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Novel Amphiphilic Architectures by Ring-Opening Metathesis Polymerization of Macromonomers

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ABSTRACT: In this study the possibilities offered by "living" ring-opening metathesis polymerization (ROMP) are exploited to engineer novel macromolecular architectures. It is indeed shown that amphiphilic branched structures of hitherto unreported topologies can be prepared by ROMP of miscellaneous macromonomers, provided the latter polymers carry an end-standing norbornene unsaturation. Janus-type architectures are, for instance, accessible by sequential ROMP of polystyrene (PS) and poly(ethylene oxide) (PEO) macromonomers; other original branched structures, whose topology makes them particularly attractive for applications such as unimolecular micelles or associative thickeners, can be obtained through homopolymerization of macromonomers based on PS-*b*-PEO diblock copolymers.

Introduction

Polymers that contain hydrophilic and hydrophobic components have aroused keen interest both from theoretical and synthetic points of view over the past years. The tendency of the hydrophobic parts to aggregate into micelles in water and also the surface active properties exhibited by such amphiphilic polymers are two features that have been thoroughly investigated and exploited in miscellaneous applications.[1] Indeed, amphiphilic polymers commonly serve as additives for the stabilization or the flocculation of dispersions; they are also used to control the rheology of aqueous formulations.

Because they are less sensitive to the ionic force and give more stable systems, nonionic amphiphilic polymers are preferred, and amongst them poly(ethylene oxide) (PEO)-based block copolymers have gained enormous popularity. All variations of copolymers of ethylene oxide with a hydrophobic component, that could be either styrene, propylene oxide, or an alkyl chain, are now available,[1] each of them being meant for a specific application; these copolymers are obtained by sequential polymerization of the corresponding monomers or by chain-end modification of PEO.

Apart from the synthesis of linear amphiphilic structures, much effort has also been devoted to the design of corresponding branched architectures. Interest in branched arrangements of hydrophilic and hydrophobic components arose with the discovery that the latter structures exhibit a quite different behavior from that observed for linear homologues: for instance, linear amphiphilic polymers tend to aggregate *via* intermolecular interaction and are known to form micelles of lesser stability than the monomolecular micelles that could be obtained with certain branched homologues.[1] It is also well established that branched systems give better surface activity for applications such as the stabilization of dispersions because of their peculiar topology.[1] On the other hand, it is reported that water soluble branched polymers that are fitted with short outer hydrophobic sequences are better viscosity enhancers of aqueous solutions than their linear homologues.[2]

Rempp and co-workers have attempted to synthesize PEO-based graft copolymers, *via* two different routes. They first resorted to the "grafting onto" method, which they implemented through deactivation of "living" PEO chains onto a partially chloromethylated polystyrene (PS) backbone.[3] The same team investigated the macromonomer method, sparing no effort to copolymerize macromonomers of PEO with miscellaneous hydrophobic comonomers.[4] These authors acknowledged that both "grafting onto" and macromonomer techniques require a tedious fractionation step meant to get rid of unreacted PEO chains; they also conceded that graft copolymers obtained in this way exhibit a rather large fluctuation in composition.

Stadler[5] also followed the "grafting onto" methodology to prepare poly(butadiene-*g*-ethylene oxide) copolymers; he therefore faced the same drawback as that mentioned by Rempp, which is the double necessity of using an excess of the polymers to be grafted and of separating them from the copolymer.

Gauthier[6] recently designed an original method to generate the so-called arborescent graft PS−PEO copolymers that combines both the "grafting onto" and the

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"grafting from" techniques. Arborescent PS samples were first obtained by repeated grafting of PS linear chains onto a chloromethylated PS substrate. The PEO corona was grown in a second step from the hydroxyl functions carried by arborescent polystyrenes. Although this experimental procedure was not conceived to afford samples of a controlled degree of branching and low compositional heterogeneity, the copolymers obtained were surprisingly shown to form stable core−shell structures.

