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Living Character of Polymer Chains Prepared via Nitroxide-Mediated Controlled Free-Radical Polymerization of Methyl Methacrylate in the Presence of a Small Amount of Styrene at Low Temperature

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ABSTRACT: This article follows a previous study (*Macromolecules* **2005**, *38*, 5485) demonstrating that the nitroxide SG1-mediated polymerization of methyl methacrylate can be achieved at 90 °C with high conversion and high quality of control by introducing a small amount of styrene. In this work, the resulting polymer was characterized and the presence of SG1-based alkoxyamine at the polymer chain-end was identified, supporting the livingness of the macromolecules. In particular, it was shown that the alkoxyamine end group was connected to a single styrene terminal unit and that the methyl methacrylate penultimate unit had a strong effect on the temperature of dissociation. Consequently, the copolymerization of methyl methacrylate with a low molar proportion of styrene could be performed at temperatures below 90 °C. The polymer was also used as an efficient macroinitiator in the polymerization of styrene and *n*-butyl acrylate, to form methyl methacrylate-based block copolymers.

Introduction

Among the available controlled free-radical polymerization techniques, nitroxide-mediated polymerization (NMP) provides the poorest degree of control over the polymerization of methacrylic esters.[1] With TEMPO, (2,2,6,6-tetramethylpiperidinyl-1-oxy), the H-transfer reaction between the nitroxide and the growing radical dominates over the reversible combination with the nitroxide, yielding an alkene chain-end along with a hydroxylamine. Polymerizations are thus unable to reach large conversions and do not produce nitroxide-terminated living polymers.[2−5] Only copolymerizations with a large ratio of styrene to methacrylate lead to rather well-defined random copolymers, but the quality of control is dramatically altered when the proportion of methyl methacrylate is increased.[6−8] The second generation of acyclic nitroxides such as SG1[9−11] (*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, Scheme 1) or TIPNO[11,12] (2,2,5-trimethyl-4-phenyl-3-azahexane 3-nitroxide) still do not permit a good control over the homopolymerization of methyl methacrylate (MMA). In the case of SG1, H-transfer between the nitroxide and the growing radical does not occur; however, the too large activation−deactivation equilibrium constant leads to a high concentration of propagating macroradicals and hence favors their irreversible self-termination together with the production of a large concentration of free nitroxide, which eventually acts as an inhibitor.[13,14] As a consequence, the polymerization stops after a very short time-period and cannot reach high conversions. A seminal work presented by Benoit et al. showed that copolymerizations of methyl methacrylate with different amounts of styrene in the

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

SG1   MAMA alkoxyamine
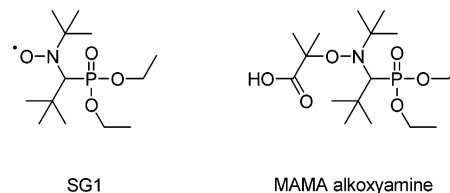
presence of TIPNO is, however, better controlled than those with TEMPO.[12]

In a recent study, the average activation−deactivation equilibrium constant, $\langle K \rangle$, was determined on a theoretical basis for controlled free-radical copolymerization operating via a reversible termination mechanism, using the terminal model or the implicit penultimate unit effect model for the propagation reaction.[15] From both the equations and the simulations, it was 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 was indeed successfully applied to the NMP of MMA at 90 °C initiated with an SG1-based alkoxyamine (Scheme 1): by adding only a few mole percent of styrene, polymerizations reached high conversions and exhibited all the features of a controlled system. The key parameter allowing the system to undergo efficient activation−deactivation cycles throughout the polymerization, and provide simultaneous growth of all chains, was supposed to be the existence of a majority of styrene-terminated macroalkoxyamines.

The purpose of this article is to go a step further by analyzing the chain ends of the poly(methyl methacrylate-*co*-styrene)

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Table 1. Experimental Conditions for the Bulk Homopolymerizations and Copolymerizations of Methyl Methacrylate with Styrene ($f_{S0} = 0.088$)

expt	MMA, g (mol)	S, g (mol)	MAMA, g (mol)	SG1, g (mol)	target DP$_n$ at 100% conversion	r,[a] %	T, °C	overall time, min
P0	80.00 (0.80)	8.00 (0.077)	4.045 (1.06×10^{-2})	0.303 (1.03×10^{-3})	83	9.7	90	40
P1	80.00 (0.80)	8.01 (0.077)	3.935 (1.03×10^{-2})	0.306 (1.04×10^{-3})	85	10.1	90	40
P2	80.15(0.80)	7.99 (0.077)	3.940 (1.03×10^{-2})	0.305 (1.04×10^{-3})	85	10.0	90	40
P3	120.33 (1.20)	12.05 (0.116)	1.426 (3.74×10^{-3})	0.129 (4.39×10^{-4})	352	11.7	90	90
P4	120.24 (1.20)	12.06 (0.116)	1.445 (3.79×10^{-3})	0.115 (3.90×10^{-4})	347	10.3	83	210
P5	119.96 (1.20)	12.02 (0.116)	1.420 (3.73×10^{-3})	0.113 (3.85×10^{-4})	353	10.3	78	320
PMMA	88.40 (0.88)	0	4.045 (1.06×10^{-2})	0.303 (1.03×10^{-3})	83	9.7	90	60

[a] $r = 100 \times [\text{SG1}]_0/[\text{MAMA}]_0$.

Table 2. Conversions and Macromolecular Characteristics of the Polymers

| expt	polym time, min	conversion, %	theoretical M_n, g mol^{-1}	experimental M_n of the raw polymer, g mol^{-1}	PDI of the raw polymer	experimental M_n of the purified polymer, g mol^{-1}	PDI of the purified polymer
P0	40	58.0	5240	5810	1.42	8280[a]	1.24[a]
P1	40	50.0	4670	5280	1.36	5870	1.33
P2	20	34.5	3320	3610	1.46	3980	1.41
	30	43.5	4085	4490	1.42	4720	1.41
	40	50.0	4660	5330	1.37	5550	1.35
P3	10	13.0	4960	7200	1.44	7720	1.37
	30	29.5	10 770	13 000	1.25	12 170	1.31
	50	39.0	14 190	17 620	1.22	17 700	1.23
	70	47.5	17 090	20 720	1.21	21 510	1.20
	90	55.5	20 000	23 950	1.21	24 850	1.21
P4	170	43.5	15 540	17 260	1.21	19 340	1.18
P5	200	29.5	10 750	12 760	1.25	15 100	1.20
PMMA	60	35.0	3350	3990	1.75	8020[a]	1.32[a]

[a] Precipitation in pure methanol (if not otherwise specified, the precipitation was performed in methanol/water (75/25 v/v)).

(P(MMA-*co*-S)) polymers prepared with 8.8 mol % of styrene in the initial comonomer mixture, following the above-described procedure, and to draw conclusions about the actual livingness of the system. We then took advantage of this knowledge in synthesizing, for the first time, well-defined P(MMA-*co*-S) polymers at low temperature, as well as methacrylate-based block copolymers entirely via nitroxide-mediated free-radical polymerization.

