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Articles

Novel Styrene−Butadiene Copolymers by Ring-Opening Metathesis Polymerization

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ABSTRACT: The possibilities offered by the ring-opening metathesis polymerization (ROMP) of macromonomers were exploited to arrange polystyrene (PS) and polybutadiene (PB) subchains in various topologies. PS_n-*b*-PB_m and PS_n-*co*-PB_m miktoarm stars were obtained by sequential and statistical polymerization of norbornene-terminated PS and PB macromonomers, whereas (PS-*b*-PB)$_n$ star block copolymers were derived by homopolymerization of the corresponding macromonomers via ROMP. Umbrella-type and dumbbell-shaped copolymers are two other architectures that were prepared through the sequential ROMP of ω-norbornenyl PS macromonomer and cyclooctadiene.

Introduction

Block copolymers with a nonlinear and asymmetric architecture attract nowadays much interest that is fueled by the synthetic challenges as well as the scope of novel applications. For instance, features such as the phase diagram, the morphology of the microphases formed and their stability, and the order−disorder transition temperature are known to be totally different for linear and branched block copolymers.[1−3] In a parallel effort to theoretical studies that were meant to describe the solution and bulk properties of these nonlinear block copolymers, synthetic methods have been developed to meet with the growing demand for well-defined samples with such characteristics. Even more than for their linear homologues, the combination of anionic polymerization with the deactivation of living ends by multifunctional chlorosilane reagents proved to be the most efficient synthetic methodology for this class of chemically and topologically asymmetric copolymers. By far, Hadjichristidis and co-workers have contributed the most to this approach, producing branched copolymers of unprecedented topology and precise molecular control.[4] A_nB_n miktoarm stars and ABC miktoarm star terpolymers are two examples of asymmetric block architectures that were synthesized by this team. Other contributions by Hadjichristidis and co-workers include H- and super H-type as well as π-type copolymers.[5,6] Using either the same kind of chemistry or a slightly different approach, other investigators have also looked into the possibilities of deriving branched block copolymers.[7−9]

In an effort to explore other chemistries to engineer original polymeric architectures, we recently resorted to the ring-opening metathesis polymerization (ROMP) of macromonomers, taking advantage of the robust and living character of ROMP. Through the homopolymerization of miscellaneous macromonomers or via their copolymerization—either sequentially or randomly—with other comonomers, structures exhibiting low conformational entropy and high compactness could be derived. Each macromonomer that was polymerized introduced one branch point in the polymer product obtained.

Depending upon the degree of polymerization of their backbone and the size of their side chains, polymacromonomers are known to adopt two types of conformation and shape:[10−13] starlike (for those having a small number of arms) or bottle-brush type (as the number of branches increases). The smaller the size of the initial macromonomer, the lower the degree of polymerization at which the resulting polymacromonomer changes its conformation from star to bottle-brush. For instance, star-shaped Janus macromolecules could be synthesized by restricting the sequential ring-opening metathesis (ROM) copolymerization of PEO and PS macromonomers to a low degree of polymerization ($\overline{DP}_n$) whereas bottle-brush conformations could be obtained from the ROMP of certain macromonomers to a high $\overline{DP}_n$.

The purpose of this paper is to look into the possibilities offered by ROMP to engineer polystyrene (PS)/polybutadiene (PB) based architectures into different topologies. Precisely, we wish to report on the synthesis of PS_n-*b*-PB_m (**1**) and PS_n-*co*-PB_m (**2**) starlike copolymers that were respectively obtained by sequential and random ROM copolymerizations of PS and PB macromonomers carried out to low $\overline{DP}_n$'s. Differing in the topology of their arms from the previous architectures **1** and **2**, (PS-*b*-PB)$_n$ (**3**, **4**) star block copolymers were synthesized by ROMP of macromonomers that were actually diblock copolymers of PS and PB.

In addition to the synthesis of these starlike architectures, other topological arrangements of PS and PB

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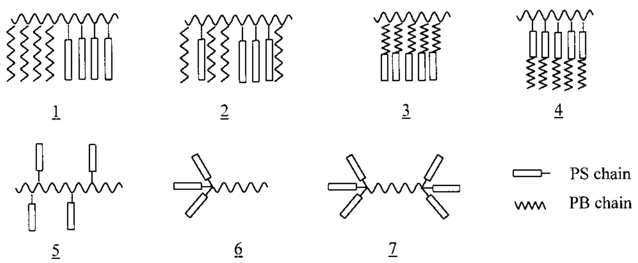

subchains were also targeted: mere PB-*g*-PS (**5**) graft copolymers could be prepared by random copolymerization of PS macromonomers with cyclooctadiene, whereas (PS)$_n$-*b*-PB (**6**) umbrella-type and (PS)$_n$-*b*-PB-*b*-(PS)$_m$ (**7**) dumbbell-shaped copolymers were derived from the sequential copolymerization of the two same entities.

In contrast to the Hadjichristidis methodology that affords precision polymeric architectures through the deactivation of living polymers by chlorosilane agents, the ring-opening metathesis polymerization—or copolymerization—of macromonomers does involves some variation in size, composition, and topology. On the other hand, the ROMP reactions are easier to carry out than the previously mentioned anionic method of Hadjichristidis. This paper discusses the conditions to minimize the variations mentioned.

Results and Discussions

In a recent addition to the field of polymacromonomers, we demonstrated that macromonomers carrying a terminal norbornene unsaturation could be polymerized under living conditions via ROMP, using Schrock's molybdenum-based initiators.[14–16] As a consequence, macromonomers could be thoroughly consumed and converted to polymacromonomers of precise size, in contrast to the synthetic difficulties associated with other chain addition processes. The choice of norbornene as the polymerizing entity in these macromonomers is of paramount importance: owing to the high ring strain of the terminal norbornene group and the unreactive character of the in-chain double bonds formed upon ring-opening polymerization, the corresponding macromonomers could be polymerized under 'living' conditions.