Amphiphilic star-shaped polymers and namely heteroarm star copolymers, constituted of PS and PEO arms, have been prepared with the expectation that the star topology would induce some peculiar solution properties.[7] Unfortunately, the lack of compositional and topological homogeneity of these samples was not propitious for thoroughly investigating their solution behavior.

These various examples of amphiphilic branched architectures eloquently show that much remains to be done to diversify the topologies accessible and improve their homogeneity. One major challenge with respect to these long-standing goals would be to design and implement novel methodologies of macromolecular engineering. In a recent addition to the field of star-shaped polymers, one of us put forward a method that enables the synthesis of ω-functionalized polystyrene stars of perfect functionality using a hexafunctional initiator.[8] Amphiphilic star and dendritic copolymers constituted of a precise number of PS and PEO blocks have been obtained by the same principle, through sequential polymerization of the corresponding monomers.[9]

Polymacromonomers (PMs) also represent an important class of branched polymers whose main characteristic is an axisymmetric distribution of branching points around the central backbone contour.[10] In contrast to the case of star polymers, little attention has been given to the synthesis of these regular multibranched systems. One major limitation associated with the homopolymerization of macromonomers is the difficulty of obtaining complete conversion and precise size control of the branched structure formed. We[11−13] recently demonstrated that macromonomers can be polymerized under truly living conditions *via* ring-opening metathesis polymerization. Provided the macromonomers are end-fitted with norbornene unsaturations, regular multibranched polymers of varying compactness and branch number can be prepared, using the fluorinated version of the Schrock molybdenum complex as initiator. The Feast team also attempted to polymerize macromonomers via ring-opening metathesis polymerization (ROMP).[14]

The original results obtained with the homopolymerization of PS[11,12] and PEO[13] macromonomers prompted us to attempt both the sequential and statistical copolymerizations of these two macromonomers. Because of the incompatibility between PEO and PS grafts, very unique morphologies should form: a Janus-type topology with one face of the polymacromonomer covered by the hydrophilic grafts and the other one with the hydrophobic grafts can be foreseen. This technique of polymerization of macromonomers can also be exploited to create other types of amphiphilic topologies. Polymerization of macromonomers that are themselves PS-*b*-PEO block copolymers should result in the formation of compact macromolecular species whose inner parts and outer layers would be chemically different. The synthetic scheme that has been followed to prepare these PS-*b*-PEO macromonomers as well as the results of their ROMP will be described and commented upon.

Results and Discussion

One of the unique features that characterize polymacromonomers (PMs) is the regularity with which branching occurs along the backbone (comblike structure); in the case of polymacromonomers that have a backbone constituted of polynorbornene, the grafts regularly dangle from the backbone every six carbon atoms. The effect of this compact arrangement of grafts on the overall shape of the polymacromonomer in a good solvent has been discussed by Tsukahara et al.[10,15] Polymacromonomers actually behave as rigid spheres whenever the backbone remains short as compared with the size of the side-tethered chains. As the backbone becomes longer and comparable in length to the grafts, the interaction between these grafts contributes to stiffen the backbone and forces the PM to gradually adopt a rodlike bottle brush shape.[16]

As we were mainly interested in generating branched PS−PEO copolymers of high compactness, that would therefore take a globular shape in a good solvent for the two types of chains, we prepared macromonomers of moderate size ($\overline{M}_n$ < 8000 g/mol) and restricted their polymerization to a backbone of short length ($\overline{DP}_n \leq 20$). We indeed intend to compare in a separate paper these polymacromonomers of small $\overline{DP}_n$ and overall globular shape with genuine PEO-*b*-PS stars that are also known to adopt a spherical form.[9] In this paper, we shall essentially focus on the synthetic aspect and namely on the methodology used to prepare and polymerize miscellaneous norbornene-ended macromonomers. The efficiency of ring-opening metathesis as a technique of production of PMs will also be examined in light of the characteristics of the PM obtained.