Experimental Part

1. Materials. Methyl methacrylate (MMA, Aldrich, 99%), *n*-butyl acrylate (BA, 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 (MAMA, so-called BlocBuilder, 99%) and the *N-tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethyl-propyl) nitroxide (SG1, 88.4%) were kindly supplied by Arkema (Scheme 1). 2,2,6,6-Tetramethylpiperidinyl-1-oxy (TEMPO, Lancaster, 98%), *tert*-butylbenzene (*t*-BuPh, Aldrich, 99%), diethyl phosphite (Aldrich, 98%), and methanol (VWR Prolabo, ≥99%) were used as received.

2. Bulk Polymerizations. The typical syntheses of the P(MMA-*co*-S) polymers at 90 °C were as follows (see Table 1): a mixture of methyl methacrylate, styrene (initial molar fraction: $f_{S0} = 0.088$) and free SG1 was deoxygenated by nitrogen bubbling during 20 min at room temperature. The alkoxyamine initiator was then added and the nitrogen bubbling was carried out for 10 more min. The mixture was then introduced into a 250 mL three-neck round-bottom flask heated at 90 °C, immersed in a thermostated oil bath and fitted with a reflux condenser, a nitrogen inlet and a thermometer. For kinetic studies and raw polymer analysis, sampling was periodically performed and the polymerization was quenched by sinking samples in an ice–water bath. The overall monomer conversion (x) was determined by gravimetry after drying the polymer samples at 65 °C, under vacuum. For preparation of the macroinitiator, the polymerization medium was first cooled in an ice–water bath to stop the polymerization and then, the polymer was purified by precipitation in methanol/water (75/25 v/v), filtered off and dried at room temperature under vacuum for several days.

Scheme 2. Determination of the Fraction of Living Chains by ESR Analysis via the Amount of Released SG1
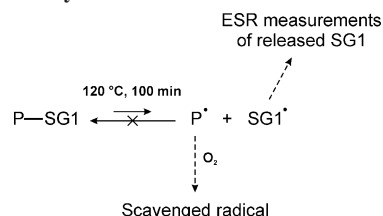
For the experiment **P0** (Table 1), the precipitation was performed in cold methanol, but such procedure led to fractionation and elimination of the shortest chains of the polymer sample as shown in Table 2 by the increase in the number-average molar mass after purification. All purified polymers were bright, white powders.

The same procedure was applied for the synthesis of a pure **PMMA** homopolymer (Table 1).

3. Electron Spin Resonance (ESR) Experiments. General Experimental Conditions. The ESR analyses were performed at the University of Aix-Marseille I on CW-EPR (Bruker EMX or MS100 Magnettech) spectrometers. Before being analyzed, the purified copolymers were carefully stored at 4 °C in the dark. Solutions of the copolymers (10^{-4} M in 500 μL of a non degassed *t*-BuPh/THF (99/1 v/v) mixture) were poured into 5 mm diameter tubes (dissolved oxygen was used as the alkyl radical scavenger).[16,17] Standard solutions of SG1 or TEMPO were also prepared in the same conditions (10^{-4} M in 500 μL of *t*-BuPh solutions) for quantitative analyses. A first analysis at room temperature was recorded for all polymer solutions to measure the concentration of residual free nitroxide.

Determination of the Proportion of Living Chains. Our study focused on two copolymerizations of methyl methacrylate and styrene carried out at 90 °C (**P2** and **P3**, Table 1). The polymer solutions prepared as described above were heated at 120 °C for 100 min (conditions to achieve more than 99% alkoxyamine dissociation). Recombination between free nitroxide and carbon centered radicals was prevented by scavenging the latter with dissolved oxygen (see Scheme 2).[16,17] Spectra were subsequently recorded at room temperature to measure the overall concentration

Table 3. Values of E_a, $k_{d,90°C}$, and $k_{d,60°C}$ for the Various SG1-Based Alkoxyamines from Ref 24

alkoxyamine	E_a, kJ mol^{-1}	$k_{d,90°C}$,^{a} s^{-1}	$k_{d, 60°C}$,^{a} s^{-1}
MMA−MMA−SG1	104	0.26	1.2×10^{-2}
S−MMA−SG1	108^b	6.9×10^{-2}	2.8×10^{-3}
MMA−S−SG1	115^c	6.8×10^{-3}	2.2×10^{-4}
S−S−SG1	125^c	2.5×10^{-4}	5.9×10^{-6}

^{a} $k_{d,T°C}$ was estimated using the E_a values and a frequency factor of 2.14×10^{14} s^{-1}. ^{b} Assuming a very weak effect of the penultimate unit (ca. 1 kJ mol^{-1}), E_a of S−MMA−SG1 is given by the E_a of MMA−SG1 (see ref 24). ^{c} Unpublished results from S. Marque.

Table 4. Theoretical Proportions of Dissociated Alkoxyamine at 60 and 90 °C, as a Function of the Alkoxyamine Type, Calculated on the Basis of $k_{d,T°C}$ Given in Table 3

sample	t, s	T, °C	considered alkoxyamine	calculated percentage of dissociated alkoxyamine, %
a	500	60	MMA−MMA−SG1	99
			S−MMA−SG1	75
			MMA−S−SG1	10
			S−S−SG1	<1
b	2000	60	MMA−MMA−SG1	99
			S−MMA−SG1	99
			MMA−S−SG1	35
			S−S−SG1	1
c	7000	60	MMA−MMA−SG1	99
			S−MMA−SG1	99
			MMA−S−SG1	78
			S−S−SG1	4
d	1000	90	MMA−MMA−SG1	99
			S−MMA−SG1	99
			MMA−S−SG1	99
			S−S−SG1	22
e	6000	90	MMA−MMA−SG1	99
			S−MMA−SG1	99
			MMA−S−SG1	99
			S−S−SG1	77
f	10 000	90	MMA−MMA−SG1	99
			S−MMA−SG1	99
			MMA−S−SG1	99
			S−S−SG1	92

of SG1. The fraction of living chains (LF) was calculated from the concentration of released nitroxide, according to eq 1, where [SG1]$_{initial}$ and [SG1]$_{final}$ respectively represent the concentration of SG1 in the solution before heating and in the solution after heating. By experience, the ESR analysis procedure gives an error smaller than 5%;[16,17] the major part of the error comes from the preparation of the sample, which might be in the 10−20% range.

$$LF = \frac{[SG1]_{released}}{10^{-4}} = \frac{[SG1]_{final} - [SG1]_{initial}}{10^{-4}} \quad (1)$$

Determination of the Chain-End Structure. This study was performed for **P2**-40′ and **P3**-10′ (Table 2). For both copolymers, six samples were prepared as described above and heated under different conditions: 60 °C for 500 s (sample *a*), 60 °C for 2000 s (sample *b*), 60 °C for 7000 s (sample *c*), 90 °C for 1000 s (sample *d*), 90 °C for 6000 s (sample *e*), and 90 °C for 10 000 s (sample *f*).

