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Synthesis and Characterization of Poly(styrene-*b*-*n*-butyl acrylate-*b*-styrene) Triblock Copolymers Using a Dialkoxyamine as Initiator

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ABSTRACT: This study investigates the ability of a novel difunctional alkoxyamine based on *N*-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1) to serve as initiator for the controlled radical polymerization of styrene (S) and *n*-butyl acrylate (*n*BuA). The efficiency of this initiator was checked using three different methods. After we set up the conditions best suited to the synthesis of perfectly difunctional poly(*n*-butyl acrylate) (P*n*BuA) samples, well-defined poly(styrene-*b*-*n*-butyl acrylate-*b*-styrene) triblock copolymers could be obtained by sequential polymerization of the corresponding monomers. However, a loss of control of the targeted structure was observed whenever the conversion of styrene exceeded 40%.

Introduction

Strongly segregated block copolymers exhibit a variety of ordered nanoscopic domains whose morphologies are controlled by the segment volume fraction and the overall molecular architecture.[1] Although some of these nanostructured materials might be of potential interest for technological use, their development critically depends on the synthetic strategies used to obtain them. For instance, ABA triblock copolymers based on poly(*n*-butyl acrylate) (P*n*BuA) as central block may be valuable substitutes for traditional poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymers because of their better resistance to oxidation and UV, but their synthesis using either anionic polymerization[2] or rare earth metal complexes[3] require very drastic experimental conditions.

Compared to traditional routes of block copolymer synthesis, living/controlled radical polymerization appears to be easier to carry out and therefore provides an opportunity to revitalize the field of block copolymers: not only can materials such as those mentioned above be obtained at lower cost but also a variety of novel block copolymers now become available.[4] On the other hand, one has to acknowledge that controlled radical polymerization does involve a nonnegligible extent of irreversible termination and is certainly not the best means to obtain block copolymers with precise segment size, very narrow molar mass distribution, and no homopolymer contamination, features that are critical for the preparation of model composite materials with controlled morphologies. For instance, Jérôme and co-workers[5] observed that fully acrylic poly(methyl methacrylate-*b*-*n*-butyl acrylate-*b*-methyl methacrylate) block copolymers obtained by atom transfer radical polymerization (ATRP) exhibit poorer mechanical properties than those prepared by the anionic method: they attributed this unexpected behavior to the broad dispersity of the radically prepared PMMA outer blocks. Other attempts were made at associating soft polyacrylic blocks with hard segments: in particular, Georges and co-workers[6] obtained at 155 °C low molar mass poly(styrene-*b*-*n*-butyl acrylate) diblock copolymers with polydispersities ranging from 1.5 to 1.7, using oxo-TEMPO as the counter-radical. Apart from nitroxide-mediated polymerization ATRP[7] and RAFT[8] are two other methodologies that have greatly contributed to the advances made in block copolymer synthesis.

As an attempt to overcome the difficulties associated with commercially available nitroxides—the necessity to work at high temperature and the use of polyacrylate samples of moderate molar mass and large polydispersities—a series of β-hydrogen-containing nitroxides were developed.[9−11] Styrene as well as *n*-butyl acrylate could be homopolymerized under living/controlled conditions between 80 and 120 °C, in particular in the presence of *N*-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide, also referred to as DEPN or SG1 (**1**). The synthesis of poly(styrene-*b*-*n*-butyl acrylate) diblock copolymers could even be accomplished with an accurate structural control, provided *n*BuA was polymerized first.[12] In the alternate case—styrene being introduced first—the diblock copolymers obtained were contaminated with residual PS macroinitiator, stressing the importance of the order of monomer addition in such sequential copolymerizations. This precluded the synthesis of well-defined poly(styrene-*b*-*n*-butyl acrylate-*b*-styrene) triblock copolymers by sequential polymerization of the corresponding monomers, starting from a monofunctional alkoxyamine.

On the basis of these results, we have explored the possibility to generate these triblock copolymers from a purposely designed SG1-based dialkoxyamine (DiF−SG1) (**2**). This synthetic route obviates the need to first polymerize styrene and should therefore afford model thermoplastic elastomers, the order of monomer addi-

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tion (*n*-butyl acrylate then styrene) being favorable in this case. In this paper, the conditions that allow the preparation of model difunctional PS and P*n*BuA homopolymers and well-defined PS-*b*-P*n*BuA-*b*-PS triblock copolymers using DiF−SG1 are described.[13]

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-dimethyl propyl]) nitroxide, 73%) was prepared as previously described[14] and used as received from ATOFINA. The adduct formed by recombination of SG1 with 1-phenylethyl radicals (SG1−PhEt, 97%), the one formed by recombination of SG1 with 1-methylcarboxyethyl radicals (SG1−EEst, 97%), and the difunctional alkoxyamine (DiF−SG1, 90%) were obtained according to a published procedure[15] and used without further purification.