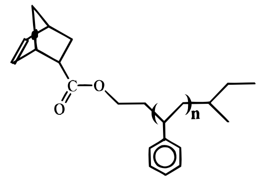
1. Synthesis of Janus-type Polymacromonomers. Polymers that exhibit a globular shape and unsymmetrical external faces are not easy to make. The only examples known to us as yet are the dendrimers of different surface functionality that were first prepared by Fréchet. This author and his team indeed took advantage of the potentialities offered by the so-called convergent method to assemble at the ultimate step two different types of dendrons[17] and derive dendrimers covered with specific groups on their two opposite faces. The purpose of the present study is to show that the sequential polymerization of two different macromonomers can also give rise to Janus-type macromolecules, but with more flexibility and under far easier conditions than those required for the synthesis of dendrimers. Indeed, the compactness cannot be varied at will in regular dendrimers and their synthesis involves the tedious repetition of the same series of reactions for each generation added.

1a. Sequential Polymerization of PS and PEO Macromonomers. The macromonomers of PS and PEO were obtained by means of anionic living polymerization through two different methods (Table 1). ω-Norbornene-ended PS macromonomers resulted from the deactivation of living anionic PS chains by 5-norbornene-2-carbonyl chloride, ethylene oxide being used as intermediate to transform the polystyrenyl carbanions into alkoxides. As to the α-norbornene-ended PEO macromonomers, they were grown from the unsaturated initiator that is obtained from the deprotonation of hydroxymethyl-5-bicyclo[2.2.1]hept-2-ene. The detailed

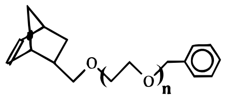
Table 1. Characteristics of *ω*-Norbornenylpolystyrene and α-Norbornenylpoly(ethylene oxide) Macromonomers

	$\overline{M}_n$ (targeted) (g/mol)	$\overline{M}_n{}^a$ (SEC-RI detector) (g/mol)	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n{}^a$ (^{1}H NMR)
PS	2700	2800	1.04	2900
PEO	1100	1500	1.05	1300
	3500	2700	1.06	2400

[a] Calibration by PS linear standards for PS macromonomer; calibration by PEO linear standards for PEO macromonomers. [b] These molar mass values were obtained upon taking the ratio of the area of the signal due to the protons of monomer units to that of the peak arising from the ethylenic protons of norbornene.



ϖ-norbornene-ended polystyrene (PS macromonomer)



α-norbornene-ended poly(ethylene oxide) (PEO macromonomer)

synthesis of these two macromonomers has been reported elsewhere.[11,13]

In the sequential polymerization of two monomers, the order in which they are assembled within the block copolymer structure is critical: between two monomers exhibiting contrasted reactivities, the molecule giving the propagating species of highest reactivity is generally polymerized first. Following this reasoning, the macromonomer of PS was first added to the reaction medium containing the Schrock initiator. Indeed, our previous investigations of the homopolymerization of PS and PEO macromonomers[11−13] showed that the macromonomer of PS is consumed faster than is its PEO homologue, attesting to its higher reactivity. The lower reactivity of the PEO macromonomer was attributed to the competition between the norbornenyl polymerizable groups and the oxygen atoms of PEO chains for coordination to the vacant site of the transition metal atom. Fifteen minutes after introduction of the PS macromonomers, PEO−norbornene was added (Figure 1).

The size exclusion chromatographic characterization of the aliquot that was withdrawn from the medium before introduction of the PEO macromonomer shows that the PS macromonomer is totally consumed, regardless of the reaction conditions used. Approximately 1 h after the beginning of the polymerization, benzaldehyde was added to quench the carbenic species in a Wittig-type reaction. The success of the sequential polymerization of the two macromonomers was checked with a size exclusion chromatographer equipped with a light-scattering detector, upon analysis of the PS polymacromonomer aliquot and of the poly[(polystyrene−oxycarbonyl−norbornene)-*b*-(poly(ethylene oxide)−oxymethylene−norbornene)] structure that should have ultimately formed. For the three experiments that have been carried out, it can be seen that both PS and PEO macromonomers have been sequentially polymerized to completion and therefore 100% crossover efficiencies have been achieved during the diblock synthesis. Indeed, inspection of the eluograms of the products obtained does not indicate the presence of any residual macromonomer or polystyrene PM contaminant (Figure 2); it also reveals a marked shift of the signal toward the lower retention volumes as compared with those seen for the polystyrene PM aliquot.