Then, the samples were cooled to room temperature and an ESR spectrum was recorded to quantify the concentration of released SG1 ([SG1]$_{released}$ = [SG1]$_{final}$ − [SG1]$_{initial}$). The latter depends directly upon the temperature, heating time and alkoxyamine structure (see Tables 3 and 4).

4. Chain Extensions. The purified P(MMA-*co*-S) and PMMA polymers were dissolved at room temperature in *n*-butyl acrylate or in styrene, in the presence or the absence of an extra amount of free SG1 (see Table 5). Those solutions were then introduced into a Schlenk tube. After degassing by three freeze−pump−thaw cycles, the polymerizations were run at 120 °C for 8 h. The samples were then sunk in an ice−water bath to quench the reaction. For both *n*-butyl acrylate and styrene, the final polymerization medium was apparently homogeneous, although cloudy, and very viscous indicating high conversions. The copolymers were recovered from the Schlenk tube via the addition of THF to reduce the viscosity, and were then dried in a ventilated oven at 70 °C until constant weight, to remove the solvent and residual monomer. They were analyzed by size exclusion chromatography.

5. Analytical Techniques. Size exclusion chromatography (SEC) was performed at 40 °C with two columns (PSS SDV, linear MU, 8 mm × 300 mm; bead diameter, 5 μm; separation limits, 400 to 2×10^6 g mol^{-1}). The eluent was THF at a flow rate of 1 mL·min^{-1}. A differential refractive index detector (LDC Analytical refractoMonitor IV) was used and molar mass distributions were derived from a calibration curve based on polystyrene (PS) standards from Polymer Standards Service. The polystyrene calibration is not appropriate for poly(methyl methacrylate) (PMMA) samples. Thus, the M_n values obtained from polystyrene conventional calibration were converted using the Mark−Houwink−Sakurada (MHS) relationship between PS and PMMA with MHS parameters determined at 35 °C: $K_{PS} = 15.8 \times 10^{-5}$ dL·g^{-1}, $\alpha_{PS} = 0.704$, $K_{PMMA} = 12.2 \times 10^{-5}$ dL·g^{-1}, and $\alpha_{PMMA} = 0.69$.[18] This technique allowed M_n (the number-average molar mass), M_w (the weight-average molar mass) and PDI = M_w/M_n (the polydispersity index) to be calculated within 5% error in comparison with a molar mass determination derived from a calibration curve based on poly(methyl methacrylate) standards (from Polymer Laboratories). In all the figures representing the experimental M_n as a function of monomer conversion, the displayed full line corresponds to the theoretical evolution of M_n calculated by eq 2.

$$M_n = MW_{alkoxyamine\ initiator} + \frac{initial\ mass\ of\ monomers}{initial\ mole\ number\ of\ alkoxyamine} \times conversion \quad (2)$$

The final polymers and copolymers were analyzed by ^{1}H NMR spectroscopy (AC250 Bruker spectrometer, 250 MHz) in CDCl$_3$ solution, at 25 °C, in 5 mm diameter probes.

The ^{31}P NMR spectra of the precipitated P(MMA-*co*-S) and **PMMA** polymers were recorded in CDCl$_3$ in 10 mm diameter tubes at 25 °C, on 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 polymer was carefully weighed and a known amount of diethyl phosphite was added as an internal reference. The

Table 5. Experimental Conditions for Chain Extensions of the SG1-Capped P(MMA-*co*-S) Copolymers at 120 °C for 8 h

initiator	macroinitiator				S, g (mol)	BA, g (mol)	target M_n at 100% conversion
	M_n, g mol^{-1}	PDI	m, g	n, mol			
P0^a	8290	1.24	0.938	1.13×10^{-4}	13.52 (0.13)^c		127 900
P1−40′^{b}	5870	1.33	0.382	6.50×10^{-5}		7.89 (0.062)^d	127 100
P4−170′^{b}	19 340	1.18	0.202	1.04×10^{-5}	2.39 (0.023)^c		248 200
P5−200′^{b}	15 100	1.20	0.199	1.32×10^{-5}	3.12 (0.030)^c		251 800
PMMA^a	8020	1.32	1.135	1.42×10^{-4}	13.52 (0.13)^c		103 500
PMMA^a	8020	1.32	1.135	1.42×10^{-4}		13.52 (0.106)^c	103 500

^{a} Purified by two precipitations in cold methanol. ^{b} Purified by one precipitation in methanol/water (75/25 v/v). ^{c} No extra SG1. ^{d} 0.441 mg (1.5 μmol) of extra SG1 was added, i.e., 2.3 mol % based on the macroinitiator.
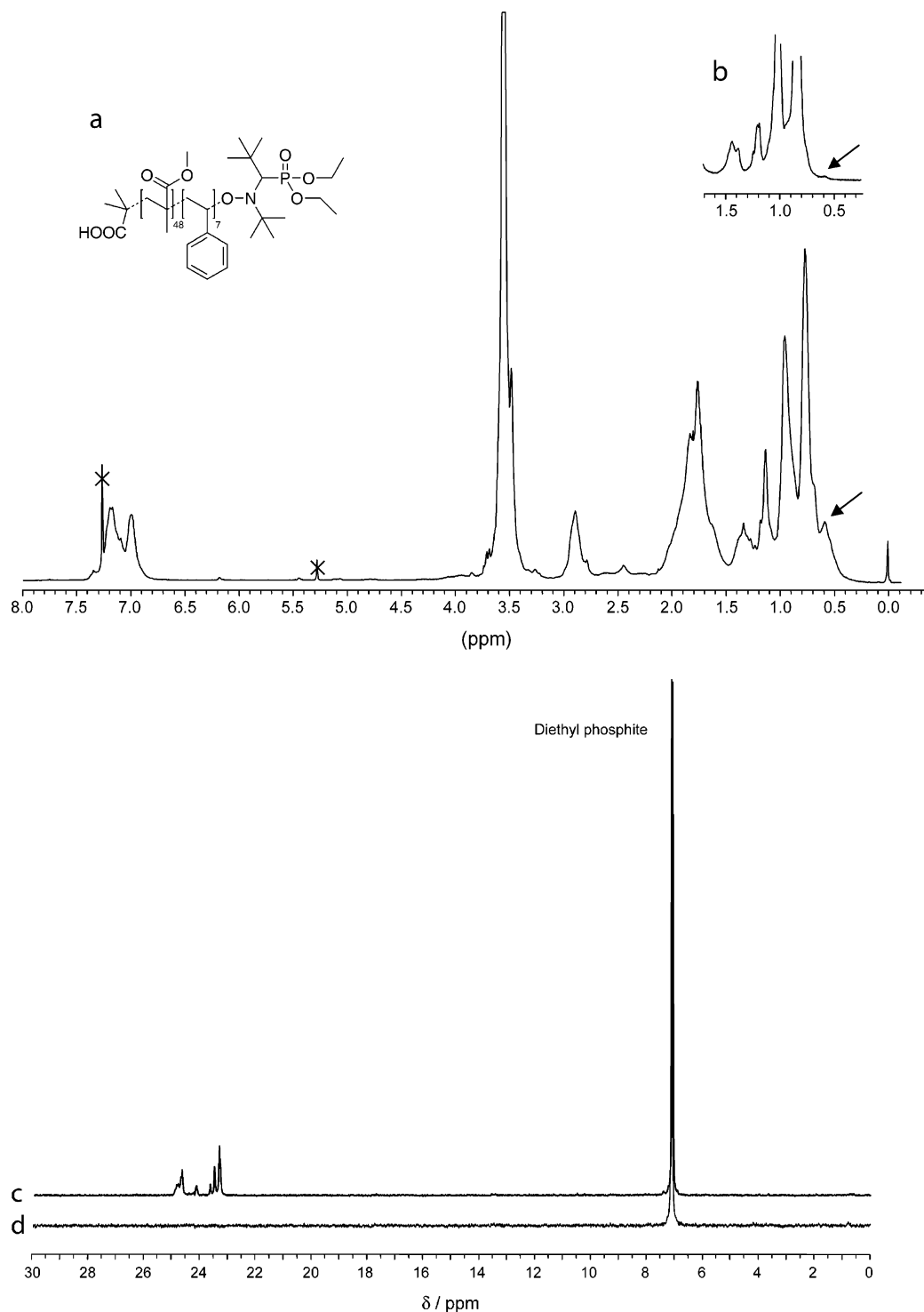
Figure 1. ^{1}H NMR spectra of (a) the poly(methyl methacrylate-*co*-styrene) copolymer **P1** and (b, inset) of the PMMA homopolymer. ^{31}P NMR spectra of (c) the poly(methyl methacrylate-*co*-styrene) copolymer **P1** and (d) the PMMA homopolymer.