Analytical Techniques. Size exclusion chromatography (SEC) was performed using a Waters apparatus equipped with four TSK gel HXL columns (25, 150, 10^3, 10^4 nm) and working at room temperature with tetrahydrofuran (THF) as eluent, at a flow rate of 1 mL/min. A differential refractive index detector and a UV detector were used, and molar masses were derived from a calibration curve based on polystyrene standards. In the case of P*n*BuA and PS-*b*-P*n*BuA-*b*-PS samples, light scattering detection (Wyatt Technology with a laser source operating at 633 nm) was used: the d*n*/d*c* (THF, 25 °C) value for P*n*BuA samples were taken to be equal to 0.057 mL/g; as to the d*n*/d*c* values for PS-*b*-P*n*BuA-*b*-PS copolymers, they were calculated taking into account the composition of these copolymers and the d*n*/d*c*'s of the corresponding homopolymers, that of PS being equal to 0.182 mL/g. 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 tend to precipitate at the top of the columns, and they were eluted as the solvent mixture was enriched in THF. P*n*BuA chains come first, then P*n*BuA/PS copolymers, and finally PS chains at the end: the eluted polymers were detected using a UV detector.

Synthesis of the α,*ω*-diSG1-Capped Polystyrene Macroinitiator. A mixture of styrene (11 mL, 9.6×10^{-2} mol), DiF−SG1 (0.178 g, 2.0×10^{-4} mol) was poured into a Schlenk flask 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 (yield = 85%), the remaining monomer was removed under vacuum at 40 °C. The molar mass of the polymer obtained was equal to 46 300 g/mol and the polydispersity index (*I*) to 1.38.

Synthesis of the α,*ω*-diSG1-Capped Poly(*n*-butyl acrylate) Macroinitiator. A mixture of *n*-butyl acrylate (5.2 mL, 3.55×10^{-2} mol), DiF−SG1 (41 mg, 4.5×10^{-5} mol), and SG1 (1.8 mg, 4.5×10^{-6} mol) was poured into a Schlenk flask 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 50 °C. The molar mass of the polymer obtained (yield = 76%) was equal to 89 600 g/mol and the polydispersity index (*I*) to 1.36.

Hydrolysis of the α,*ω*-diSG1-Capped Polystyrene Macroinitiator. About 3 g of α,*ω*-functionalized PS (53 200 g/mol, $I = 1.2$; 5.6×10^{-5} mol) was dissolved in THF (50 mL) in the presence of KOH (6 mL, 1 M solution in methanol; 6×10^{-3} mol) in large excess. The reaction was carried out at 60−70 °C (reflux) for 30 min, and then the polymer obtained was precipitated in methanol. About 90% of PS was recovered and its molar mass as analyzed by SEC was equal to 27300 g/mol ($I = 1.2$).

Table 1. Polymerization of Styrene and *n*-Butyl Acrylate from Mono- and Difunctional Alkoxyamines (SG1−EEst and DiF−SG1, Respectively)

expt	F[a]	[initiator]$_0$ (mol/L)[b]	time (h)	ρ[c] (%)	$M_{\mathrm{n,calcd}}$[d] (g/mol)	$M_{\mathrm{n,expt}}$[e] (g/mol)	*I*[f]	*f*[g]
A1	1, S	2.08×10^{-2}	3	78	35 000	33 300	1.15	1
A2	2, S	1.78×10^{-2}	3	85	42 500	46 300	1.38	0.92
A3	1, BuA[h]	1.76×10^{-2}	3	68	34 000	38 500	1.16	0.88
A4	2, BuA[h]	8.69×10^{-3}	3	76	76 000	89 600	1.36	0.85

[a] Functionality of the alkoxyamine used (1 for SG1-EEst and 2 for DiF−SG1) and monomer polymerized (S = styrene and BuA = *n*-butyl acrylate). [b] Initial concentration of alkoxyamine. [c] Conversion evaluated by gravimetry. [d] Number-average molar mass calculated from conversion and initial initiator concentration. [e] Number-average molar mass measured by size exclusion chromatography using THF as eluent, refractive index detection, and polystyrene standards in the case of PS samples and light scattering detection in the case of PnBuA samples (d*n*/d*c* = 0.057 mL/g). [f] Polydispersity index from SEC. [g] Initiation efficiency evaluated from the ratio of $M_{\mathrm{n,calc}}$ over $M_{\mathrm{n,exp}}$. [h] A slight excess of SG1 has been used (0.05 molar equiv per alkoxyamine function) to prevent the loss of control during the polymerization.