For the calculation of the molar masses of these Janus-type PS−PEO copolymers, it was assumed that their refractive index increment is a linear function of their composition:[2]

$$\frac{\mathrm{d}n}{\mathrm{d}c} = W_{\mathrm{PS}}\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{PS}} + W_{\mathrm{PEO}}\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{PEO}}$$

(This assumption was found to apply on two copolymer samples of different types: first on a [PEO-*b*-PS]−norbornene macromonomer and second on a statistical copolymer of PS and PEO macromonomers. W_{PS} and W_{PEO} are the weight fractions of PS and PEO in the copolymer.) As for the expected molar masses, they were calculated upon postulating a 100% efficiency of the Schrock initiator. The two sets of molar masses—experimental and targeted—tend to fall in reasonable agreement (Table 2), if one takes into account the fact that even a small variation of the initiator used can induce a large modification of the molar mass of the PM. Despite this feature, which is related to the size of the macromonomer, it is noteworthy that molar masses remain narrowly distributed with polydispersity indexes lower than 1.3.

It was also attempted to first polymerize the macromonomers of PEO and wait until its complete conversion before adding the macromonomer of PS. In the latter case and regardless of the experimental conditions used, a double distribution of molar masses was observed in the SEC eluograms. Even though both types of macromonomers are entirely consumed by the ROM process, the rather poor crossover efficiency actually stems from the low reactivity of the carbenic species carried by the PEO macromonomers. Only a small proportion of growing poly(ethylene oxide) PM participated in the crossover process probably because the rate of the latter reaction was too slow as compared with the rate of propagation of the PS macromonomer. The deactivation of a fraction of active poly(ethylene oxide) PM by possible impurities contained in the PS macromonomers can be ruled out: indeed, despite repeated purifications and freeze-dryings of the latter macromonomer the crossover results did not show any improvement. The lack of reactivity of the carbenic species carried by the macromonomer of PEO prevented us from attempting the synthesis of the triblock copolymer, poly[(polystyrene−oxycarbonyl−norbornene)-*b*-(poly(ethylene oxide)−oxymethylene−norbornene)-*b*-(polystyrene−oxycarbonyl−norbornene)].

1b. Statistical Copolymerization of PEO and PS Macromonomers. The PEO and PS macromonomers used in these statistical copolymers were prepared under conditions similar to those previously described. For this series of experiments, again three molar ratios of PEO to PS macromonomers were selected and the amount of initiator was adjusted so as to obtain $\overline{\mathrm{DP}}_n$'s between 5 and 20 (Table 3).

The copolymerization was triggered by addition of the requested amount of the Schrock initiator into the solution containing the two macromonomers. Approximately 1 h after the beginning of the polymerization, the carbenic species were deactivated by reaction with benzaldehyde and the copolymer was recovered by precipitation. Characterization by size exclusion chromatography (SEC) revealed that both PEO and PS macromonomers have been polymerized to completion. As for the molar masses of the samples prepared, they were drawn from the light-scattering detector connected to the size exclusion chromatographer, assuming a

