as was expected from the results found with methyl methacrylate and from the calculated $\langle K \rangle$ value. Moreover, chain transfer reactions to the solvent could not be detected as the experimental M_n data remained on the theoretical line and did not shift toward lower values, as was observed in the case of acrylic acid.[8] The same copolymerization carried out with a larger concentration of MAA (4.31 mol L^{-1} instead of 3.27 mol L^{-1}, same target M_n, experiment 3; see Table 1 and Figure 2) was significantly faster and underwent thermal autoacceleration after 50 min (temperature increase to 90−100 °C).

In a second step, the polymerization temperature was then lowered to 73 °C, to decrease the polymerization rate and then allow the monomer concentration to be increased. Two reactions were performed at $[\mathrm{MAA}]_0 = 3.27$ mol L^{-1} (experiment 4) and $[\mathrm{MAA}]_0 = 4.31$ mol L^{-1} (experiment 5) (Table 1). It should be noted here that the initiator concentration was slightly different for both experiments, the purpose being to target the same final M_n. The polymerization rate was faster for the highest initiator and monomer concentrations (experiment 5, Figure 2), but no thermal autoacceleration was observed. In all cases, irrespective of the temperature, an initial conversion jump to 10−15% was observed, indicating a delay before the pseudo-equilibrium conditions are reached (a shift of the x-axis due to the possible start of the polymerization before the chosen $t = 0$ (see the Experimental Part) might also partially explain the shape of the conversion−time plots). The experimental M_n values increased linearly with monomer conversion and were in good agreement with the theoretical ones (Figure 3). Once again, this supports the absence of irreversible chain transfer reactions to the solvent. The polydispersity indices continuously decreased with monomer conversion, to reach a value just below 1.4 at 80% conversion. Interestingly, they were initially much higher at 83 °C than at 73 °C. This is directly related to the equation giving PDI as a function of monomer conversion in nitroxide-mediated free-radical polymerization, established for batch systems with constant concentration of propagating radicals (eq 2).[19]

$$\mathrm{PDI} = 1 + \frac{1}{\mathrm{DP_n}} + (2x^{-1} - 1)\frac{k_\mathrm{p}[\mathrm{initiator}]_0}{k_\mathrm{c}[\mathrm{free\ SG1}]} \qquad (2)$$

In this equation, $\mathrm{DP_n}$ is the number-average degree of polymerization at a given conversion x, k_p is the rate constant of propagation (average value in a copolymerization), k_c is the rate constant of reversible deactivation of the propagating radicals by SG1 (average value in a copolymerization), and [free SG1] is the actual SG1 concentration at the conversion x. Since, in contrast to k_p, the deactivation rate constant, k_c, is only slightly affected by the temperature,[20] the ratio $k_\mathrm{p}/k_\mathrm{c}$ increases significantly when the temperature is increased. This explains why the PDI are much larger at 83 °C for the lowest conversions, when the concentration of SG1 is not very different in both systems (same initial concentration). When the polymerization progresses, [free SG1] increases due to the persistent radical effect,[21] which is more pronounced at the highest temperature because the activation−deactivation equilibrium constant is larger. This counterbalances the $k_\mathrm{p}/k_\mathrm{c}$ effect and might explain why the final PDIs are not so different for both temperatures.

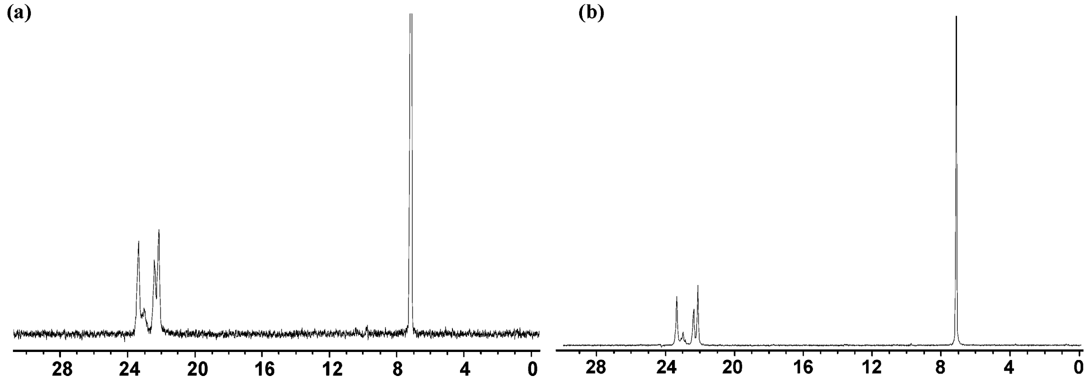

Figure 6. ^{31}P NMR spectrum of the final copolymers **5** (a) and **6** (b).

