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Synthesis of Stars and Starlike Block Copolymers from a Trialkoxyamine Used as Initiator

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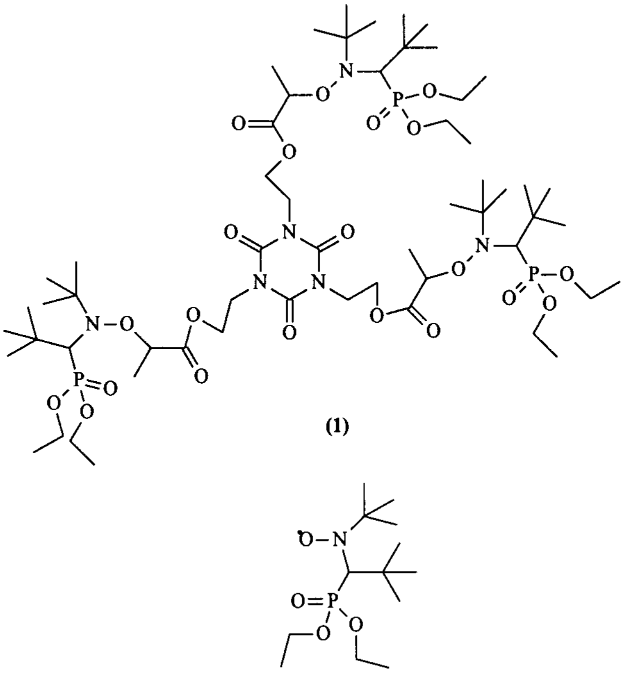
ABSTRACT: This study investigates the efficiency of a novel trifunctional alkoxyamine (**1**) based on *N*-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1) (**2**) as initiator for the controlled radical polymerization of styrene (S) and *n*-butyl acrylate (*n*BuA). Three factors, namely the concentration of SG1 initially introduced in excess, the monomer conversion, and—in the specific case of PS samples—the monomer autopolymerization, were found to control the quality of the star samples obtained. Well-defined T-(PBuA-*b*-PS)$_3$ star block copolymers could also be synthesized by sequential copolymerization using the same trifunctional initiator.

Introduction

Nitroxide-mediated free-radical polymerization has emerged in the past decade as a powerful tool of macromolecular engineering. Block[1] and graft[2] copolymers as well as star-shaped[3] polymers could indeed be prepared using either TEMPO or other commercially available nitroxides to control the chain growth. Later it was discovered that β-hydrogen-containing nitroxides[4,5a] can not only promote the controlled polymerization of styrenic monomers but also that alkyl acrylates, dienes, etc., polymeric architectures that were not accessible with TEMPO-based alkoxyamines as initiators, now become available. For instance, we showed[5b] that well-defined PS-*b*-P*n*BuA-*b*-PS triblock copolymers can be obtained by sequential polymerization from a difunctional alkoxyamine[6] based on one of these β-hydrogen-containing nitroxides, namely (*N*-*tert*-butyl-*N*-[1-diethylphosphono-2,2-dimethyl]propyl nitroxide) (SG1).

This paper discusses the ability of the trialkoxyamine (**1**) to bring about the controlled polymerization of styrene and *n*-butyl acrylate from its three initiation sites. The conditions that permit the synthesis of well-defined star-shaped block copolymers were thoroughly investigated. Two factors were more specifically examined: the conversion beyond which star−star coupling becomes detectable and the amount of excess SG1 required for a controlled propagation to occur.

Scheme 1. Structure of the T-(SG1)$_3$ Trialkoxyamine (1) and SG1 (2)



Experimental Part

Materials. Styrene (S) and *n*-butyl acrylate (*n*BuA) were purchased from Aldrich (99 and 98%, respectively) and distilled under reduced pressure over calcium hydride. SG1 (*N*-*tert*-butyl-*N*-[1-diethylphosphono-2,2-dimethylpropyl] nitroxide) was prepared as previously described[7] and used as received from ATOFINA.

Analytical Techniques. Size exclusion chromatography (SEC) was performed using a Waters apparatus equipped with four TSK gel HXL columns of 5 μm (25, 150, 10^3, and 10^4 nm) and working at room temperature with tetrahydrofuran (THF) as eluent, at a flow rate of 1 mL/min. A light scattering detector (DAWN-F laser photometer operating at 633 nm, Wyatt Technology) was used for the determination of molar masses; for star block copolymers the molar masses were calculated taking into account the composition of the sample and the d*n*/d*c* values of the corresponding homopolymers ($dn/dc_{(\mathrm{PnBuA,THF,25}\ °\mathrm{C})} = 0.057$ and $dn/dc_{(\mathrm{PS,THF,25}\ °\mathrm{C})} = 0.182$). Liquid adsorption chromatography (LAC) was performed using a similar apparatus except for the pump which delivered a mixture of hexane and THF whose composition varied with time. With pure hexane, the chains tended to precipitate at the top of the columns and were eluted as the eluent mixture was enriched with THF: PBuA chains come first, then PBuA/PS copolymers, and PS chains at the end; polymers were detected using a UV detector.