chemical shift scale was calibrated on the basis of the added diethyl phosphite at 7.1 ppm.[19]

Results and Discussion

1. Theoretical Approach of the Livingness of the P(MMA-*co*-S) Copolymers. A high degree of livingness of a (co)polymer prepared by SG1-mediated polymerization is characterized by a high proportion of SG1-terminated chains. In our previous article, we presented the analytical expressions giving the proportion of each individual type of dormant chain, depending

on the last monomer unit(s), for both the terminal model and the implicit penultimate unit effect model for propagation.[15] Using the terminal model as an illustration, eq 3 expresses the proportion of styrene-terminated dormant chains, $[S-N]/C$, where the activation−deactivation equilibrium constants of methyl methacrylate (MMA) and styrene (S) are K_{MMA} and K_S, the propagation rate constants are $k_{p,MMA}$ and $k_{p,S}$, the reactivity ratios are r_{MMA} and r_S, the respective molar fractions of MMA and S in the comonomer mixture are f_{MMA} and f_S, the macromolecular alkoxyamine concentrations are $[MMA-N]$ and
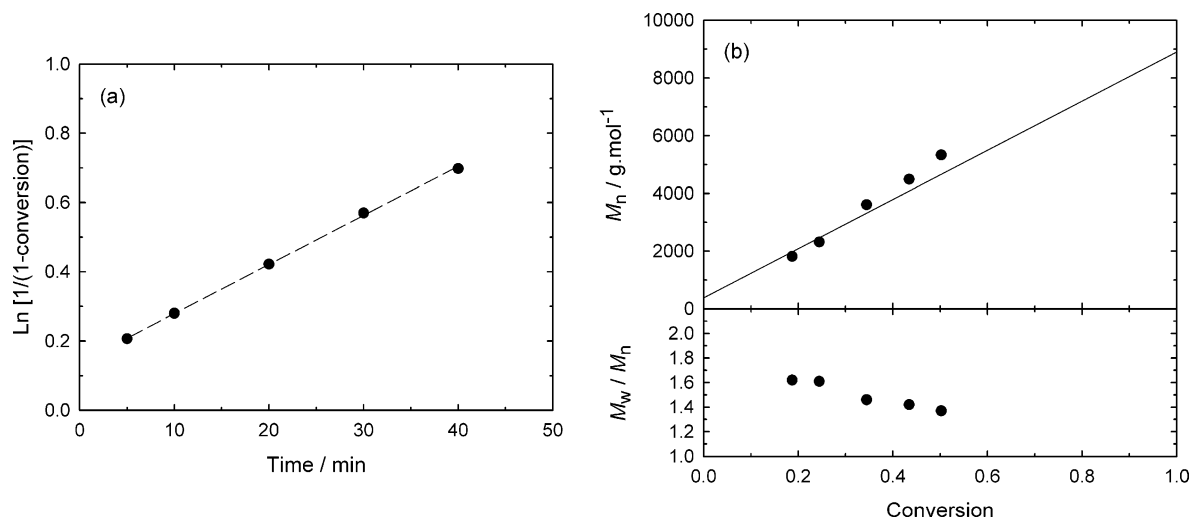
Figure 2. Bulk copolymerization of methyl methacrylate and styrene (initial molar fraction of styrene: $f_{S0} = 0.088$) at 90 °C, in the presence of 1.10×10^{-1} mol L^{-1} of MAMA (**P2**, $M_{n(x=1)} = 8900$ g mol^{-1}), 10.0 mol % of added free SG1 based on the initiator. Key: (a) $\ln[1/(1 - x)]$ vs time (x = overall conversion); (b) number-average molar mass, M_n, and polydispersity index, PDI, vs conversion. The full line represents the theoretical M_n.

[S−N] (i.e., the concentration of dormant chains with respectively a MMA and a S terminal monomer unit; with N as nitroxide) and the overall concentration of dormant chains is C (C = [MMA−N] + [S−N]).

$$\frac{[\text{S−N}]}{C} = \frac{K_{\text{MMA}} r_S k_{p,\text{MMA}} f_S}{K_{\text{MMA}} r_S k_{p,\text{MMA}} f_S + K_S r_{\text{MMA}} k_{p,S} f_{\text{MMA}}} \quad (3)$$

Using the same parameters as those used in ref 15 for the copolymerization of methyl methacrylate with styrene at 90 °C, it appears that in the initial conditions [S−N]/C = 95 mol % when 4.4 mol % of styrene is added in the comonomer mixture ($f_{S0} = 0.044$) and goes up to 98 mol % if $f_{S0} = 0.088$.[20] It is therefore anticipated that a majority of the dormant chains should be terminated by a styrene−SG1 unit instead of a MMA−SG1 unit. In addition, the polymeric MMA−SG1 bond is expected to be too weak to remain stable for long time at room temperature, owing to the too large activation−deactivation equilibrium constant. Thus, it is reasonable to assume that the recovered SG1-terminated P(MMA-*co*-S) copolymer should mainly contain the terminal styryl−SG1 moiety. Moreover, from both the reactivity ratios and small initial proportion of styrene in the comonomer feed, which was $f_{S0} = 0.088$ in this work, it can be inferred that isolated styrene subunits predominate over dyads or even longer sequences. The chain-end structure is therefore expected to be MMA−S−SG1. We would now like to illustrate this result by the chain-end analysis of P(MMA-*co*-S) copolymers prepared by SG1-mediated bulk polymerization and to apply it to the synthesis of various block copolymers in order to assess livingness and architectural feasibility.