Synthesis of the PS-*b*-P*n*BuA-*b*-PS Block Copolymer from the α,*ω*-diSG1-Capped Poly(*n*-butyl acrylate) Macroinitiator. A mixture of α,*ω*-diSG1 P*n*BuA ($M_n = 72\,000$ g/mol, $I = 1.23$) macroinitiator (1.4 g, 2.4×10^{-5} mol) and styrene (10 mL, 8.7×10^{-2} mol) were poured into a Schlenk flask and degassed by three freeze−thaw cycles under vacuum, before being immersed in an oil bath thermostated at 120 °C for a given time (0.25, 0.5, and 1 h). For instance, after 15 min of polymerization, the conversion of styrene was 10% and the molar mass of the polymer obtained was equal to 95 200 g/mol and the polydispersity index (*I*) to 1.36.

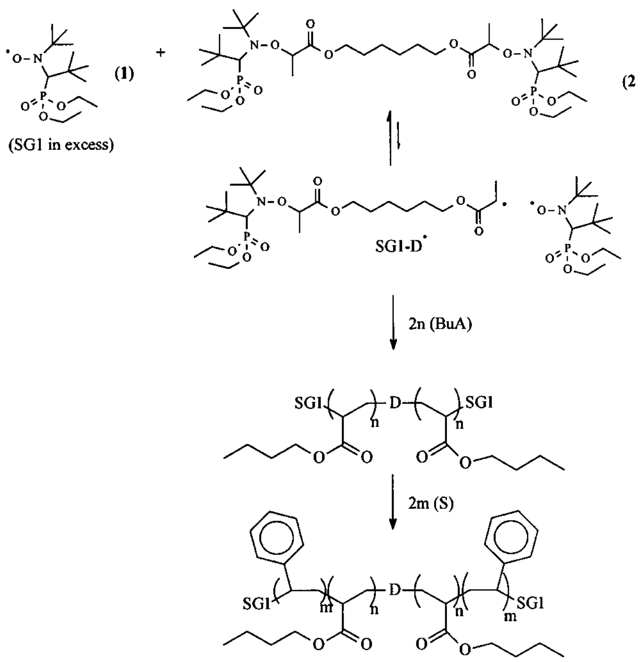
Results and Discussion

Before using the dialkoxyamine DiF−SG1 (**2**) to obtain PS-*b*-P*n*BuA-*b*-PS triblock copolymers by sequential polymerization (Scheme 1), its efficiency as a difunctional initiator was first investigated. Styrene and *n*-butyl acrylate were thus polymerized separately at 120 °C, in the presence of various amounts of (**2**) and a slight excess of nitroxide (**1**), in particular with *n*BuA as monomer. In this way, the polymerization could be slowed to a few hours—instead of minutes—and the extent of irreversible termination due to the Fischer[16] effect minimized.

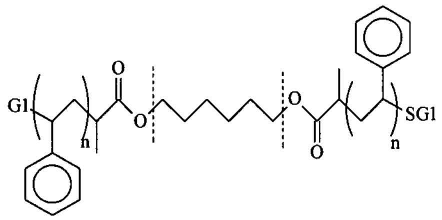
Determination of the Initiating Efficiency of DiF−SG1. In addition to the simple comparison of the sample actual molar mass with the targeted value (which obviously lacks precision), two other methods were contemplated as a means to check the efficiency of the initiating step. In the first method, the polymers obtained from this dialkoxyamine were subjected to a basic treatment aimed at hydrolyzing the central ester functions introduced by **2**, the molar mass ratio between the precursors and the hydrolyzed chains being an indicator of the efficiency step. In a second method, styrene and *n*-butyl acrylate were polymerized in the presence of a mixture of SG1-based mono- and dialkoxyamines with the view of generating two populations of linear chains whose comparison by SEC would serve to derive the actual functionality of the longest chains.