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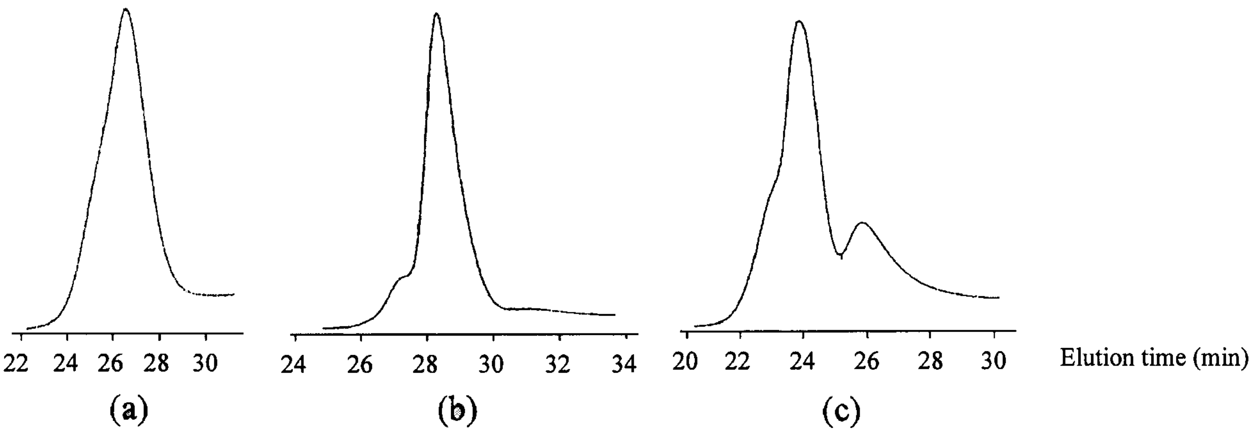

Figure 1. SEC traces of PS stars A2 (48%) (a), A3 (70%) (b), and A6 (80%) (c).

Table 1. Polymerization of Styrene at 120 °C Using T-(SG1)$_3$ as Initiator with Various Proportions of SG1 in Excess

expt	$[SG1]_0$ (eq)[a]	$[T\text{-}(SG1)_3]_0$ (mol/L)[b]	time (h)	ρ^c (%)	$M_{n,th}{}^d$ (g/mol)	$M_n{}^e$ (g/mol)	I^f	LP[g]
A1	0	3.02×10^{-2}	2	87	26 100	21 200	1.2	0
A2	0	1.20×10^{-2}	1	48	36 000	33 800	1.24	0
		+ styrene[h]	3	76	114 000	100 900	1.32	-
A3	0	6.05×10^{-3}	2.6	70	105 000	101 500	1.33	-
A4	0.077	3.13×10^{-3}	2.75	61	176 900	193 300	1.37	11
A5	0.28	3.02×10^{-2}	3.25	67	20 100	16 300	1.10	-
			5.25	96	28 800	22 900	1.15	-
A6	0.6	3.24×10^{-3}	7	88	246 400	177 900	1.21	25
A7	0.8	6.05×10^{-3}	2.6	35	52 500	37 100	1.12	16
			5.3	75	112 500	81 000	1.15	19
A8	0.8	3.02×10^{-3}	3.8	38	114 000	106 100	1.16	25
			5.6	56	168 000	143 400	1.20	30
A9[i]	0.077	3.02×10^{-3}	5	55	165 000	180 500	1.27	-
A10[i]	0.077	3.02×10^{-3}	7	44	132 000	152 600	1.23	-

[a] Initial concentration of nitroxide in molar equivalent per function of initiator. [b] Initial concentration of alkoxyamine T-(SG1)$_3$. [c] Conversion evaluated by gravimetry. [d] Theoretical number-average molar mass calculated from conversion and initial concentration of initiator. [e] Number-average molar mass of the main peak measured by size exclusion chromatography using THF as eluent and light scattering detection ($dn/dc = 0.182$). [f] Polydispersity index from SEC traces using refractometric detection. [g] Weight proportion of the linear chains (LP) from SEC traces. [h] Second addition of styrene in equal amount to the first one after 1 h polymerization. [i] Temperature of polymerization taken equal to 100 °C.