2. ^{31}P and ^{1}H NMR Analysis of a P(MMA-*co*-S) Copolymer. To analyze the chain-end by NMR spectroscopy, a low molar mass P(MMA-*co*-S) copolymer was synthesized at 90 °C (**P1**, see the experimental part and Table 1). From the SEC analysis, the raw copolymer **P1** exhibited a M_n of 5280 g mol^{-1} and a polydispersity index of 1.36 (Table 2). This M_n value was close to the theoretical one ($M_{n,th} = 4670$ g mol^{-1}) calculated from the monomer over alkoxyamine initial molar ratio multiplied by the fractional conversion (0.50) and showed an initiation efficiency of 88%. After 2 precipitations in methanol/water (75/25 v/v), the copolymer **P1** exhibited a M_n of 5870 g mol^{-1} and a polydispersity index of 1.33. In parallel,

a **PMMA** homopolymer (without any initial addition of styrene) was synthesized by SG1-mediated polymerization following the same experimental procedure as for the copolymer. The reaction was performed during 1 h but a plateau in monomer conversion (at 35%) was obtained within the first 5 min, as also observed by Guillaneuf et al.[14] The final raw polymer exhibited a rather high PDI of 1.75 with a M_n of 3990 g mol^{-1}, close to the theoretical one ($M_{n,th} = 3350$ g mol^{-1}). After precipitation in pure methanol, the M_n increased to 8020 g mol^{-1} with a PDI of 1.32.

Both the purified P(MMA-*co*-S) **P1** and **PMMA** polymers were analyzed by ^{1}H and ^{31}P NMR spectroscopy to investigate the chain-end structure. The ^{1}H NMR spectrum of the P(MMA-*co*-S) copolymer **P1** presented in Figure 1a exhibits characteristic peaks, which undoubtedly demonstrate the incorporation of styrene in the copolymer: aromatic styrene peaks at 6.8−7.3 ppm and three characteristic peaks of the poly(methyl methacrylate) methoxy protons in the 2.2−3.7 region. These peaks respectively represent the MMA-centered triads with zero (3.3−3.7 ppm), one (2.9 ppm) and two (2.4−2.5 ppm) MMA−S dyads.[21,22] From the integration of the styrene aromatic region with respect to the methyl ester peak of the MMA units, one can estimate the copolymer composition at 12.5 mol % of styrene units, i.e. a distribution of the units corresponding to P(MMA$_{48}$-*co*-S$_7$). For short polymer chains, the ^{1}H NMR peaks corresponding to the end group should be visible. This is qualitatively illustrated by the presence of a shoulder at 0.5−0.6 ppm, which likely corresponds to the methyl groups of the SG1 nitroxide (ω-end group), as it is in good agreement with the spectrum of SG1-terminated polystyrene.[10] For comparison, a selected part of the ^{1}H NMR spectrum of the **PMMA** homopolymer is also presented in Figure 1b, in which no SG1 methyl group peak is observed, supporting the nonliving character of such homopolymer. In both cases, the α-end group (methyl of the initiating radical) is not visible as its peak is within the polymer peak at the 1.5−2.0 ppm region.

These results were qualitatively and quantitatively confirmed by the ^{31}P NMR analyses. The presence of the SG1 end group was detected in the 23−25 ppm region for the copolymer (Figure 1c), whereas no signal was obtained for the homopolymer (Figure 1d). The multiplicity of the peak might be accounted for by the diastereoisomer existing in the terminal styrene−SG1 structure, as well as by the influence of the penultimate
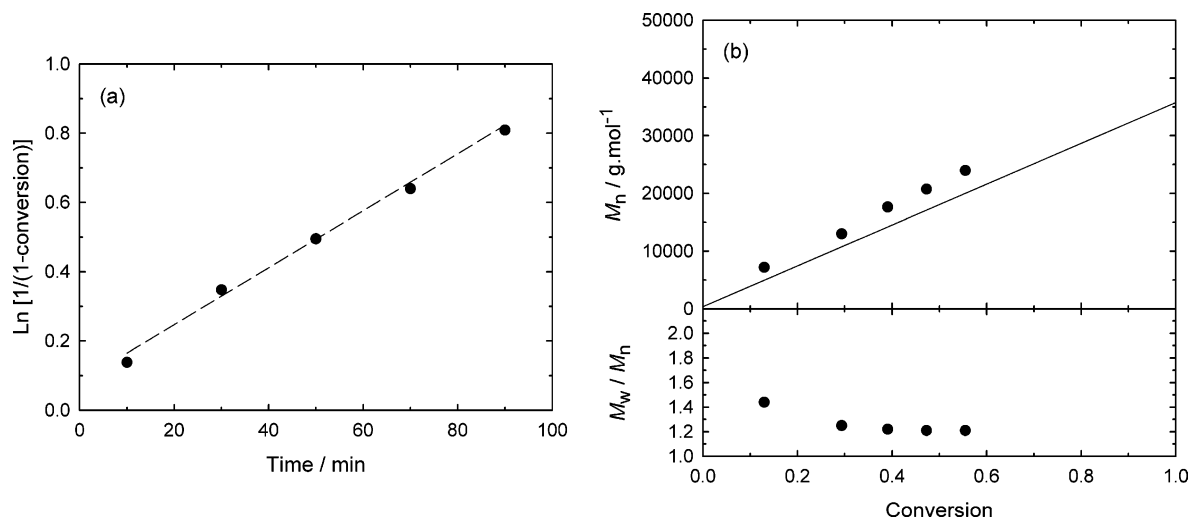
Figure 3. Bulk copolymerization of methyl methacrylate and styrene (initial molar fraction of styrene: $f_{S0} = 0.088$) at 90 °C, in the presence of 2.64×10^{-2} mol L^{-1} of MAMA (**P3**, $M_{n(x=1)} = 35\ 750$ g mol^{-1}), 11.7 mol % of added free SG1 based on the initiator. Key: (a) ln[1/(1 − x)] vs time (x = overall conversion); (b) number-average molar mass, M_n, and polydispersity index, PDI, vs conversion. The full line represents the theoretical M_n.