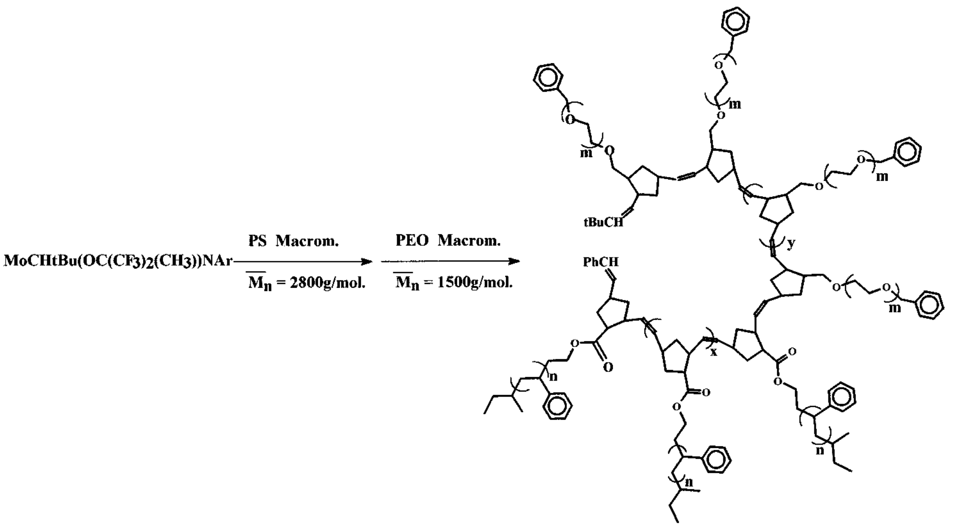


Figure 1. Synthetic scheme to obtain polymacromonomer by sequential polymerization of PS–norbornene and PEO–norbornene macromonomers.

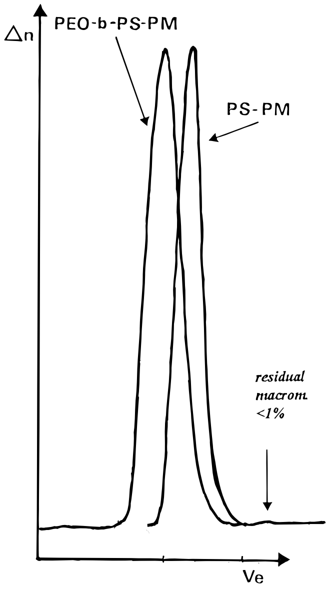


Figure 2. SEC traces of the polymacromonomer obtained from the sequential polymerization of PS–norbornene and PEO–norbornene macromonomers.

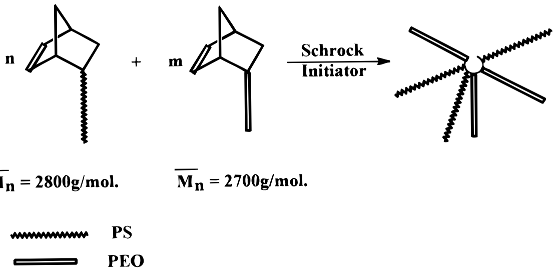
Table 2. Characterization of Poly[(polystyrene–oxycarbonyl–norbornene)-*b*-(poly(ethylene oxide)–oxymethylene–norbornene)] with a Size Exclusion Chromatographer Equipped with a Light-Scattering Detector

PS/PEO/ initiator	conversion (%)	$\overline{M}_n$[a] (targeted) (g/mol)	$\overline{M}_n$ (SEC-LS detector) (g/mol)	$\overline{M}_w/\overline{M}_n$ (SEC-LS detector)
10/10/1	100	43 000	64 000	1.26
10/5/1	100	35 500	33 260	1.17
5/10/1	100	29 000	49 500	1.10

[a] $\overline{M}_n = 2800\overline{DP}_{n,PS} + 1500\overline{DP}_{n,PEO}$.

linear variation of the refractive index increment with the composition. The values of the molar masses are found to be in rather good agreement with the targeted values, except in one case for which a slight discrepancy can be noted.