Synthesis of the Adduct of SG1 to 1-Phenylethyl Radicals (SG1-PhEt).[7,8] A solution of SG1 (2.03 g, 5 mmol) and 1-phenylethyl bromide (1.35 mL, 10 mmol) in benzene (8 mL) was transferred under an inert atmosphere to a mixture of CuBr (1.32 g, 10 mmol), 2,2′-bipyridine (3.18 g, 20 mmol), and Cu(0) (0.31 g, 5 mmol) in benzene (8 mL), according to the procedure described by Matyjaszewski.[7] After 2 days stirring at room temperature, the mixture was filtered and washed with a 5% (w/v) aqueous solution of $CuSO_4$. The organic phase was dried over anhydrous Na_2SO_4, and the remaining solvent was removed under reduced pressure. The oil obtained was purified by silica gel chromatography (pentane/ethyl acetate).

Synthesis of the Trifunctional Alkoxyamine T-(SG1)$_3$.[8] In a 250 mL three-neck flask equipped with a magnetic stirrer, 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (2.64 g, 15 mmol) was suspended in 50 mL of dry THF containing triethylamine (2.9 mL, 20 mmol). The mixture was cooled to 0 °C, and 2-bromopropionyl bromide (4.31 g, 20 mmol) dissolved in 10 mL of THF was added dropwise over a period of 1 h and then the reaction was stirred at room temperature for 24 h. The salt formed was removed by filtration, and the crude ester obtained was washed with a water−methanol mixture and dried over anhydrous $MgSO_4$: 1,3,5-tris(2-bromopropionyloxyethyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione was obtained in 80% yield as a yellowish viscous liquid. To transform the latter compound to the corresponding trialkoxyamine T-(SG1)$_3$, the same procedure as that described for SG1-PhEt was followed.

Synthesis of the T-(PS-SG1)$_3$ Polystyrene Star. A mixture of styrene (20 mL, 0.174 mol), T-SG1 (91 mg, 6.25×10^{-5}mol), and SG1 (5.6 mg, 1.4×10^{-5}mol) was poured into a Schlenk and degassed by three freeze−thaw cycles under vacuum and then immersed in an oil bath thermostated at 120 °C for 3 h. After polymerization, the remaining monomer was removed under vacuum at 40 °C (61% yield). The molar mass of the polymer obtained was equal to 193 300 g/mol, and the polydispersity index was $I = 1.37$.

Synthesis of the T-(PBuA-SG1)$_3$ Macroinitiator. A mixture of *n*-butyl acrylate (15 mL, 0.102 mol), T-SG1 (0.125 g, 8.6×10^{-5} mol), and SG1 (5.3 mg, 1.3×10^{-5} mol) was poured into a Schlenk and degassed by three freeze−thaw cycles under vacuum and then immersed in a oil bath thermostated at 120 °C for 1 h. After polymerization, the remaining monomer was removed under vacuum at 50 °C. The molar mass of the polymer obtained (29% yield) was equal to 45 400 g/mol and its polydispersity index equal to $I = 1.18$.

Hydrolysis of the T-(PS-SG1)$_3$ Polystyrene Macroinitiator. About 1 g of PS star ($M_n = 193\,300$ g/mol, $I = 1.37$, 5.17×10^{-6} mol) was dissolved in THF (30 mL) in the presence of KOH (0.3 mL,1 M solution in methanol) in excess. The reaction was carried out at 60−70 °C (reflux) for 30 min, and then the polymer obtained was precipitated in methanol and analyzed by SEC ($M_n = 52\,200$ g/mol, $I = 1.12$, yield over 90%).

Synthesis of the T-(PBuA-*b*-PS-SG1)$_3$ Starlike Block Copolymer from the T-(PBuA-SG1)$_3$ Macroinitiator. A mixture of T-(PBuA-SG1)$_3$ ($M_n = 41\,200$ g/mol, $I = 1.18$) precursor (1.0 g, 2.42×10^{-5} mol) and styrene (5 mL, 4.36×10^{-2} mol) was poured into a Schlenk and degassed by three freeze−thaw cycles under vacuum and then immersed in a oil bath thermostated at 120 °C for a given time (0.5, 1, and 2 h). For instance, after 30 min of polymerization, the molar mass of the polymer obtained was equal to 96 900 g/mol and its polydispersity index equal to 1.32 (18% conversion of styrene).