Table 6. Estimations of the Fraction of Living Chains (LF) by ESR Analysis of the Amount of Released SG1 after Heating the Polymers at 120 °C for 100 min

expt	polymerization time, min	[SG1]$_{initial}$,[c,d] mol L^{-1}	[SG1]$_{final}$,[c,e] mol L^{-1}	[SG1]$_{released}$,[f] mol L^{-1}	LF,[g] %
P2	20[a]	1.45×10^{-6}	9.14×10^{-5}	9.00×10^{-5}	90
	30[b]	8.18×10^{-6}	7.86×10^{-5}	7.04×10^{-5}	70
	40[b]	2.36×10^{-6}	1.09×10^{-4}	1.07×10^{-4}	107
P3	10[a]	5.09×10^{-6}	8.14×10^{-5}	7.63×10^{-5}	76
	30[a]	5.45×10^{-6}	9.71×10^{-5}	9.17×10^{-5}	92
	50[a]	7.45×10^{-6}	8.14×10^{-5}	7.40×10^{-5}	74
	70[a]	7.36×10^{-6}	1.11×10^{-4}	1.04×10^{-4}	104
	90[b]	3.18×10^{-6}	1.21×10^{-4}	1.18×10^{-4}	118

[a] 500 μL of a nondegassed *t*-BuPh/THF (99/1 v/v) 10^{-4} M solution of the purified polymer. [b] 400 μL of a nondegassed *t*-BuPh/THF (99/1 v/v) 10^{-4} M solution of the purified polymer. [c] Calculated from SG1 and TEMPO standard tubes (500 μL of *t*-BuPh 10^{-4} M solutions of SG1 and TEMPO). [d] Amount of free SG1 before heating. [e] Values measured after heating at 120 °C for 100 min. [f] [SG1]$_{released}$ = [SG1]$_{final}$ − [SG1]$_{initial}$. [g] LF calculated according to eq 1 with an error in the 10−20% range.

units and by tacticity effects. The proportion of chains containing a SG1 end group was estimated at 75 ± 10 mol %. This proportion is high and indicates a high degree of livingness of the P(MMA-*co*-S) copolymer. However, it is lower than that given by eq 3 (i.e. 98 mol % with 0.088 mol % of styrene initially introduced, as calculated with the terminal model for propagation). The proportion of dead chains, i.e., the persistent radical effect (PRE),[23] is actually not taken into account in the theoretical model and may explain this difference. Moreover, the theoretical value is based on low conversion, and it should decrease when conversion increases.[15]

From the results, no living character should be expected from the **PMMA** homopolymer whereas the P(MMA-*co*-S) copolymer should be an efficient macroinitiator for the synthesis of block copolymers.

3. Living Character of the P(MMA-*co*-S) Copolymers Estimated by ESR. To undoubtedly provide proof of the living character and to deeply analyze the chain-end structure, ESR experiments were performed on various P(MMA-*co*-S) copolymers, with different chain lengths.

(a) Proportion of Living Chains. We focused our attention on two bulk copolymerizations of methyl methacrylate and styrene ($f_{S0} = 0.088$), which only differed in the initial concentration of MAMA initiator and consequently in the
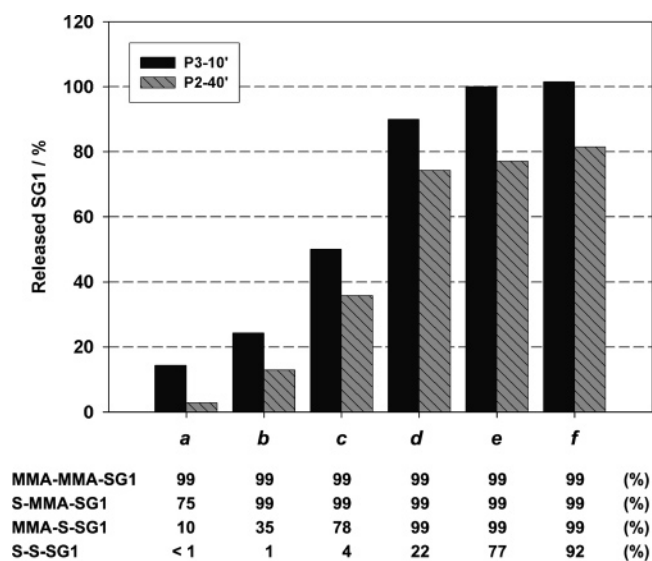

	a	b	c	d	e	f	
MMA-MMA-SG1	99	99	99	99	99	99	(%)
S-MMA-SG1	75	99	99	99	99	99	(%)
MMA-S-SG1	10	35	78	99	99	99	(%)
S-S-SG1	< 1	1	4	22	77	92	(%)

Figure 4. Percentage of released SG1 for the copolymers **P2**-40′ and **P3**-10′, from ESR measurements and discrimination between the different chain-ends as a function of the heating conditions (see Table 4; for the figure to be more legible, the calculated percentage of dissociated alkoxyamine are reported on the *x* axis).