All the macromonomers used in this study were prepared via anionic pathways and were end-capped with a norbornene unsaturation. The recourse to living anionic polymerization to obtain macromonomers can indeed secure controlled molar masses, polydispersity indices close to 1, and high functionalization yield, provided the synthetic scheme is well designed. In the following section, the synthesis of α- and ω-norbornene terminated PS-*b*-PB blocks macromonomers is described in more detail. As to α-norbornenyl PS and ω-norbornenyl PB macromonomers, they were synthesized in a fashion similar to that reported in previous communications.[17,18]

In this work, the PB macromonomers that we intended to copolymerize either sequentially or randomly contained reactive double bonds of *cis*-1,4, *trans*-1,4, and 1,2-vinyl types. Both types of unsaturation are known to undergo metathesis processes in the presence of metal−alkylidene complexes. However, in a previous contribution[18] devoted to the ROMP of polybutadiene macromonomers, we showed that Mo(NAr)(CHtBu)(OtBu)$_2$ is a catalyst that is selective enough to only react with the macromonomer norbornene unsaturation, triggering its ring-opening polymerization without reacting with the acyclic internal double bonds of the PB chains. It is only above 90% conversion of macromonomer that some degradation was observed due to the reaction of growing metal−alkylidene species with the acyclic double bonds. The experimental conditions to polymerize macromonomers of PB to high conversion under controlled conditions appear to have been achieved.

Table 1. Characteristics of PS$_n$-*b*-PB$_m$ Miktoarm Stars

PS/PB/ init. ratio	PB content expected (% w,w)	$\bar{M}_n$^{a} targeted (g/mol)	($\delta n/\delta c$) expected	($\delta n/\delta c$) measd	$\bar{M}_n$^{b} (LS) (g/mol)	$\bar{M}_w/\bar{M}_n$ (SEC)
25/22.5/1	55	89 100	0.155	0.149	88 200	1.41
10/25/1	77	70 200	0.145	0.142	68 600	1.45
25/10/1	35	62 100	0.168	0.165	87 800	1.32

^{a} $\bar{M}_{n,\mathrm{targeted}} = 1620(\overline{\mathrm{DP}})_{n,\mathrm{PS}}) + 2160(\overline{\mathrm{DP}}_{n,\mathrm{PB}})$. ^{b} Molar masses obtained from SEC equipped with an LS detector.

1. PS$_n$-*b*-PB$_m$ and PS$_n$-*co*-PB$_m$ Miktoarm Starlike Copolymers (1, 2). In this section, we shall be concerned with the synthesis of two types of PS/PB-based miktoarm star copolymers that were respectively obtained by sequential and statistical copolymerization of PS and PB macromonomers. These two types of structures were prepared with the goal of generating materials with different morphologies and properties.

a. PS$_n$-*b*-PB$_m$ Miktoarm Stars (1) by Sequential Polymerization of PS and PB Macromonomers. We recently showed that Janus-type copolymers could be obtained by sequential ROMP of norbornenyl-terminated PS and PEO macromonomers.[19] One of the purposes of the present study is to show that the sequential polymerization of α-norbornenyl-PS and ω-norbornenyl-PB macromonomers can also give rise to Janus-type macromolecules.

Three miktoarm starlike copolymers were thus synthesized by sequential ROMP of PS ($\bar{M}_n$ = 1600 g/mol) and PB ($\bar{M}_n$ = 2200g/mol) macromonomers.

The PS macromonomer was first polymerized using Schrock's alkylidene complex Mo(NAr)(CHtBu)(OtBu)$_2$. After consumption of the PS macromonomer, which was complete within 30 min, its PB homologue was added to the living PS polymacromonomer. After complete conversion of the second macromonomer (about 2 h), a small amount of benzaldehyde was introduced into the reaction medium to deactivate the alkylidene active species via a Wittig-type reaction. Analyses by size exclusion chromatography (SEC) of aliquots withdrawn from the reaction medium prior to the introduction of PB macromonomer and after polymerization of the latter showed that the conversion of both macromonomers was close to unity, regardless of the PS/PB molar ratio used (Table 1). The SEC trace of the last aliquot also showed a marked shift of the copolymer peak toward shorter elution volumes and did not exhibit any broadening, shoulder or side peak that would result from unexpected side reactions. Moreover, the characterization of the resulting copolymers by ^{1}H NMR showed excellent agreement between the PS/PB composition in the copolymer and that in the initial mixture. For the determination of the actual molar masses of these copolymers, laser light scattering (LS) was utilized. Refractive index increments for the copolymer solutions were obtained by classical methods and compared with values calculated assuming additivity of the two components (Table 1). Good agreement is observed

Table 2. Characteristics of PB_n-*co*-PS_m Miktoarm Stars

PS/PB/init. ratio	PB content expected (% w,w)	$\bar{M}_n$[a] targeted (g/mol)	$(\delta n/\delta c)$ expected	$(\delta n/\delta c)$ measd	$\bar{M}_n$[b] (LS) (g/mol)	$\bar{M}_w/\bar{M}_n$ (SEC)
25/25/1	57	95 000	0.156	0.153	96 300	1.61
25/10/1	35	62 000	0.169	0.169	61 000	1.44
10/25/1	77	71 000	0.149	0.144	57 800	1.36

[a] $\bar{M}_{n,\ \mathrm{targeted}} = 1600(\overline{DP}_{n,PS}) + 2200(\overline{DP}_{n,PB})$ [b] Molar masses obtained from SEC equipped with an LS detector

between the expected and measured refractive index increments. This finding, coupled with the excellent correspondence between the experimentally measured and targeted molar masses, suggest that these miktoarm starlike copolymers exhibit little compositional heterogeneity.

b. PS_n-*co*-PB_m Miktoarm Stars (2) by Statistical Polymerization of Norbornenyl PS and PB Macromonomers. Three copolymers, corresponding to various molar ratios of PB ($\bar{M}_n = 2200$ g/mol) and PS ($\bar{M}_n = 1600$ g/mol) macromonomers, were synthesized by statistical copolymerization. The two macromonomers were first mixed together in toluene and subsequently added to the Schrock alkylidene complex Mo(NAr)(CHtBu)-$(OtBu)_2$. After 10 min of reaction, benzaldehyde was added to the reaction medium to quench the growing active species. For the three copolymerization experiments, complete conversion of both PS and PB macromonomers was achieved, as confirmed by SEC analyses using UV and RI detectors. The SEC traces exhibited narrow and symmetrical molar mass distributions. The polymacromonomer samples were also analyzed by SEC equipped with an LS detector: the molar masses obtained were found to be in good agreement with the targeted values (Table 2).