Table 2. Polymerization of *n*-Butyl Acrylate at 120 °C from T-(SG1)$_3$ in the Presence of SG1 in Various Proportions

expt	[SG1]$_0$ (eq)[a]	[T-(SG1)$_3$]$_0$ (mol/L)[b]	time (h)	ρ[c] (%)	$M_{n,th}$[d] (g/mol)	M_n[e] (g/mol)	I[f]	SSC (%)[g]
B1	0.037	5.83×10^{-3}	2.2	54	81 000	84 000	1.17	0
			5	92	138 000	103 800	1.39	30
B2	0.05	5.83×10^{-3}	1	29	43 500	45 400	1.18	0
			2	52	78 000	76 500	1.19	0
			3	65	97 500	93 400	1.39	16
			4	79	118 500	151 100	1.40	32
B3	0.1	3.64×10^{-2}	3.1	60	14 400	15 600	1.09	0
B4	0.116	2.08×10^{-3}	2.25	39	163 800	119 700	1.42	0
B5	0.117	1.53×10^{-2}	4.3	68	38 800	40 300	1.11	0
B6	0.13	2.03×10^{-3}	6	30	129 000	86 800	1.28	0

[a] Initial concentration of nitroxide in molar equivalent per function of the initiator. [b] Initial concentration of alkoxyamine T-(SG1)$_3$. [c] Conversion evaluated by gravimetry. [d] Theoretical number-average molar mass calculated from conversion and initial concentration of initiator. [e] Number-average molar mass calculated from polydispersity index measured by size exclusion chromatography using refractometric detection and weight-average molar mass measured by light scattering detection (THF as eluent and d*n*/d*c* = 0.057). [f] Polydispersity index from SEC, using refractometric detection. [g] Proportion of the population resulting from star–star coupling (SSC) as measured from SEC traces.

Results and Discussion

Synthesis of Three-Arm PS Stars from T-(SG1)$_3$. Polystyrene stars of various sizes were synthesized from neat styrene at 120 °C using T(SG1)$_3$ as initiator. In experiments D4 to D8, some SG1 was deliberately added to check whether there is a correlation between the quality of the samples synthesized and the amount of free SG1 available in the reaction medium.

Table 1 shows that stars (samples A1 and A2) exhibiting rather low polydispersity indexes, and no contamination by either linear chains or coupled species can be obtained, provided low to moderate molar mass ($<10^5$ g mol^{-1}) samples are targeted. Even though this entailed the presence of rather large initial concentration in **1** and in polymeric radicals in the reaction medium, no major complication such as that due to star–star coupling could be detected up to conversion as high as 87%. This excellent control of molar mass indicates that the initiator efficiency is high with little loss of active sites.

In contrast, the synthesis of well-defined PS stars of large size appears more complicated to master: because such samples imply longer polymerization times (>3 h), the amount of linear chains formed by autopolymerization reaches nonnegligible values (>10%). In addition, the samples tend to broaden as their molar mass and the monomer conversion increase (M_n = 193 300 g mol^{-1}, I = 1.37, conversion of 61%) and be eventually contaminated with species of uncontrolled functionality (Figure 1b) because of the star–star coupling phenomenon. The sample shown in Figure 2 was then subjected to a basic treatment in order to hydrolyze the three ester functions of its core: the chains isolated after hydrolysis which correspond to the branches of the star precursor exhibit a rather narrow molar mass distribution (I = 1.19, M_n = 52 200 g/mol), suggesting that the broadened molar mass distribution of the mother sample was essentially due to the recombination between stars.

The introduction of free SG1 in the reaction medium helped to narrow the molar mass distribution of the samples on one hand but provoked an extension of the polymerization times on the other: this resulted in the increase of the concentration of thermally produced linear chains (Figure 1c). The best compromise was actually obtained upon decreasing the temperature to the range of 100 °C and maintaining a small excess of SG1: under these conditions, the production of thermally initiated chains could be drastically reduced, and the initiation step remained fast enough in comparison to the incorporation of monomer units to provide well-defined samples (A9 and A10).