targeted final chain lengths (**P2** and **P3**, Tables 1 and 2). Both copolymerizations exhibited all the characteristics of a controlled system (see Figures 2 and 3) with the following: (i) a linear evolution of ln[1/(1 − x)] vs time owing to the initially added free nitroxide; (ii) a linear increase of M_n with monomer conversion, close to the theoretical line; (iii) a simultaneous decrease of the polydispersity indices with conversion. Although such features demonstrated the controlled nature of the polymerization, they did not provide any information on the living character of the polymers, i.e. on the presence of an alkoxyamine group at all chain-ends. The degree of livingness (proportion of living chains in the copolymer, LF) was then determined by ESR analyses, by measuring the concentration of SG1 that was released after heating in conditions such that all alkoxyamines would dissociate. The results are listed in Table 6 for a series of purified polymers and show a high proportion of living chains, unambiguously above 75% (variations with the polymerization time cannot be discussed with accuracy owing to the experimental error). Such results are in good agreement with
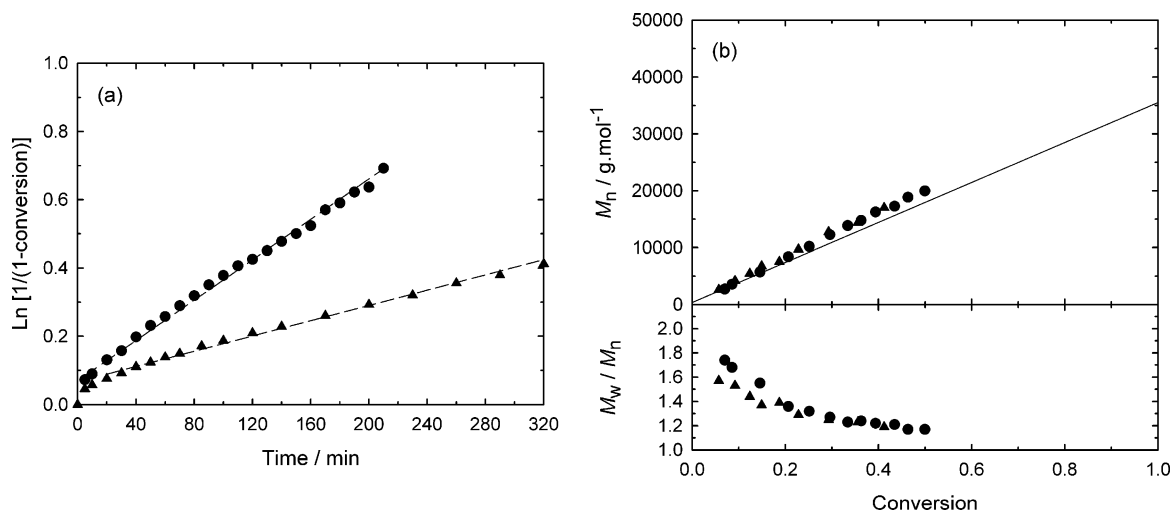
Figure 5. Bulk copolymerization of methyl methacrylate and styrene (initial molar fraction of styrene: $f_{S0} = 0.088$) at 83 (**P4**, ●) and 78 °C (**P5**, ▲), in the presence of 2.66×10^{-2} mol L^{-1} of MAMA ($M_{n(x=1)} = 35\,520$ g mol^{-1}), 10.3 mol % of added free SG1 based on the initiator. Key: (a) ln[$1/(1 - x)$] vs time (x = overall conversion); (b) number-average molar mass, M_n, and polydispersity index, PDI, vs conversion. The full line represents the theoretical M_n.
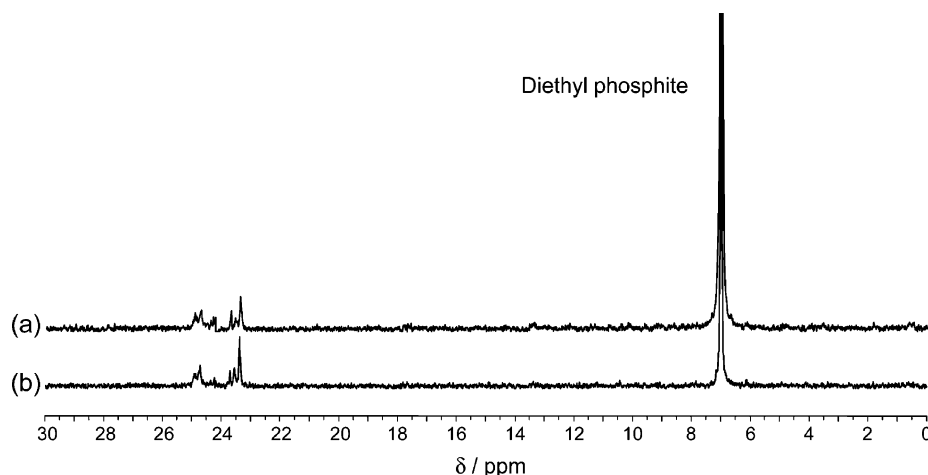
Figure 6. ^{31}P NMR spectra of the purified copolymers **P4**-170′ (a) and **P5**-200′ (b).

the ^{31}P NMR analysis of the copolymer **P1** and did not depend on the chain length.

(b) Chain-End Structure. There are four possible types of chain-ends considering both the terminal and the penultimate units (S−S−SG1, MMA−S−SG1, S−MMA−SG1 and MMA−MMA−SG1). Because there is a significant difference in the bond dissociation energies between the styrene-based alkoxyamine and its methacrylate-based counterpart[24] and also a strong penultimate unit effect on the alkoxyamine dissociation rates,[24] the proportion of each species can be estimated through specific heating conditions before performing the ESR analysis. Two temperatures have been selected to accomplish this. The first one, 60 °C, should be high enough to allow quantitative dissociation of all MMA−SG1 terminated macroalkoxyamines but too low for the quantitative dissociation of the S−SG1 terminated ones. The second temperature, 90 °C, should be high enough to allow quantitative dissociation of both the MMA−SG1 and the S−SG1 alkoxyamines (see Table 4). Then, we have used theoretical estimations of the dissociation rate constants at 60 and 90 °C for the four types of alkoxyamines,[24] knowing that such reactions follow first-order kinetics in total scavenging conditions[25] (Table 3). From the data, it was possible to determine appropriate heating times, to allow discrimination between the different chain-ends (Table 4). For this purpose, 6 samples were prepared for the polymers **P2**-40′ and **P3**-10′ and

heated in the different conditions (a−f) as previously described in the experimental part. Figure 4 displays the proportion of released SG1 with respect to the molar concentration of polymer chains initially introduced into the probes, as a function of the heating conditions. The low proportions of released SG1 observed in samples a and b (Figure 4) are in good agreement with the expected amounts given in Table 4 for the decay of MMA−S−SG1. Therefore, it is clear that the MMA−MMA−SG1 and S−MMA−SG1 chain-ends were in minor proportion, which is fully consistent with the large dissociation rate constant of the alkoxyamine and also with the large activation−deactivation equilibrium constant, K_{MMA}, for the SG1-mediated homopolymerization of methyl methacrylate.[13,14] An important amount of SG1 was released in samples c and d. According to the theoretical prediction and to the previous results of samples a and b, the nitroxide was mainly issued from the MMA−S−SG1 alkoxyamine homolysis. Last, one can notice that there was no significant increase between the samples d, e, and f, meaning that the proportion of S−S−SG1 chain-ends was rather low. All results confirm the existence of a majority of styrene-terminated macroalkoxyamines, the key parameter allowing the control of the polymerization. Moreover, one can go a step further by affirming that the majority of the chains are terminated by a MMA−S−SG1 sequence. Finally, it should be pointed out that in samples f (in which all chain-ends are
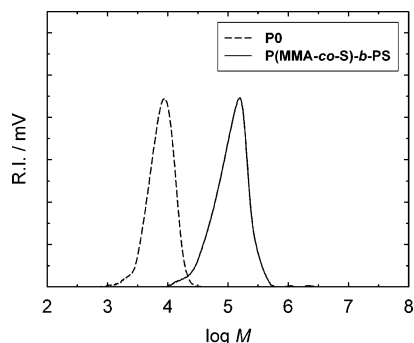
Figure 7. Size exclusion chromatogram of the poly(methyl methacrylate-*co*-styrene)-*b*-polystyrene block copolymer resulting from chain extension of the copolymer **P0**.
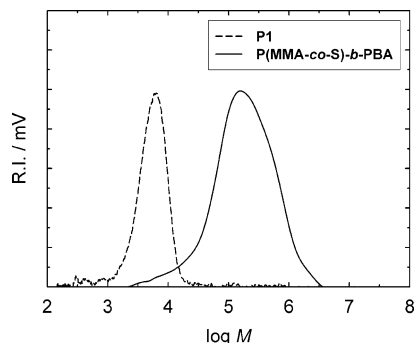

Figure 8. Size exclusion chromatogram of the poly(methyl methacrylate-*co*-styrene)-*b*-poly(*n*-butyl acrylate) block copolymer resulting from chain extension of the copolymer **P1**-40′.

dissociated), the proportion of released SG1 is above 80%, agreeing with the proportion of living chains determined before.