The comparison of the experimental molar masses (Table 1) for both mono- and difunctional samples shows that the two sets of data are in agreement with those targeted; however, one can observe that the samples that derive from the dialkoxyamine (**2**) exhibit larger polydispersity indices than those evaluated for their monofunctional homologues: 1.3−1.4 instead of 1.1. According to our interpretation, this merely reflects the fact that growing monofunctional species can undergo irreversible recombination only once, being definitively deactivated; in contrast, their difunctional homologues

Scheme 1. Synthesis of PS-*b*-PnBuA-*b*-PS Triblock Copolymer from DiF−SG1 (2) Dialkoxyamine



Scheme 2. Bonds Sensitive to Basic Hydrolysis in Difunctional PS Samples



may participate in recombination more than one time. All difunctional chains that undergo recombination still retain their difunctional character but double their average molar mass. This might be the reason for the slight broadening of the molar mass distribution that is observed.

The hydrolysis of difunctional PS samples (Scheme 2) resulted in samples of lower PDI and molar mass corresponding to roughly half of the values determined for their precursor (Figure 1, Table 2). The efficiency of the initiation step as calculated by this method was higher than 0.9.

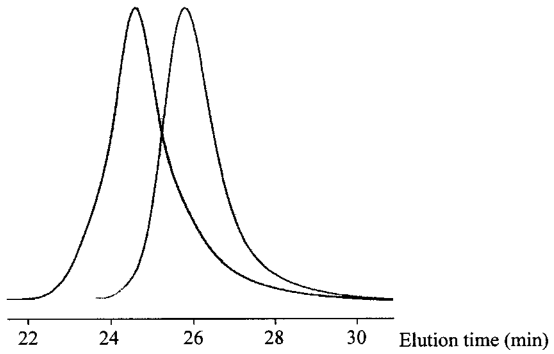


Figure 1. SEC traces of the sample of polystyrene synthesized from DiF−SG1, before and after hydrolysis of its core.

Table 2. Hydrolysis of Polystyrene Samples Synthesized from the Difunctional Alkoxyamine (2)

	starting PS sample				after hydrolysis			
expt	$M_{n,calc}$[a] (g/mol)	M_n[b] (g/mol)	M_w[c] (g/mol)	I[d]	M_n[b] (g/mol)	M_w[c] (g/mol)	*I*[d]	*F*[e]
B1	45 000	53 200	63 800	1.2	27 300	32 200	1.2	2.0
B2	84 000	72 900	87 500	1.2	34 800	40 800	1.2	2.1
B3	113 500	108 100	144 400	1.3	49 300	61 200	1.2	2.0

[a] Number-average molar mass calculated from conversion and initiator initial concentration. [b] Number-average molar mass measured by size exclusion chromatography using THF as eluent and polystyrene standards. [c] Weight-average molar mass measured by the same method. [d] Polydispersity index from SEC. [e] Average functionality of the PS starting sample expressed as the ratio of $M_{w,hydrolyzed\ PS}$ over $M_{w,starting\ PS}$.

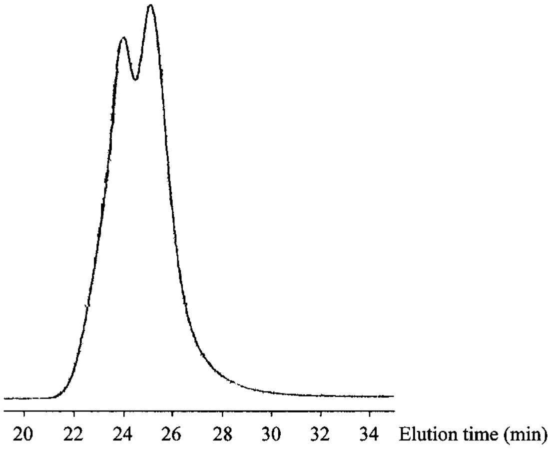


Figure 2. SEC traces of the sample C2 (Table 3).

Unfortunately, the same procedure could not be applied to PnBuA samples because of the lack of selectivity of hydrolysis; indeed, the ester functions carried by the chains (Scheme 1) were also cleaved—if not totally, at least partially—in addition to those of the initiating moiety, making the molar mass determination of the resulting samples meaningless.

Since the evaluation of the sample functionality through hydrolysis of their central core was ineffective for poly(*n*-butyl acrylate), the latter structural information was checked using a mixture of mono- and dialkoxyamine as initiator in a 2/1 ratio. Should the initiating step have occurred with the same efficiency for both mono- and dialkoxyamine, the two populations of chains formed should exhibit the same weight fraction in the SEC traces and a molar mass ratio of 2. This is exactly what was actually observed upon characterization of these bipopulated samples (Figure 2, Table 3). The weight fraction of each population in the corresponding SEC traces indeed revolved around 0.5 as expected and their respective molar mass values at the peak apex appears to differ by a factor of 2.