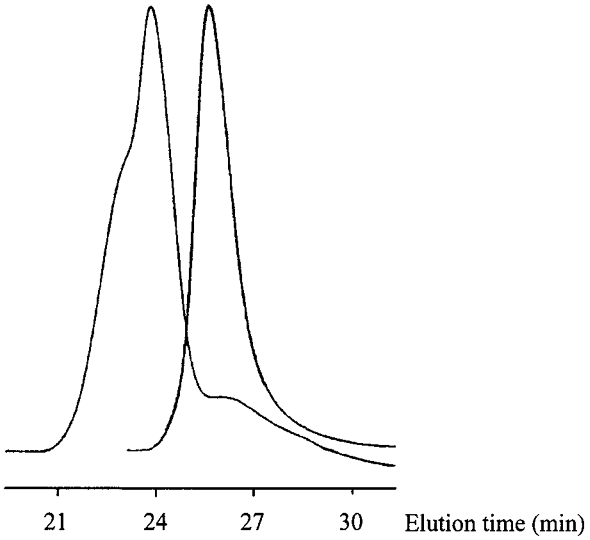

Figure 2. SEC traces of the PS stars synthesized from T-(SG1)$_3$ before (on the left) and after (on the right) hydrolysis of the three central ester functions.

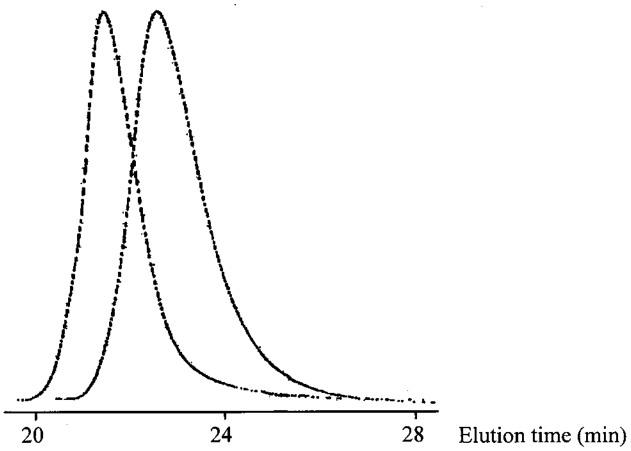

Figure 3. SEC traces of PS star synthesized at 100 °C.

Synthesis of Three-Arm P*n*BuA Stars from T-(SG1)$_3$. In contrast to PS stars which may contain linear chains when synthesized above 100 °C, PBuA star samples should not be contaminated with linear species: the only complication that may occur and alter the

Table 3. Polymerization of *n*-Butyl Acrylate Using Mixtures of Mono- and Trifunctional Alkoxyamines and a Slight Excess of SG1 (0.05 Molar Equivalent per Active Center); Characterization of Polymers Obtained

expt	$[1]_0/[3]_0{}^a$	time (h)	ρ^b (%)	$M_{n,th}{}^c$ (g/mol)	$M_w{}^d$ (g/mol)	I^e	F^f
C1	1	1.75	64	44 800	55 800	1.42	-
C2	3	3.25	81	172 400 57 400	162 000 53 500	1.13 1.09	3.0

[a] Ratio of initial concentration of alkoxyamines used (1 is AM-SG1 and 3 is T-(SG1)$_3$). [b] Conversion evaluated by gravimetric measurements. [c] Number-average molar mass calculated from conversion and initiator initial concentration. [d] Number-average molar mass measured by size exclusion chromatography using THF as eluent and light scattering detection. In the case of C2, two peaks were detected, whose corresponding mass average molar mass is indicated. [e] Polydispersity index from SEC. [f] Functionality from the ratio of the M_w of the two peaks.

Table 4. Polymerization of Styrene at 120 °C from T-(PBuA-SG1)$_3$ Precursors at Different Conversion Rates

		precursor		PS blocks							
expt	Pr^a	ρ^b (%)	$M_n{}^d$ (g/mol)	T	$[\mathrm{Pr}]_0{}^e$ (mol L^{-1})	time (h)	ρ^c (%)	$M_{n,th}{}^f$ (g/mol)	$M_n{}^g$ (g/mol)	I^h	PS^i (%)
D1a	B2	29	41 200	120	5.04×10^{-3}	0.5	18	72 400	96 900	1.32	54
D1b						1	32	97 600	120 500	1.57	59
D1c						2	60	148 000	151 000	1.74	73
D2	B3	60	15 600	120	1.32×10^{-2}	0.5	20	27 600	29 300	1.18	
						1.3	50	53 700	45 200	1.26	
D3	B3	60	15 600	110	6.36×10^{-3}	1.75	27	52 300	44 600	1.24	
D4	B5	68	40 300	120	7.56×10^{-3}	0.5	25	65 500	103 400	2.4	
D5	B5^d	68	40 300	120	2.48×10^{-3}	1	25	128 500	132 600	1.89	
D6	B5^d	68	40 300	110	2.48×10^{-3}	1.75	22	115 800	112 100	1.47	
D7	B6	30	86 800	120	2.65×10^{-3}	0.5	10	109 400	97 100	1.36	
						1.25	16	129 800	113 500	1.37	