Statistical copolymerization reactions that occur *via* a nonliving process generally yield polymeric materials with some compositional heterogeneity, except in the case of the azeotropic composition for reactivity ratios lower than 1 or when the reactivity ratios of the two comonomers are close to 1. As the ring-opening metathesis polymerization has been proven to proceed *via* a truly "living" process, the chances to observe some compositional heterogeneity are minimal. To evaluate the extent of compositional fluctuation in our copolymer samples, we therefore compared the SEC eluograms obtained with UV and refractive index (RI) detections, respectively. As UV specifically detects the polystyrene part in the copolymer, any dissymmetry in the molar mass distribution and difference from the RI detection can be taken as a clue of the sample heterogeneity. The SEC traces whether they arise from RI or UV detections are found to perfectly align for the three copolymer samples, confirming their homogeneity.



This feature, though, does not necessary mean that truly random copolymers were obtained. Only the determination of the reactivity ratios would have informed us about the distribution of PEO and PS grafts along the PM backbone and the tendency of the copolymerization system to blockiness. But it was beyond this work to carry out such an investigation.

2. Synthesis and ROMP of [PEO-*b*-PS]-Norbornene Macromonomers. Globular shape macromolecules that would present the same features as those exhibited by certain assemblies of molecules such as the micelles or the latices, with a bulk part different from the external surface, are scarce. To our knowledge the only examples of molecules with such characteristics come again from the work of Fréchet on dendrimers. He[18] indeed described the synthesis of hydrophobic aryl ether dendrimers that turned to behave as unimolecular micelles because of the presence of hydrophilic carboxylic acid functions on their outer surfaces.

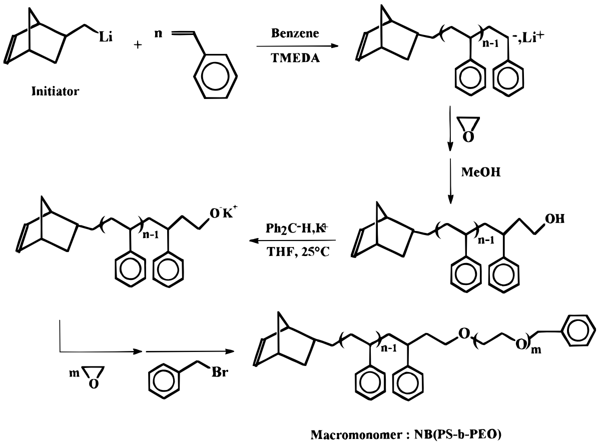
One of the purposes of this paper is to demonstrate that polymers with similar qualities—a globular shape,

Table 3. Characterization of Poly[(polystyrene−oxycarbonyl−norbornene)-*co*-(poly(ethylene oxide)−oxymethylene−norbornene)] with a Size Exclusion Chromatogapher Equipped with a Light-Scattering Detector

PS/PEO/ initiator	% PS	conversion (%)	$\overline{M}_n$[a] (targeted (g/mol)	$\overline{M}_n$ (SEC-LS detector) (g/mol)	$\overline{M}_w/\overline{M}_n$ (SEC-LS detector)
10/10/1	50	100	55 000	56 500	1.16
10/5/1	66	100	41 500	58 600	1.20
5/10/1	33	100	41 000	40 000	1.10

[a] $\overline{M}_n = 2800\overline{DP}_{n,PS} + 2700\overline{DP}_{n,PEO}$.

Scheme 1



inner and outer parts of quite different chemical nature—are also accessible by the macromonomer route. The difficulty in such an endeavor lies more in the synthesis of the appropriate macromonomer than in its polymerization, which can be effected by the ring-opening metathesis process, provided the macromonomer is fitted with a norbornenyl unsaturation.