Synthesis of a Triblock Copolymer PS-*b*-P*n*BuA-*b*-PS from DiF−SG1. The difunctional character of P*n*BuA samples grown from DiF−SG1 being established, the synthesis of PS-*b*-P*n*BuA-*b*-PS triblock copolymers could be contemplated.

Two different strategies were considered for obtaining well-defined triblock copolymers samples in bulk, with short outer PS blocks (Table 4). A difunctional P*n*BuA macroinitiator was either used in small amounts (in that case the polymerization of styrene was discontinued at low conversion (samples D5, D6)) or introduced in high concentration with the view of consuming styrene to higher conversion (samples D1−D4). This macroinitiator was mixed with neat styrene and heated to 120 °C, with

Table 3. Polymerization of *n*-Butyl Acrylate Using Mixtures of Mono- and Difunctional Alkoxyamines and a Slight Excess of SG1 (0.05 molar equiv per Alkoxyamine Function), Showing the Characterization of the Polymers Obtained

expt	[**1**]$_0$/[**2**]$_0$[a]	time (h)	ρ[b] (%)	peak mass[c] (g/mol)	R[d] (%)
C1	1/1	1.75	69	37 100[f]	
C1	1/1	3	93	108 000 209 000	45
C1′ [e]	1/1	3	44	111 900 235 800	53
C2	2/1	3.25	79	61 700 1 065 000	55

[a] Ratio of initial concentration of alkoxyamines used (1 is SG1-EEst and 2 is DiF−SG1). [b] Conversion evaluated by gravimetry. [c] Peak mass as given by size exclusion chromatography using THF as eluent and refractive index detection. [d] Proportion of low molar mass population. [e] Styrene has been polymerized from (B1) PBuA macroinitiator. [f] Only 1 peak detected.

the SG1 introduced in slight excess in the reaction medium during the polymerization of the first P*n*BuA block being left during the polymerization of styrene to help control the growth of the PS outer blocks.

As could be anticipated, the best defined samples were those generated through the first approach (samples D5 and D6). Provided the conversion in styrene was limited to 40%, the samples isolated exhibit an unimolecular and rather narrow molar mass distribution (I < 1.4). Although this corresponded to the growth of rather short PS outer blocks, their SEC traces (Figure 3) showed a marked shift compared to that of the precursor.

As to the sample that was obtained by the second approach at high conversion in styrene (sample D3, Table 4), it exhibited a bimodal and broad molar mass distribution (I = 2.7) because of extensive couplings/recombinations between growing chains.

Beyond these positive results, one can wonder whether the samples eventually obtained are contaminated with diblock species resulting from incomplete initiation by the P*n*BuA dialkoxyamine. Unfortunately, this question could not be experimentally answered: as previously mentioned, the copolymer central block could not be selectively cleaved without affecting the chain ester functions. However, the results from a previous study[12] on the synthesis of 5.3×10^4 g mol^{-1} P*n*BuA-*b*-PS diblock copolymer from a P*n*BuA macroinitiator of 4×10^4 g mol^{-1} showed the remarkable efficiency (f) of the blocking process, a value of $f = 1.97$ being obtained for styrene conversion as low as 19%.

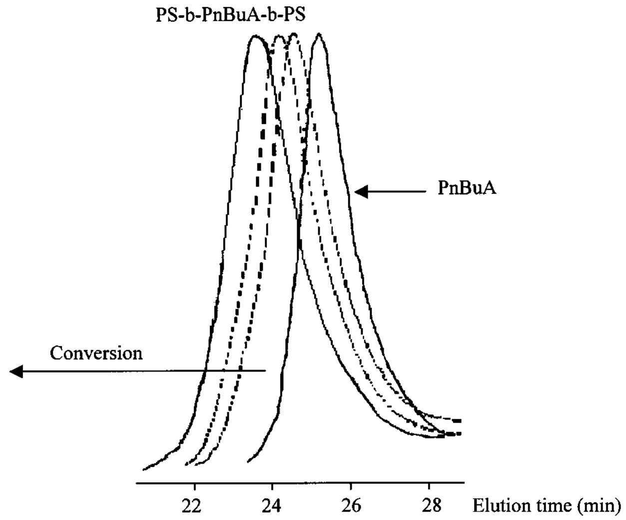


Figure 3. SEC traces of PnBuA macroinitiator and PS-*b*-PnBuA-*b*-PS block copolymers corresponding to the samples D6 with 32, 44, and 55% content of PS.