[a] Reference of the PBuA precursor described in Table 2. [b] Conversion of the PBuA block. [c] Conversion by gravimetry, knowing the amount of macroinitiator. [d] Molar mass of the PBuA star from light scattering ($dn/dc = 0.057$). [e] Initial concentration of PBuA precursor. [f] Theoretical number-average molar mass calculated from conversion and initial concentration of initiator. [g] Number-average molar mass measured by size exclusion chromatography using refractometric detection and polystyrene standards. [h] Polydispersity index from SEC, refractometric detection. [i] PS content in the star formed.

trifunctional character of these stars is their mutual couplings. Poly(*n*-butyl acrylate) stars of various sizes were thus synthesized from neat *n*BuA at 120 °C using T-(SG1)$_3$ as initiator; unlike the case of styrene, the presence of an excess of SG1 was necessary to keep control over the propagation of poly(*n*-butyl acrylate) chains.[7] The amount of SG1 purposely introduced was varied, and its influence on the quality of the resulting star samples was examined.

It can be seen from Table 2 that the presence of free SG1 is essential to the preparation of well-defined and narrowly distributed P*n*BuA stars. Should the excess of SG1 introduced be too low, the recombination of growing polymeric radicals and therefore their irreversible termination were favored: the samples obtained under these conditions were contaminated with species of higher functionality whose proportion increased with conversion. Even though the use of SG1 in large excess resulted in longer polymerization times, there was no other option but to provide growing radicals with enough SG1 to prevent their early termination, specially when high molar mass and high conversion were targeted.

Despite these constraints, well-defined P*n*BuA stars could be obtained in the range of 10^5 g mol^{-1} in reasonable times (<6 h). To check the efficiency of the initiation step, a mixture of tri- (**1**) and monofunctional (SG1-PhEt, see Experimental Part) alkoxyamines in a 1:3 ratio was used to trigger the polymerization of *n*BuA. As expected, the SEC traces of the resulting sample showed the presence of two populations whose respective weights were found equal using the program “origin” (Figure 4).

Such a perfect agreement between the expected and experimental molar masses (Table 3) for the two populations of chains suggests that initiation occurred with an ideal efficiency for both mono- and trifunctional (**1**) alkoxyamines.

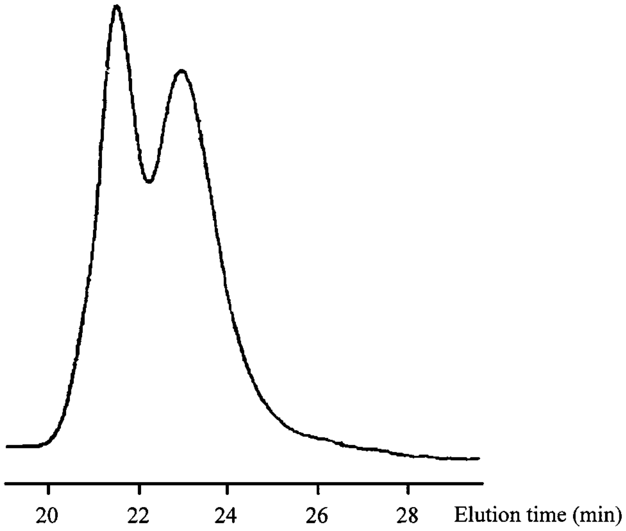

Figure 4. SEC traces of the sample C2 mentioned in Table 3.

When used separately to initiate the polymerization of *n*-butyl acrylate, the two alkoxyamines afford, for a same initial concentration, the same rate of polymerization (Figure 5) and samples whose molar masses differ by a factor of 3. This is an additional argument in favor of perfectly trifunctional star samples.