To obtain polymacromonomers constituted of a hydrophobic bulk part and a hydrophilic corona, one has to first prepare a macromonomer made of two amphiphilic blocks and whose terminal unsaturation should be specifically attached to the hydrophobic block. Scheme 1 depicts the synthetic procedure that has been followed to obtain these [PEO-*b*-PS]−norbornene macromonomers. Because of the peculiar position of the unsaturation with respect to the two blocks, the most straightforward method to derive such macromonomers would be to successively grow the PS and the PEO blocks from a norbornene-containing initiator. A norbornene-based carbanionic initiator was thus developed for this purpose.[12]

Upon addition of the norbornene-containing lithiated initiator into the flask filled with a benzene solution of styrene, the reaction medium immediately turned red, attesting to the formation of polystyryl carbanions. To speed up the chain growth and prevent the carbanionic species from aggregating, tetramethylethylenediamine (TMEDA) was introduced in the reaction medium. The polymerization was effected at 25 °C for 1−2 h, depending upon the molar mass targeted.

As for the growth of the second PEO block, it was carried out in two steps. An excess of ethylene oxide was first introduced into the reaction medium containing living (polystyryl)lithium so as to end-cap these chains with a lithium alkoxide. This reaction is indeed known to be selective[20] enough not to proceed beyond the addition of only one ethylene oxide, the lithium alkoxide formed exhibiting very limited selectivity toward the latter cyclic monomer—unless heating at elevated temperature or using polar solvents (DMSO). The hydroxyl function that is generated in this way at the polystyrene chain end was then deprotonated by (diphenylmethyl)potassium, and the potassium alkoxide formed was used to polymerize ethylene oxide.

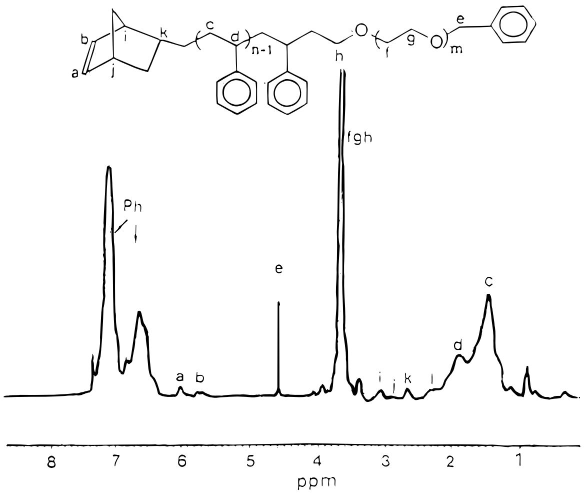


Figure 3. ^{1}H NMR spectrum of a norbornene terminated PS-*b*-PEO macromonomer.

Table 4. Characteristics of [PEO-*b*-PS]−Norbornene Macromonomers

$\overline{M}_{n,PS}$[a] (UV-RI detector) (g/mol)	$\overline{DP}_{n,PS}$[b] (targeted)	$\overline{DP}_{n,PEO}$[c] (NMR)	$\overline{M}_{n,calcd}$[d] (g/mol)	$\overline{M}_{n,PS\text{-}b\text{-}PEO}$[a] (UV-RI detector) (g/mol)	$\overline{M}_w/\overline{M}_n$
1800	16	136	7800	6900	1.03
2300	20	36	3900	5530	1.02
2300	20	69	5400	6870	1.03

[a] Calibration by PS linear standards. [b] $\overline{DP}_n$ targeted for this α-norbornenyl ω-hydroxy PS macromonomer. [c] $\overline{DP}_n$ of the PEO block in the [PEO-*b*-PS]−norbornene macromonomer. [d] $\overline{M}_{n,calc} = (104(\overline{DP}_{n,PS})_{SEC} + 44(\overline{DP}_{n,PEO})_{NMR}) + 198$.