4. Polymerizations at Temperature below 90 °C. Knowing that the copolymers P(MMA-*co*-S) are essentially terminated by a MMA−S−SG1 sequence and that the methyl methacrylate penultimate unit induces a significant increase in the dissociation rate constant of the S−SG1 alkoxyamine (Table 3), we have decided to test our copolymerizations at temperatures below 90 °C, for which the homopolymerization of styrene is extremely slow (conversion below 2% after 210 min at 80 °C). In this way, copolymerizations were attempted at 83 °C and at 78 °C (**P4** and **P5** respectively, Table 1). The results are presented in Figure 5. The first and most important point is that the polymerizations indeed occurred at 83 and 78 °C, in perfect agreement with the aforementioned expectations. They were slower than those performed at 90 °C, but the quality of control was improved (better initiating efficiency and lower PDI values) as shown in Figure 5b. The purified copolymers **P4**-170′ (conversion = 43.5%; M_n = 19 340 g mol^{-1}, PDI = 1.18) and **P5**-200′ (conversion = 29.5%; M_n = 15 100 g mol^{-1}, PDI =

1.20) were furthermore analyzed by ^{31}P NMR spectroscopy to study the chain-end structure (Figure 6). The presence of SG1 end groups was detected in the 23−25 ppm region. From the peak integration and from the respective molar amount of polymer and internal reference, the proportion of chains containing a SG1 end group (LF) was estimated: LF$_{\textbf{P4}-170'}$ = 75 ± 10% (83 °C) and LF$_{\textbf{P5}-200'}$ = 90 ± 10% (78 °C). As for copolymerizations carried out at 90 °C, the proportion of living chains is high, in the 70−90% range, and those copolymers might also be efficiently used as macroinitiators for the synthesis of block copolymers.

It is noteworthy, in these experiments, that the temperature could be reduced owing to the existence of the MMA−S−SG1 terminal sequence and to the effect of the penultimate MMA unit on the alkoxyamine dissociation rate. In other words, a too large proportion of styrene, which would favor the formation of S−S dyads or longer sequences instead of isolated units, might be prejudicial.

5. Syntheses of Block Copolymers Using SG1-Capped P(MMA-*co*-S) Macroinitiators. (a) Chain Extension of Copolymers Synthesized at 90 °C. Our study focused on **P0** and **P1**-40′ (Tables 1 and 5) and high molar mass block copolymers were targeted so as to allow a complete shift of the SEC peaks with chain extension (a narrow molar mass distribution was not the goal of those experiments). In both cases, block copolymers were indeed obtained, as shown by the shift of the SEC traces toward higher molar masses, with respect to that of the macroinitiators (Figures 7 and 8). In the case of styrene, a complete shift was observed indicating a high reinitiation efficiency; the P(MMA-*co*-S)-*b*-PS block copolymer had M_n = 85 200 g mol^{-1} and the polydispersity index was 1.53. With *n*-butyl acrylate, because of the low activation−deactivation equilibrium constant and the high propagation rate constant, chain extension should be performed with an initial addition of free SG1 to better control the polymerization.[26,27] So, 2.3 mol % of free SG1 based on the macroinitiator **P1**-40′ were added. The resulting P(MMA-*co*-S)-*b*-PBA block copolymer had M_n = 140 900 g mol^{-1} and the polydispersity index was 2.44. This rather high PDI might be explained by a too low amount of free SG1 initially introduced and a too high target molar mass which favors side reactions (irreversible terminations and chain transfer to the polymer).

For comparison, chain extensions from the **PMMA** homopolymer have also been performed with *n*-butyl acrylate and styrene following the same procedure. As expected from the lack of SG1 chain-end, no significant *n*-butyl acrylate conversion was achieved (2.5%) indicating no reinitiation and thus no polymerization. In the chain extension with styrene, an additional trace was found in the high molar mass region of the size exclusion chromatogram (M_n = 130 000 g mol^{-1}, PDI = 2.0);
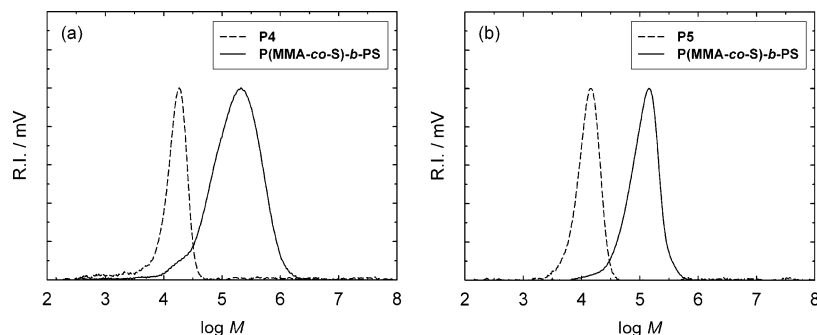

Figure 9. Size exclusion chromatograms of the poly(methyl methacrylate-*co*-styrene)-*b*-polystyrene block copolymers resulting from chain extension of the copolymers **P4**-170′ (a) and **P5**-200′ (b).

this was assigned to polymer generated by thermal-self-initiation of styrene at high temperature.

(b) Chain Extension of the Copolymers Synthesized at 83 °C and 78 °C. The copolymers **P4**-170′ and **P5**-200′ were used as macroinitiators for the polymerization of styrene (Table 5). In both cases, block copolymers were obtained, as shown by the shift of the SEC traces toward higher molar masses, with respect to that of the macroinitiators (Figure 9). With **P4**-170′, the P(MMA-*co*-S)-*b*-PS block copolymer had $M_n = 144\,500$ g mol^{-1} and PDI = 1.93. With **P5**-200′, the P(MMA-*co*-S)-*b*-PS block copolymer had $M_n = 99\,330$ g mol^{-1} and PDI = 1.41. However, a small shoulder for the block copolymer initiated by the **P4**-170′ macroinitiator is noticed, indicating remaining unreacted macroinitiator. This was not the case for the copolymer initiated with **P5**-200′. This can be explained by the high degree of livingness of **P5**-200′ (LF = 90 ± 10%) compared to that of **P4**-170′ (LF = 75 ± 10%), as previously determined by ^{31}P NMR spectroscopy.

Conclusion

Polymers with a very high molar fraction of methyl methacrylate prepared via SG1-mediated polymerization in the presence of a few percents of styrene were subjected to ^{1}H, ^{31}P NMR and ESR analyses in order to identify and quantify the chain-end structure. It undoubtedly appeared that these P(MMA-*co*-S) copolymers exhibit a high degree of livingness and that the chain-end structure was a MMA−S−SG1 sequence. Such structure was successfully used to reinitiate the polymerization of styrene and *n*-butyl acrylate, hence leading to the formation of block copolymers. The synthesis of such methyl methacrylate-rich block copolymers entirely via nitroxide-mediated radical polymerization represents a significant progress in the field. Moreover, the dissociation rate constant was enhanced with respect to that of PS−SG1 macroalkoxyamine, due to the MMA penultimate unit effect. This allowed the polymerization temperature to be decreased down to 78 °C, which is unprecedented in nitroxide-mediated polymerizations.

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