To conclude this part, a temperature of 73 °C and a MAA concentration of 4.3 mol L^{-1} seem to be the most-suited conditions for the synthesis of the poly(methacrylic acid-*co*-styrene) copolymers.

Effect of the Initiator Concentration. For experiment 6 (Table 1), the alkoxyamine initiator concentration was increased by a factor of 2 to target a copolymer with M_n twice as low as in the previous experiment 5. From the graph representing the conversion vs time (Figure 4a), it appears that the kinetics were not significantly different for both reactions and therefore did not strongly depend upon the initiator concentration. This is not really surprising as the [free SG1]$_0$/[initiator]$_0$ ratio, which was maintained the same, close to 0.1 for both experiments, actually governs the polymerization rate.[22,23] With this initiator concentration, the M_n values followed the theoretical line (Figure 4b) and the polydispersity indices decreased to 1.4.

Effect of the Solvent. As mentionned above, methacrylic acid-based radicals are much less reactive in hydrogen abstraction than those derived from acrylic acid, and the polymerization of MAA is then less affected by chain transfer reaction to the solvent. Consequently, any kind of polar solvent might be suitable for the polymerization. The copolymerization of methacrylic acid with a small amount of styrene ($f_{\mathrm{S},0} = 0.088$) was then carried out in ethanol (experiment 7, Table 1), and the results, displayed in Figure 4, indeed fulfill the expectations. Figure 4a shows that the polymerization rates in ethanol and in 1,4-dioxane (experiment 5) are not very different, and Figure 4b underlines the good agreement between the theoretical and the experimental M_ns, which confirms the absence of transfer reaction to ethanol.

Effect of the Proportion of Styrene. According to eq 1, a proportion of styrene as low as 0.04 might be sufficient to significantly decrease the average activation−deactivation equilibrium constant. To check the possibility of reducing the proportion of styrene, the polymerization of methacrylic acid was carried out in the presence of 4.0 mol % of styrene, in ethanol at 73 °C (experiment 8, Table 1). For this experiment, the evolution of conversion with time was followed by both gravimetry and ^{1}H NMR. The results underline that gravimetry generates an overestimation of the conversions. Nevertheless, Figure 5a,b shows that the copolymerization was still well controlled, even though the PDIs were not as low as in the previous experiments with higher styrene content. In particular, the continuous and complete shift of the size exclusion chromatograms toward the high molar mass region was a very encouraging characteristic.

2. Assessment of the Living Character of the Poly(methacrylic acid-*co*-styrene) Copolymers by ^{31}P NMR. ^{31}P NMR was used to analyze the chain-end structure of the two final copolymers **5** and **6** synthesized at 73 °C, after purification by precipitation in diethyl ether. From the SEC analysis, the raw copolymers **5** (55% conversion) and **6** (53% conversion) had respectively $M_\mathrm{n} = 5460$ and 2920 g mol^{-1} with PDI = 1.39 and 1.41, whereas after purification, M_n was 5640 and 3210 g mol^{-1}, respectively, and PDI was 1.37 and 1.38. Consequently, the purification step did not lead to fractionation of the material, and analysis of the resulting copolymers should give reliable information. For both copolymers, the characteristic peaks of the SG1-based alkoxyamine end group were observed at 22−24 ppm (Figure 6). From the peak integration (see the Experimental Part), the percentage of chains terminated by the alkoxyamine group was above 90%. Such result is a clear indication of the living character of the copolymers, which might allow efficient chain extension toward the synthesis of well-defined block copolymers.

3. Synthesis of Amphiphilic Poly(methacrylic acid-*co*-styrene)-*b*-polystyrene Block Copolymers. In a first step, to confirm the ^{31}P NMR quantitative analysis, the copolymer **5** was used as a macroinitiator in the homopolymerization of styrene in 1,4-dioxane solution at 120 °C (see experiment 9 in Table 2): a high molar mass was targeted (i.e., 36 840 g mol^{-1}) to ensure a complete shift of the SEC peak and allow clear conclusion on the crossover efficiency. The results, displayed in Figure 7a, show indeed a complete shift of the peak, in particular the absence of a shoulder on the low molar mass side, which indicates the absence of unreacted macroinitiator. The characteristics of the resulting copolymer were particularly satisfactory as $M_\mathrm{n} = 17\,680$ g mol^{-1} and PDI = 1.12 at 43% styrene conversion for a theoretical M_n of 19 060 g mol^{-1}.