We could not precisely know whether the copolymerization occurred randomly or exhibited a tendency for blockiness, since we did not monitor the consumption of the two macromonomers as a function of time. However, differential scanning calorimetry (DSC) characterization of the sample corresponding to 70 (PS)/30 (PB) weight composition by (determined by NMR) gave a single glass transition temperature (T_g = 40 °C), indicating that the copolymer was not blocky in nature. Since the miktoarm starlike copolymer did not exhibit evidence of phase separation, we conclude that the distribution of the two macromonomers is random. PS and PB chains of such a short size are indeed known to be miscible.[20] Interestingly, the sample that was obtained by sequential copolymerization of the two same macromonomers exhibited, for the same nominal PS/PB composition, three glass transition temperatures (−94, +58, +100 °C), reflecting the existence of three discrete mesophases. This result demonstrates the influence of the topology of PS and PB arms to the occurrence of phase separation in these miktoarm star copolymers.

2. Block Copolymers with a Starlike Structure (3, 4). Stars whose arms are block copolymers were first obtained by deactivation of living anionic ends with a stoichiometric amount of an appropriate multifunctional chlorosilane. Living $(PI\text{-}b\text{-}PS)^-Li^+$ diblock was reacted with $SiCl_4$ to generate tetraarm star block copolymers.[21] Even though star-shaped polymers can be synthesized through ROMP of macromonomers to low $\overline{DP}_n$'s, the resulting materials are not expected to exhibit a precise number of arms, unlike those derived by the previously described methodology. Notwithstanding this minor limitation, the macromonomer technique has advantages such as the possibility to polymerize a range of unsaturated species, including block copolymers. Provided the starting block copolymer is end-capped with norbornenyl unsaturation, star-shaped block copolymers can be obtained by ROMP.

a. Synthesis of α- and ω-Norbornenyl (PS-*b*-PB) Macromonomers by Means of Anionic Polymerization. PS-*b*-PB macromonomers were prepared by sequential anionic polymerization of styrene and butadiene following two different pathways. Because of the higher electroaffinity of butadiene, styrene was polymerized first in the two synthetic schemes.

The first route is based on the deactivation of growing polybutadienyl anions by 5-carbonyl chloride bicyclo [2.2.1] hept-2-ene (Scheme 1a). The second route made use of a norbornene-based anionic initiator, namely 5-lithiomethyl bicyclo [2.2.1] hept-2-ene (Scheme 1b).

The macromonomers synthesized by these two pathways exhibit different 1,2-vinyl contents. Route a—corresponding to ω-norbornenyl macromonomers—afforded samples with low 1,2-vinyl content (15%) while route b—α-norbornenyl macromonomers—gave rise to samples with up to 53% of 1,2-vinyl content because it included the use of a higher dielectric constant solvent,[22] ether.

PS-*b*-PB diblock macromonomers fitted with a terminal norbornenyl entity either through their PS or their PB block were derived in this way. Three macromonomers with different proportions of the two blocks were thus synthesized and their characteristics are shown in Table 3.

Their actual molar masses were measured using ^{1}H NMR (Figures 1 and 2) and laser light scattering. The relatively good agreement observed between calculated and experimental refractive index increments, associated with a rather good correspondence between experimental molar masses obtained by ^{1}H NMR and LS, suggests that the samples are homogeneous in composition. These results demonstrate that the various reactions that are shown in the synthetic schemes occurred as expected with no detectable side reactions.

b. Homopolymerization of α- and ω-(PS-*b*-PB) Macromonomers. A first series of polymerizations was carried out using the ω-norbornenyl (PS-*b*-PB) macromonomer that was characterized by a molar mass of 5200 g/mol and a low content of 1,2-vinyl unsaturations (*p*, which represents the ratio of the concentration of 1,2-vinyl unsaturation to that of norbornenyl unsaturation being equal to 6). The samples obtained were analyzed by SEC equipped with a LS detector. As shown in Table 4, the experimental molar masses are in good agreement with the targeted values.

As in the case of ω-norbornenyl PB macromonomer, the polymerization could be taken to 90% conversion without detecting any side reactions, regardless of the $\overline{DP}_n$ targeted. Since the content of 1,2 vinyl groups was low in these macromonomers, the growing metallaalkylidene species had little opportunity to react with these acyclic unsaturations.

The second part of this study, devoted to the ROMP of macromonomers was concerned with the homopolymerization of α-norbornenyl (PS-*b*-PB) macromonomers; the latter species exhibited a molar mass of 4200 g/mol

Scheme 1. Synthesis of (b) α-norbornenyl and (a) ω-norbornenyl PS-b-PB Macromonomers