Synthesis of a Starlike Block Copolymer T-(PBuA-*b*-PS)$_3$. Some of the well-defined T-(PBuA-SG1)$_3$ star samples then served as precursors for the synthesis of star-shaped T-(PBuA-*b*-PS)$_3$ block copolymers. A first experiment (D2) was carried out at 120 °C using a precursor of small molar mass (1.5×10^3 g mol^{-1}) to trigger the polymerization of styrene. Two aliquots were withdrawn at different conversion and analyzed by SEC. The resulting samples exhibited a narrow, unimodal, and symmetrical molar mass distribution and appeared

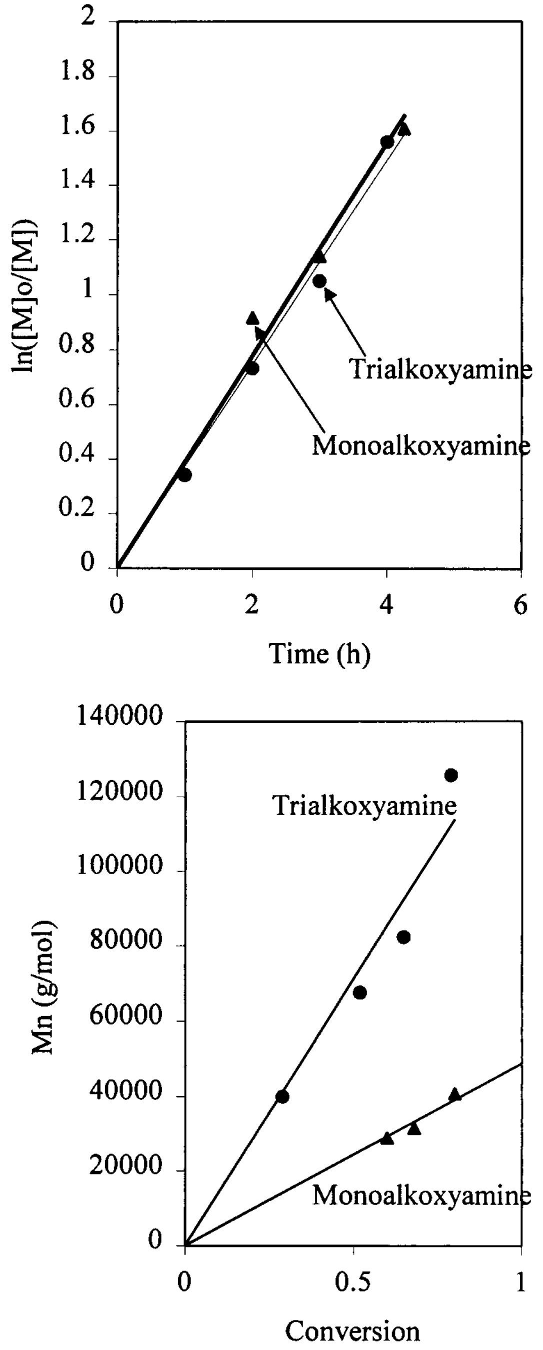

Figure 5. Polymerization of styrene and *n*-butyl acrylate from mono- and trifunctional alkoxyamines. Evolutions of ln([M]$_0$/[M]) and of the number-average molar mass as a function of time and conversion, respectively.

not be contaminated with species of higher functionality. Even the copolymer sample isolated after crossing 50% conversion in styrene is well-defined with a polydispersity index of 1.26.

The use of T-(PBuA-SG1)$_3$ of larger molar mass (40 × 10^3 and 45 × 10^3 g mol^{-1}) resulted in a totally different picture. With such precursors, the polymerization of styrene had to be discontinued at rather low conversion (<20%) for the resulting T-(PBuA-*b*-PS–SG1)$_3$ block copolymer samples to exhibit the expected structure and a narrow distribution of molar mass. Under these conditions, well-defined star-shaped copolymers could be prepared in the range of 10^5–1.3 × 10^5 g mol^{-1} molar mass with various contents in PS and PBuA (Table 4). Above 20% conversion in styrene, star–star coupling was systematically observed, and ill-defined samples (D1b,c, D4, D5) were eventually obtained regardless of the initial concentration in T-(PBuA-SG1)$_3$ precursor. Decreasing the temperature of the reaction medium to 110 °C (D3) helped to curb the recombination between stars (Figure 6), but the high molar mass sample isolated (D6) still contained coupled materials of functionality higher than 3. To account for this unexpected result, one has to consider the possibility for the reaction medium to phase separate into nanoscale microdomains as the PS blocks get longer.