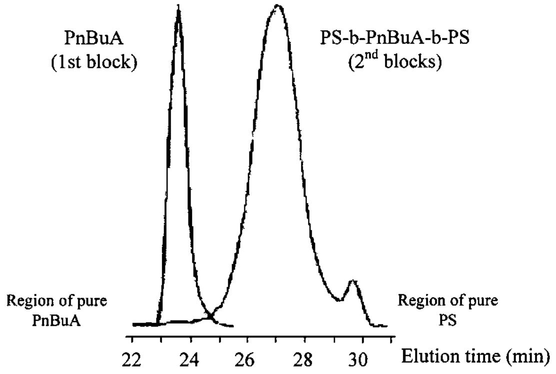


Figure 4. LAC traces of PnBuA macroinitiator (on the left) and PS-*b*-PnBuA-*b*-PS block copolymer of the sample D6 for 55% conversion (on the right).

Characterization of the triblock copolymer sample C6 by liquid adsorption chromatography (LAC) (Figure 4) using hexane/THF mixture as solvents confirms that all P*n*BuA chains did initiate the polymerization of styrene: the LAC chromatogram of such samples does not indicate the presence of residual P*n*BuA chains, and the shift toward the region of copolymers containing styrene and *n*-butyl acrylate units is clearly seen. However, the same LAC analysis demonstrates that some PS homopolymers arising from the thermal autopolymeriza-

Table 4. Synthesis of Triblock Copolymers PS-*b*-PnBuA-*b*-PS from a Difunctional PnBuA Macroinitiator Which Has Been Polymerized in the Presence of a Slight Excess of SG1, at 120 °C in Bulk

	first PBuA block			synthesis of PS blocks						
expt	SG1 (equiv)[a]	M_n[b] (g/mol)	I[c]	time (h)	ρ[d] (%)	$M_{n,\mathrm{targeted}}$ (g/mol)	M_n[b] (g/mol)	$M_{n,\mathrm{LS}}$[e] (g/mol)	I[c]	PS[f] (%)
D1	1	51 700	1.40	0.25	20	172 000	59 700	66 800	1.40	33
D2	0.1	52 400	1.43	0.25	15	200 000	62 100	69 500	1.40	30
D3	*0.05*	*144 100*	*1.66*	*5.75*	*76*	*200 000*	*162 100*	*181 400*	*2.70*	*24*
D4	0.02	87 700	1.58	0.25	10	200 000	100 000	111 900	1.60	26
D6	0.115	72 000	1.23	0.25	10	380 000	85 100	95 200	1.36	32
				0.5	18		99 500	111 300	1.43	44
				1	31		131 500	147 100	1.47	55

[a] Excess of SG1 in molar equivalents per active center. [b] Number-average molar mass measured by size exclusion chromatography with a refractometric detection using THF as eluent. [c] Polydispersity index from SEC. [d] Dry extract from gravimetry measurement. [e] Number-average molar mass measured by SEC with light scattering detection using THF as eluent, the d*n*/d*c* being deduced from the copolymer composition (d*n*/d*c*(PS) = 0.182 and d*n*/d*c*(PnBuA) = 0.057). [f] Composition of the copolymer measured by proton nucleic magnetic resonance (^{1}H NMR). [g] Sample obtained at high conversion in styrene and therefore ill-defined.

tion of styrene are present in the sample, which corresponds to 30% conversion of styrene.

Characterization of the same triblock copolymer sample by differential scanning calorimetry (DSC) (sample C6, Table 4) indicates that it underwent microphase separation as revealed by the two glass transition temperatures (T_g) measured: $T_{g,\mathrm{PnBuA\ block}} = -45$ °C and $T_{g,\mathrm{PS\ blocks}} = 70$ °C (PS = 55%). The study of their mechanical properties is underway.

Conclusion

Although it entailed the use of SG1 in slight excess (5%), DiF−SG1 was found to be an excellent difunctional initiator for the SG1-controlled polymerization of styrene and *n*-butyl acrylate. Provided the polymerization is discontinued before complete conversion, homopolymer samples of controlled size and narrow molar mass distribution could be obtained.

Likewise, well-defined PS-*b*-P*n*BuA-*b*-PS triblock copolymers that contained 20−30% of PS could be generated upon discontinuing the polymerization of styrene at moderate conversion (40%).

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