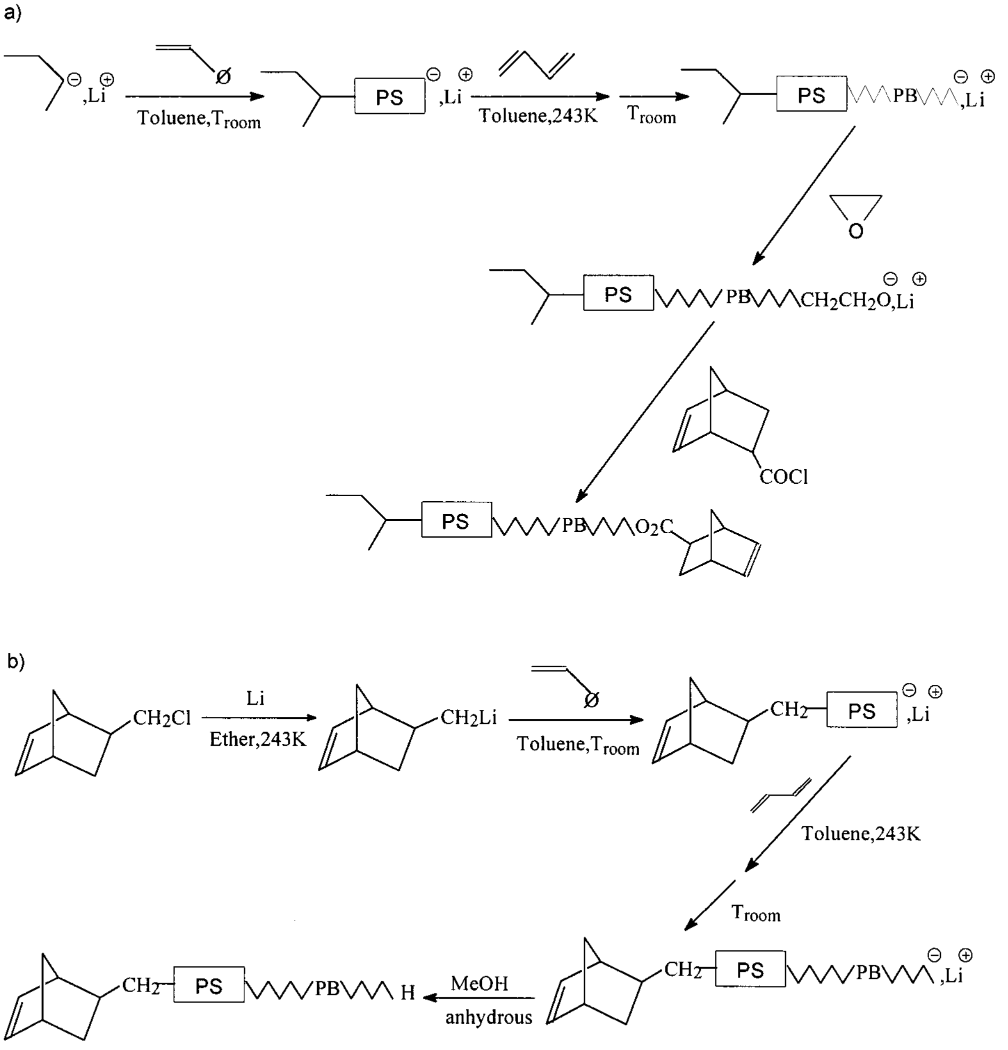

Table 3. Characteristics of Norbornene-Terminated (PS-*b*-PB) Macromonomers

macromonomer	PS/PB targeted (%w/w)	$\bar{M}_n$ targeted (g/mol)	$\bar{M}_n$ ^{1}H NMR (g/mol)	% 1,2^b/p^c	PS/PB measd^d (%w/w)	($\delta n/\delta c$) expt	($\delta n/\delta c$) measd	$\bar{M}_n$ LS^e (g/mol)	$\bar{M}_w/\bar{M}_n$ (SEC)
ω-^{a}	50/50	6300	5200	13/6	51/49	0.159	0.151	5800	1.03
α-	50/50	4700	4200	46/16	53/47	0.159	0.152	5500	1.18
	20/80	4700	3100	53/25	17/83	0.140	0.135	3400	1.05

[a] 100% functionalization as determined by ^{1}H NMR by taking the ratio of the signal due to the protons of the initiator fragment (*sec*-BuLi, $\delta = 0.9$ ppm) to that arising from ethylenic protons of norbornene unit ($\delta = 5.8-6.2$ ppm) (see Figure 1). [b] Percent of 1,2-unsaturations determined by ^{1}H NMR. [c] p: ratio of the concentration of 1,2-vinyl double bonds to that of norbornenyl unsaturations. [d] Determined by ^{1}H NMR. [e] Determined by SEC equipped with a laser light scattering (LS) detector.

and a higher value of p—equal to 16—as compared to their ω-norbornenyl homologues (Table 3).

As shown in Table 5, the experimental molar masses of the (PS-*b*-PB)$_n$ samples obtained generally exhibited good agreement with the targeted values, with any difference between two sets of data likely due to the lack of precision in the amount of initiator actually introduced. On the other hand, we observed that this (PS-*b*-PB) macromonomer could be polymerized to high conversion (~90%), unlike its α-norbornenyl PB homologue ($\bar{M}_n = 6900$ g/mol, $p = 15$) whose ROMP did not exceed 80% conversion because of chain transfer and chain scission reactions.[18] Of note, a difference was observed in the evolution of the two reaction media as a function of time. In the case of PB macromonomers with high vinyl content, the resulting polymacromonomer was found to undergo substantial degradation over the course of the reaction,[18] its trace in the SEC chromatogram decreased steadily in favor of a broad distribution of low molar mass species. The higher the 1,2-vinyl content in the PB macromonomer, the more pronounced the degradation of the PB polymacromonomer. Unlike the previous case, the polymacromonomer obtained from α-norbornenyl (PS-*b*-PB) block copolymers did not undergo any detectable degradation with time as shown in Figure 3, although its $\overline{DP}_n$ and vinyl content were approximately the same as those of its PB homologues. The presence of a PS block between the polymerizing unsaturation and the PB block may account for this result.