The synthesis of an amphiphilic poly(methacrylic acid-*co*-styrene)-*b*-polystyrene diblock copolymer was then undertaken. The aim was to demonstrate the possibility of designing copolymers with similar characteristics as those of the well-defined poly(acrylic acid)-*b*-polystyrenes prepared in the past for stabilization of emulsion polymerizations.[24] Among the various structures investigated for the latter, the copolymers with 50 acrylic acid subunits and 10−16 styrene subunits were particularly efficient.[25,26] Therefore, a chain extension was performed from the purified copolymer **5**, targetting a low molar mass for the polystyrene block (experiment 10 in Table 2). As for experiment 9, the SEC characteristics of the resulting copolymer, based on polystyrene calibration, were in correct agreement with the theoretical calculations: the raw copolymer **10** (44% styrene conversion; theoretical M_n of 6400 g mol^{-1}) had $M_\mathrm{n} = 7250$ g mol^{-1} with PDI = 1.36. After purification, M_n was 7310 g mol^{-1} with PDI = 1.33 (Figure 7b). Then, knowing that the macroinitiator had a M_n of 5640 g mol^{-1} and that the molar proportion of styrene was 10.0 mol % according to ^{13}C NMR spectroscopy (in correct accord with the 11 mol % calculated from the reactivity ratios given in Table 3),

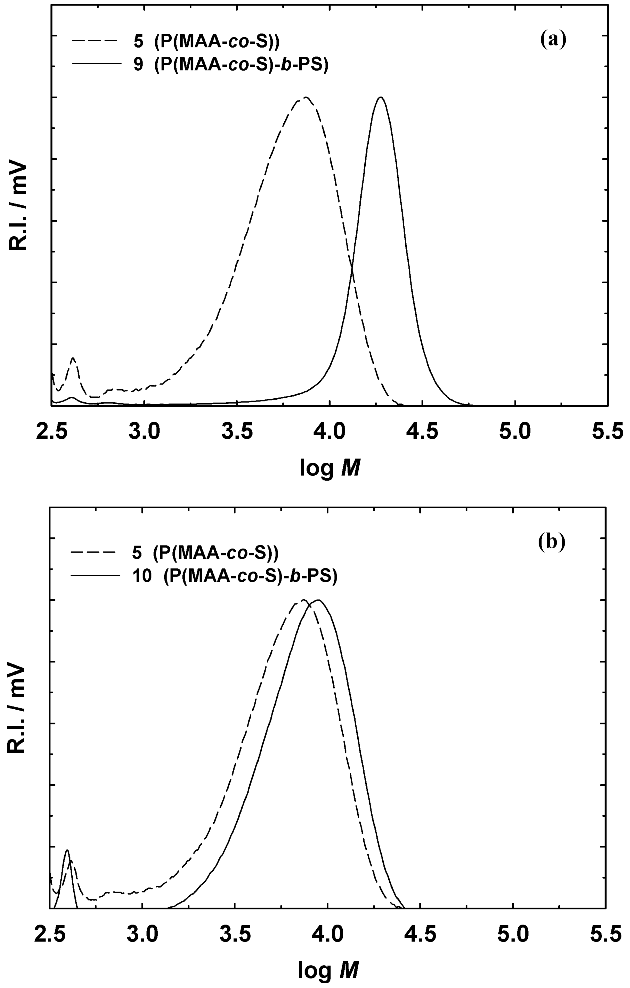

Figure 7. Size exclusion chromatograms of the poly(methacrylic acid-*co*-styrene)-*b*-polystyrene resulting from chain extension of the copolymer **5**: (a) experiment 9; (b) experiment 10 (see Table 2).

the distribution of the monomer subunits in the copolymer **5** could be determined: P(MAA_{54}-*co*-S_6). From the overall composition of the purified diblock copolymer **10**, also determined by ^{13}C NMR analysis, the final structure was P(MAA_{54}-*co*-S_6)-*b*-PS_8. The length of the second block was then in perfect agreement with the calculated value based on the conversion of styrene of 44% in the second polymerization step.

Conclusion

In a similar way as with methyl methacrylate, this work demonstrates that methacrylic acid can be polymerized at a temperature below 90 °C using a SG1-based alkoxyamine initiator in the presence of a small proportion of styrene, to yield well-defined polymers with controlled molar mass. With 1,4-dioxane or ethanol as a solvent, no chain transfer reaction to the solvent could be detected. The presence of an alkoxyamine chain end was assessed by ^{31}P NMR and by chain extension experiments, by which we showed that the polymers could be used as efficient macroinitiators in the polymerization of styrene, allowing well-defined, amphiphilic diblock copolymers to be synthesized. A wide variety of functional methacrylate monomers are often used in free-radical polymerizations, and their advantage over acrylates is the reduced reactivity of the propagating radical, allowing many side reactions to be avoided. This work opens the door to the nitroxide-mediated polymerization of such monomers, combining the benefits of the polymerization method with those of the monomers.

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