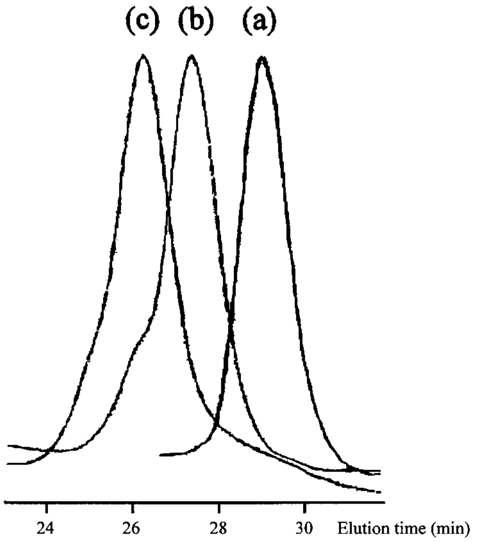

Figure 6. SEC traces of T-(PBuA-*b*-PS-SG1)$_3$ samples as described in Table 4: (a) PBuA precursor (E4), (b) T-(PBuA-*b*-PS-SG1)$_3$ (D2, 20% conversion, T = 120 °C), and (c) T-(PBuA-*b*-PS-SG1)$_3$ (D3, 27% conversion, T = 100 °C).

In such samples that involve P*n*BuA and PS blocks of larger size, the incompatibility between the two polymers occurs soon after the conversion in styrene crosses the threshold of 10–20%, changing the initial homogeneous solution into a milky medium. Under such heterogeneous conditions, the growing PS radicals whose mobility is likely restricted to the PS-rich phase have obviously more opportunities than in a homogeneous medium to be deactivated by other growing branches. This appears to be the main reason for the marked tendency of these PS radicals to recombine in such block copolymer synthesis. For the synthesis of well-defined T-(P*n*BuA-*b*-PS-SG1)$_3$ star block copolymers by this nitroxide-mediated route, it is therefore essential to discontinue the polymerization of styrene at low conversion (<20%).

Some of the star-block samples were subjected to liquid adsorption chromatography (LAC) analysis using a mixture of hexane and THF as solvents. The characterization of the sample D7 (Figure 7) shows that all T-(PBuA-SG1)$_3$ chains have initiated the polymerization of styrene and that all T-(PBuA-PS-SG1)$_3$ stars molecules exhibit the same composition, in the range of 0–16% conversion. It can also be seen that the star-block sample isolated at 16% conversion is contaminated with a small amount of linear PS chains arising from the autopolymerization of styrene.

Conclusion

A trialkoxyamine T-(SG1)$_3$ was purposely synthesized to subsequently serve as a trifunctional initiator for the controlled polymerization of styrene and *n*-butyl acry-

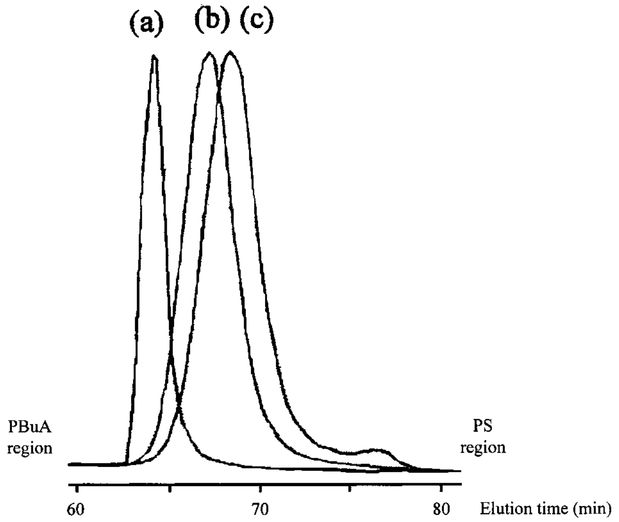

Figure 7. LAC analysis of T-(PBuA-*b*-PS)$_3$ (D7). From the left to the right: (a) T-(PBuA)$_3$ macroinitiator (E7), T-(PBuA-*b*-PS)$_3$ diblock copolymer (10 and 16% conversion, (b) and (c), respectively).

late. Well-defined triarmed PS and P*n*BuA stars could be obtained but the experimental conditions used differ from one monomer to the other. In the case of styrene, precautions were taken to avoid the presence in detectable amounts of linear chains produced by self-polymerization and of coupled species of functionality higher than 3. Setting the temperature of the reaction medium at 100 °C helped to prevent these two complications. As to the preparation of P*n*BuA-based star polymers, it required the addition of free SG1 for the propagation to occur under controlled conditions. It was also necessary to discontinue the polymerization before complete conversion to obtain well-defined triarmed P*n*BuA stars. T(P*n*BuA-*b*-PS-SG1)$_3$ star block copolymers of narrow distribution could also be derived in the range of 10^5 g mol^{-1} by sequential polymerization of the two monomers, that of styrene being carried out at 110 °C and discontinued at low conversion. As for star–star coupling, it was again the main side reaction responsible for the loss of control of the star functionality at high conversion.

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References and Notes

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