To better demonstrate the *protecting* role played by the PS block, a second series of experiments was carried out using α-norbornenyl (PS-*b*-PB) macromonomers

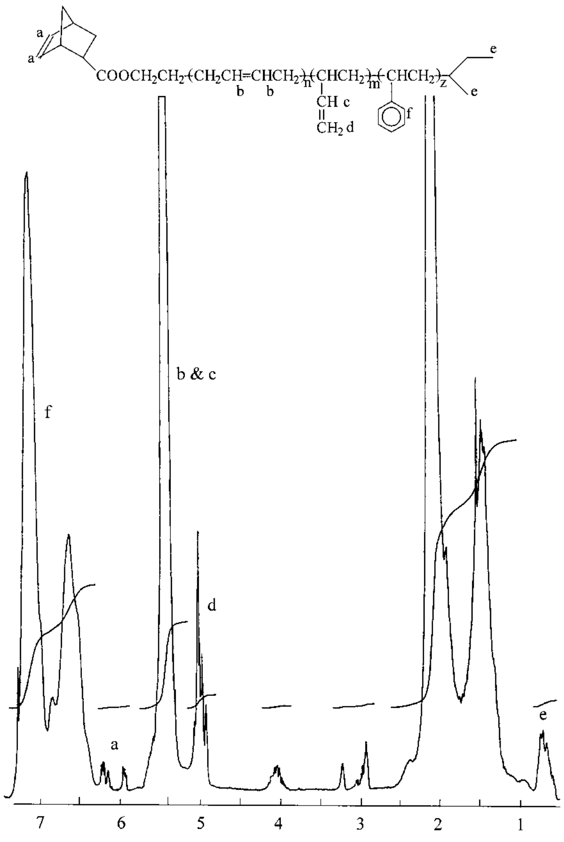

Figure 1. ^{1}H NMR spectrum of a ω-norbornenyl (PS-*b*-PB) macromonomer in CDCl3 ($\overline{M}_n$ = 5200 g/mol).

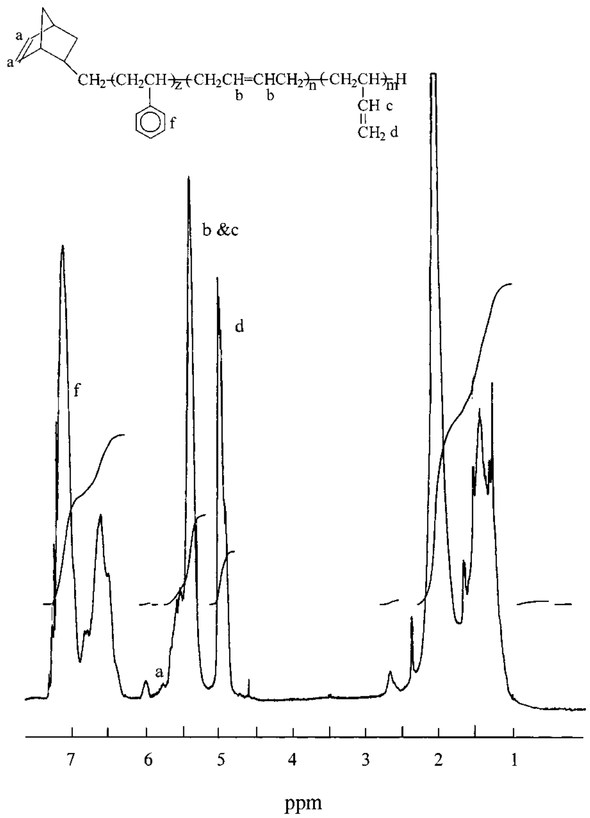

Figure 2. ^{1}H NMR spectrum of a α-norbornenyl (PS-*b*-PB) macromonomer in CDCl3 ($\overline{M}_n$ = 4200 g/mol).

Table 4. Characteristics of (PS-*b*-PB)$_n$ Star Block Copolymer Obtained from ω-Norbornenyl (PS-*b*-PB) Macromonomer of 5200 g/mol Molar Mass and *p* Equal to 6

$\overline{DP}_n$ targeted	convn^a (%)	$\overline{M}_n \times 10^3$ targeted^b (g/mol)	$\overline{M}_n \times 10^3$ expt^c (g/mol)	$\overline{M}_w/\overline{M}_n$ (SEC)
10	86	44.7	46.1	1.24
25	88	114	75.7	1.40
50	92	239	184	1.38

[a] Conversion determined by SEC equipped with a RI detector. [b] $\overline{M}_{n,\text{targeted}} = \overline{M}_{n,\text{macro}} \times \overline{DP}_n \times$ conversion. [c] $\overline{M}_{n,\text{expt}} = \overline{M}_{w,LS}/I_{SEC-RI}$ where $\overline{M}_{w,LS}$ is the molar mass obtained from SEC equipped with a laser light scattering (LS) detector and *I* is the polydispersity index given by SEC equipped with a RI detector.

Table 5. Characteristics of (PB-*b*-PS)$_n$ Star Block Copolymers Obtained from a α-Norbornenyl (PS-*b*-PB) Macromonomer of 4200 g/mol Molar Mass and *p*^{d} Equal to 16

$\overline{DP}_n$ targeted	convn^a (%)	$\overline{M}_n \times 10^3$ targeted^b (g/mol)	$\overline{M}_n \times 10^3$ expt^c (g/mol)	$\overline{M}_w/\overline{M}_n$ (SEC)
10	89	37.4	41.9	1.39
25	87	91.4	84.3	1.36
50	87	183	124	1.36

[a] Conversion determined by SEC equipped with a RI detector. [b] $\overline{M}_{n\text{targeted}} = \overline{M}_{n\text{macro}} \times \overline{DP}_n \times$ conversion. [c] $\overline{M}_{n,\text{exp}} = \overline{M}_{w,LS}/I_{SEC-RI}$ where $\overline{M}_{w,LS}$ is the molar mass obtained from SEC equipped with a laser light scattering (LS) detector and *I* is the polydispersity index given by SEC equipped with a RI detector. [d] *p*: ratio of the concentration of 1,2-vinyl double bonds to that of norbornenyl unsaturations.

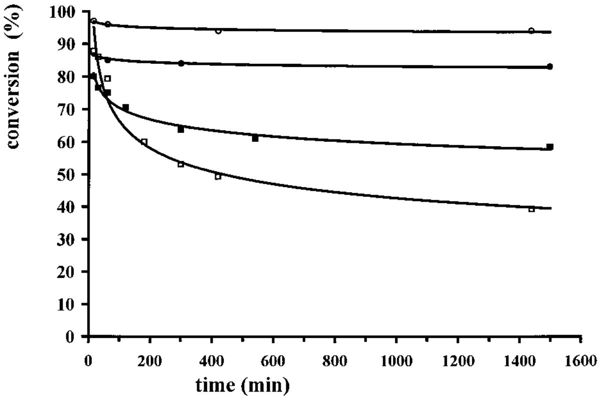

Figure 3. Degradation as a function of time of polymacromonomers obtained from α-norbornenyl-(PS-*b*-PB) of $\overline{M}_n$ = 4200 g/mol and *p* = 16 (●) and $\overline{M}_n$ = 3100 g/mol and *p* = 25 (○) compared with the behavior of polymacromonomers obtained from norbornenyl−PB of *p* = 17 (■) and *p* = 20 (□).

characterized by a PS block ($\overline{DP}_n$ = 5) of very short size and a large value of *p*—equal to 25—(Table 6). Despite a high 1,2-vinyl content, the ROMP of these macromonomers could be taken nearly to completion, in contrast to 75−80% conversion obtained for pure PB macromonomers of similar 1,2-vinyl content.[18] As shown in Figure 3, no degradation of the (PS-*b*-PB)$_n$ polymacromonomer with time was observed. Thus, even a PS segment of very short size between the polynorbornene backbone and the PB side block can help to prevent side reactions, resulting from the presence of 1,2-vinyl unsaturation, from occurring.

3. Synthesis of PB-*g*-PS Graft Copolymers, (PS)$_m$-*b*-PB Umbrella-like and (PS)$_n$-*b*-PB-*b*-(PS)$_m$ Dumbbell-Shaped Copolymers (5−7). Umbrella-like or dumbbell shaped architectures were obtained by statistical (**5**) or sequential (**6**, **7**) copolymerization of a ω-norbornenyl−PS macromonomer ($\overline{M}_n$ = 2700 g/mol)

Table 6. Characteristics of (PB-*b*-PS)$_n$ Star Block Copolymers Obtained from a α-norbornenyl (PS-*b*-PB) Macromonomer of 3100 g/mol Molar Mass and p Equal to 25

$\overline{DP}_n$ targeted	convn[a] (%)	$\bar{M}_n \times 10^3$ targeted[b] (g/mol)	$\bar{M}_n \times 10^3$ expt[c] (g/mol)	$\bar{M}_w/\bar{M}_n$ (SEC)
10	96	30	36	1.15
25	97	75	67	1.24
50	97	150	98	1.32

[a] Conversion determined by SEC equipped with a RI detector. [b] $\overline{M}_{n\text{targeted}} = \underline{\overline{M}}_{n\text{macro}} \times \overline{DP}_n \times$ conversion. [c] $\bar{M}_{n,\text{expt}} = \bar{M}_{w,\text{LS}}/I_{\text{SEC-RI}}$ where $\bar{M}_{w,\text{LS}}$ is the molar mass obtained from SEC equipped with a laser light scattering (LS) detector and *I* is the polydispersity index given by SEC equipped with a RI detector. p: ratio of the concentration of 1,2-vinyl double bonds to that of norbornenyl unsaturations

Table 7. Characteristics of PB-*g*-PS Graft Copolymers

PS/COD/I ratio	% PB expected	% PB ^{1}H NMR	$\bar{M}_n \times 10^3$ SEC	$(\delta n/\delta c)$ expected	$\bar{M}_n \times 10^3$ targeted	$\bar{M}_w \times 10^3$ (LS)
11/630/1	69	63	48	0.153	98	107
22/626/1	52	43	59	0.179	127	94

with a molecular monomer, namely cyclooctadiene (COD). Because of the lower reactivity of COD compared with that of the norbornenyl unsaturation carried by the macromonomer, the fluorinated Schrock complex $Mo(NAr)(OCH(CF_3)_2CH_3)_2(CHtBu)$ was found to be an appropriate catalyst for this series of experiments. Since the reactivity of this complex was high—it can indeed provoke metathesis reactions with the acyclic unsaturation of the PB backbone—it was necessary to work with high initial COD concentration and quench the polymerization prior to complete conversion.[23]

a. PB-*g*-PS Graft Copolymers by Statistical Copolymerization of *ω*-Norbornenyl PS Macromonomer with COD (5). The ROM copolymerization of PS macromonomers with COD is expected to produce graft copolymers with PS as side chains and 1,4-PB as the backbone. The number of branches per chain depends on the feed ratio and the relative reactivity of two reactants. Studies reported so far[24] on the reactivity of macromonomers show that reactivity is affected by their lack of compatibility with the growing backbone. In the present study, the copolymerization of these two entities should not be influenced by the compatibility factor because of the small size of the PS macromonomer.

Two copolymers were actually synthesized by statistical ROMP of PS macromonomer ($\bar{M}_n = 2700$ g/mol) and COD (Table 7). Both PS macromonomer and COD were completely consumed within 3 min. The good agreement between the actual composition (checked by NMR) and the expected one and the excellent match between the polymacromonomer molar masses and the targeted values indicate that these graft copolymer samples exhibited little heterogeneity in composition, despite the likely large difference between the reactivities of norbornenyl unsaturation and COD.

b. (PS)$_n$-*b*-PB Umbrella-like Copolymers by Sequential Polymerization of *ω*-Norbornenyl PS Macromonomer and COD (6). The so-called umbrella-like copolymers consist of an arrangement of *n* B blocks with one A block of much larger size in a miktoarm star architecture. For instance, in the samples prepared by Wang et al.[25] several branches of PB were associated with only one large block of PS through the deactivation (coupling) of living anionic PB ends onto chlorosilane-terminated PS chains.

In the present work, it is shown that sequential ROMP of norbornenyl macromonomers and an appropriately chosen cycloolefin is also an elegant means to derive umbrella-like star copolymers. Four umbrella—star copolymers were thus prepared by sequential polymerization of PS macromonomers and COD (Table 8). In a first series of experiments (Table 8, entries 1 and 2), a PS macromonomer of 2700 g/mol was used. In a toluene solution containing the same Schrock complex as the one previously mentioned, this macromonomer was polymerized to complete conversion within 1 h as indicated by SEC characterization of the medium aliquot. COD was then added to the living medium. After a few minutes of reaction, a small amount of benzaldehyde was introduced in the reaction medium to deactivate the growing metal—alkylidene species. Analyses of the reaction medium by SEC and gas chromatography prior to the introduction of COD and after polymerization of the latter showed that the conversion of PS macromonomer was close to unity before addition of COD, and that the conversion of COD was complete. The SEC chromatogram of the final aliquot indeed showed a shift toward smaller elution volumes, as compared with that of the previous sampling. As to the distribution of molar masses of these umbrella-like copolymers, they were rather large, reflecting the slow initiation rate of COD by the living metal—alkylidene species carried by PS macromonomers. However, the polydispersity of these samples could be marginally narrowed (entry 2) through the dropwise addition of COD instead of introducing the cyclo-olefin (entry 1) at once. The use of macromonomers of larger size ($\bar{M}_n$ = 11 000 g/mol; Table 8, entry 3) in these sequential polymerizations resulted in ill-defined samples (bimodal distribution) with a nonnegligible proportion of PS polymacromonomer that was found to be unable to initiate the polymerization of COD and that remained unreacted. Similar results, namely bimodal distribution and incomplete conversion, were obtained upon modifying the order of addition of the reactants and polymerizing COD first.

To obtain umbrella-like copolymers with a monomodal distribution and controlled molar masses, it is therefore essential to first polymerize the macromonomer and then slowly add COD.

c. (PS)$_n$-*b*-PB-*b*-(PS)$_m$ Dumbbell-Shaped Polymers by Two Successive Polymerizations of Macromonomers between That of COD (7). Dumbbell-shaped copolymers can be viewed as double stars that are linked through a linear block; they were obtained using living umbrella stars to initiate the polymerization of *ω*-norbornenyl PS macromonomers.

The synthesis of these dumbbell-shaped copolymers thus involved first the polymerization of PS macromonomer followed by the addition and polymerization of COD and subsequent addition and polymerization of PS macromonomer (entry 4, Table 8).

To avoid possible redistribution reactions as the conversion of COD neared completion, the second addition of PS macromonomer was made before the molecular cyclo-olefin was totally consumed. Under these experimental conditions, the SEC chromatograms of the three aliquots, corresponding respectively to the PS polymacromonomer, the PB-*b*-(PS)$_m$ umbrella-like star, and the resulting (PS)$_n$-*b*-PB-*b*-(PS)$_m$ dumbbell-

Table 8. Characteristics of $(PS)_n$-*b*-PB Umbrella-Type and $(PS)_n$-*b*-PB-*b*-$(PS)_m$ Dumbbell-Shaped Copolymers

entry no.	$\bar{M}_{n,macro.PS}$ (g/mol) SEC	% PB targeted	% PB NMR	$\bar{M}_n \times 10^3$ targeted (g/mol)	$\bar{M}_n \times 10^3$ SEC (g/mol)	$\bar{M}_w/\bar{M}_n$ SEC	t (min)	convn (%)	$\bar{M}_n$ calcd NMR
1	2700	0		68	35	1.3	60	100	
		80		230	65	1.9	10	99	
2	2700	0	0	67	34	1.35	60	100	
		67	60	203	67	1.7	10	99	167 500
3	11000	0	0	67	66	1.2	60	100	
		67	60	203	100	1.7[a]	10	99	167 500
4	2700	0	0	64	23	1.3	30	100	
		66	40	188	31	1.7	10	99	106700
		47	40	264	39	1.4	30	100	310000

[a] Bimodal distribution.

shaped copolymer, exhibited symmetrical traces, each of them being shifted toward lower elution volumes as compared with the previous ones. This indicates that initiation of each of these sequential polymerizations occurred quantitatively. Given the rather large polydispersity indices exhibited by these umbrella-like stars as well as by the dumbbell-shaped copolymers, no attempt was made to characterize these architectures by SEC equipped with an LS detector. Owing to their heterogeneity in composition, we did not consider it meaningful to determine the molar masses of these samples by this technique and compare them with the targeted values. Rather, we chose to rely on NMR to evaluate the $\bar{M}_n$ of these samples, knowing that of their precursors. By this method of characterization, a rather good agreement between expected and actual values of molar masses could indeed be obtained for all samples.

Conclusions

This paper explores a novel route toward the synthesis of various styrene/butadiene based copolymer architectures. Through ROMP of the appropriate macromonomers, miktoarm stars, and star block copolymers could be derived with little heterogeneity in size, composition and number of arms. Even though this methodology is not suited to generate precision architectures, it appears to be an interesting alternative to other reported synthetic strategies such as the combination of anionic polymerization and deactivation by chlorosilanes. The versatility of ROMP was further used to engineer umbrella-like and dumbbell-shaped architectures whose structures, however, were found to be less precisely defined than the previous structures.

Experimental Part

Materials. 1,3-Butadiene (Aldrich, purity 99%) was stirred over *sec*-BuLi (Janssen Chemica, 1.3 M in cyclohexane) at −30 °C for 3 h and subsequently cryodistilled prior to use.

Methanol was dried over $MgSO_4$ and distilled over Mg/I_2 after filtration.

Styrene was distilled and stored over CaH_2 and cryodistilled prior to use.

Undecane and cyclooctadiene were dried over CaH_2 before being cryodistilled over Na prior to use.

Ethylene oxide was cryodistilled after being stirred over sodium at −30 °C for 3 h.

Toluene was dried over polystyryllithium and then cryodistilled.

5-Carbonyl chloride bicyclo[2.2.1]hept-2-ene, 5-chloromethyl bicyclo[2.2.1]hept-2-ene,[17] and $Mo(NAr)(CHC(CH_3)_2Ph)(OtBu)_2$[26] were synthesized according to literature methods.

sec-BuLi and lithium (Aldrich, ~30 wt % dispersion in mineral oil) were used without further purification.

α- and ω-norbornenyl PS and ω-norbornenyl PB were prepared according to procedures described in previous papers.[15,17,18]

Methods. All reagents were stored and used under an inert atmosphere of nitrogen.

All anionic polymerizations were carried out under a slight nitrogen overpressure using a glass reactor equipped with a nitrogen inlet, magnetic stirring bar, sampling device, and burets designed to introduce solvent, initiator, monomers, and deactivator.

All macromonomers were dried under high vacuum before their polymerization.

All ring-opening metathesis polymerizations were carried out in a glovebox under moisture-free conditions at room temperature. ^1H NMR spectra were obtained using a Brucker AC200 spectrometer.

The size exclusion chromatography (SEC) equipment consisted of a JASCO HPLC pump type 880-PU, TOSOHAAS TSK gel columns, a Varian refractive index (RI) detector, and a JASCO 875 UV/vis absorption detector, with THF being the mobile phase. The columns were calibrated with narrow polystyrene standards. The actual molar masses of polymacromonomer samples were calculated from the response of the multiangle laser light scattering detector (Wyatt Technology) that was interfaced with the SEC.

DSC traces were obtained with a Perkin-Elmer DSC7 calorimeter equipped with a Perkin-Elmer TAC 7/DX thermal analysis controller or a Mettler DSC30 calorimeter equipped with a Mettler TC10A processor and a TA3000 thermal analysis controller. Samples were heated at a heating rate of 10 °C/min.

Synthesis of ω-Norbornenyl (PS-*b*-PB) Macromonomer ($\bar{M}_n$ = 6300 g/mol Targeted). In a typical reaction, 150 mL of toluene was cryodistilled in a three-neck flask equipped with a magnetic stir bar. *sec*-BuLi (2.5 mL, 3.3×10^{-3} mol) was added at once, under N_2, before styrene (12 mL, 0.10 mol). The polymerization was allowed to proceed for 1 h at room temperature before adding, at −30 °C, butadiene (17.6 mL, 0.20 mol). The reaction medium was then allowed to stir overnight at room temperature. After addition of 1 mL of ethylene oxide, 5-carbonyl chloride bicyclo[2.2.1]hept-2-ene (2−3 equiv) was introduced in the medium. The macromonomer was recovered by precipitation in a mixture of anhydrous methanol/pyridine. Two or three additional precipitations in methanol were necessary to remove the excess unreacted 5-carbonyl chloride bicyclo[2.2.1]hept-2-ene.

Synthesis of α-Norbornenyl (PS-*b*-PB) Macromonomer ($\bar{M}_n$ = 4700 g/mol Targeted). About 150 mL of toluene and styrene (11 mL, 9.6×10^{-2} mol) were cryodistilled in a three-neck flask equipped with a magnetic stirring bar. The initiator solution containing 5-lithiomethyl bicyclo[2.2.1]hept-2-ene (10 mL, 4.2×10^{-3} mol) was added at once at −30 °C, after filtration of the residual lithium and salts present. The polymerization was allowed to proceed for 1 h. Butadiene (16.1 mL, 0.19 mol) was added next at −30 °C. The reaction medium was then warmed to room temperature and the polymerization was allowed to proceed overnight. Deactivation of the reaction medium was performed by addition of 3 mL of anhydrous methanol. The solution was then filtered, concentrated and poured into excess methanol to yield the expected macromonomer by precipitation.

Polymerization of α or ω-Norbornenyl (PS-*b*-PB) Macromonomers. A 9.1 μmol sample of initiator, Mo(NAr)(CHtBu)$(OtBu)_2$, was weighed out and introduced into a flask containing 2 mL of toluene. Then 9.1×10^{-5} mol of the appropriate macromonomer was dissolved in 8 mL of toluene and this solution was added to the initiator flask solution under stirring. Deactivation of the medium was performed after 1 h of reaction at room temperature by addition of 0.1 mL of benzaldehyde. Precipitation by methanol yielded the pure polymacromonomer.

Statistical Copolymerization of PB and PS Macromonomers. In a typical experiment, 368 mg (2.27×10^{-4} mol) of PS macromonomer ($\bar{M}_n = 1600$ g/mol) and 499 mg (2.27×10^{-4} mol) of PB macromonomer ($\bar{M}_n = 2200$ g/mol) were dissolved in 8 mL of toluene and then poured into a flask containing 5 mg (9.09×10^{-6} mol) of Mo(NAr)(CHtBu)$(OtBu)_2$ of complex. Deactivation of the reaction medium was performed after 10 min of polymerization at room temperature by addition of 0.1 mL of benzaldehyde. The statistical copolymacromonomer was recovered by precipitation in methanol.

Sequential Copolymerization of PB and PS Macromonomers. In a typical experiment, 368 mg (2.27×10^{-4} mol) of PS macromonomer ($\bar{M}_n = 1620$ g/mol) was first polymerized at room temperature in 10 mL of toluene in the presence of 5 mg (9.09×10^{-6} mol) of Mo(NAr)(CHtBu)$(OtBu)_2$. After 30 min, 491 mg (2.27×10^{-4} mol) of PB macromonomer ($\bar{M}_n = 2160$ g/mol), dissolved in 2 mL of toluene, was introduced into the reaction medium. After polymerizing PB macromonomer for 2 h at room temperature, 0.1 mL of benzaldehyde was added to deactivate the metal−alkylidene species. Precipitation in methanol afforded the expected block copolymacromonomer.

Statistical Copolymerization of PS Macromonomer with COD. In a typical experiment 880 mg (3.2×10^{-4} mol) of PS macromonomer ($\bar{M}_n = 2700$ g/mol) and 2 mL of COD (1.6×10^{-2} mol) were dissolved in 18 mL of toluene and poured into a flask containing 10 mg (1.3×10^{-5} mol) of Mo(NAr)(CHtBu)$(OC(CF_3)_2CH_3)_2$ dissolved in toluene. At the end of the reaction that lasted about 3 min at room temperature, the polymerization (about 3 min) was deactivated by addition of 0.1 mL of benzaldehyde. Aliquots removed from the medium were analyzed by SEC and gas chromatography.

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