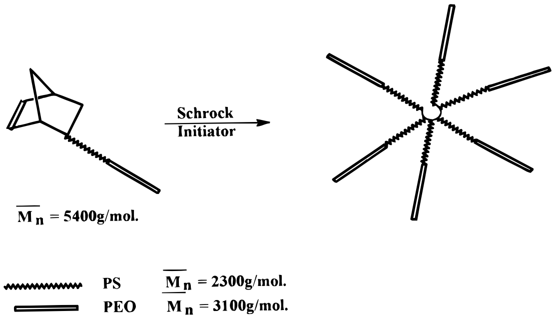
The α-norbornene ω-hydroxy polystyrene precursors were subjected to characterization by SEC and ^{1}H NMR, prior to the growth of the PEO block (Table 4). They were found to exhibit polydispersity indexes close to unity, and the values determined by SEC for their molar masses come to a rather good agreement with those targeted, confirming the excellent efficacy of this novel carbanionic initiator. The molar masses of the PS-*b*-PEO macromonomer were simply drawn from ^{1}H NMR characterization (Figure 3); the size of the PS block being known, it was easy to deduce the balance between the two blocks in the copolymer (Table 4). The three copolymer samples were also analyzed to check for the possible presence of homopolymers, either PEO or PS. Not only were the copolymers free of any contaminant but they all also exhibited a sharp distribution of molar masses (Table 4).

The ROMP experiments were conducted on only one macromonomer, that constituted of an equal balance of PS and PEO. Again, it was decided not to attempt high $\overline{DP}_n$'s, the values targeted ranging from 5 to 21.

The polymacromonomers obtained were then characterized with a size exclusion chromatographer coupled with a light-scattering detector (Table 5). The remarkable selectivity of ROMP and its straightforward character were again verified: not only was 100% conversion

Table 5. Characteristics of Poly([PEO-*b*-PS]−norbornene) Obtained from a [PEO-*b*-PS]−Norbornene Macromonomer of 5400 g/mol

[macromonomer]/[initiator]	conversion (%)	$\overline{M}_n$ (targeted) (g/mol)	$\overline{M}_n$ (LS detector) (g/mol)	$\overline{M}_w/\overline{M}_n$ (LS detector)
5	100	27 000	40 300	1.13
9	100	51 000	60 250	1.40
21	100	114 000	136 500	1.37



accomplished but a good control of the polymacromonomer molar mass was also achieved. The values determined by light scattering, using a refractive index increment that includes the contribution of PS and PEO, fell, indeed in good agreement with the expected ones.

Even though their behavior in water has yet to be investigated, it is clear that the peculiar topology of these PS-*b*-PEO polymacromonomers makes them particularly suitable for applications such as unimolecular micelles.

Thanks to the versatility and the selectivity of the macromonomer technique, the PS/PEO balance as well as the $\overline{\mathrm{DP}}_n$ of the PM can be varied at will, enabling the synthesis of unimolecular micelles of controlled size.

3. Synthesis and ROMP of [PS-*b*-PEO]−Norbornene Macromonomers. Water soluble polymers that contain a small proportion of hydrophobic units are known to enhance the viscosity of aqueous solutions through hydrophobic intermolecular association; they are referred to as associative thickeners.[2]

Branched structures constituted of such hydrophobically modified water soluble chains are bound to bring about even higher viscosity enhancement, because of their particular topology. Unfortunately, branched polymers with such features are generally poorly defined, giving little incentive to use them in aqueous formulations. Well-controlled branched architectures whose hydrophobic and hydrophilic parts would be distributed in a precise topology would be of genuine interest for such applications. It came to us that the macromonomer technique would be well suited for the preparation of branched polymers exhibiting such features. To allow intermolecular association to efficiently develop between the hydrophobic parts, it is essential to place these hydrophobic sequences or blocks at the periphery of the branched system, on its external surface.

Hydrophilic PMs that would be prepared by ROMP and whose external corona would be hydrophobically modified would certainly fulfill the criteria of control and precise definition of the structure formed.

The first step in such an endeavor consists in the synthesis of the appropriate macromonomer. As this macromonomer is meant to be polymerized by ring-opening metathesis, it should bear a norbornene unsaturation and contain a main hydrophilic PEO block followed by an external PS block. To obtain this PS-*b*-PEO−norbornene macromonomer, we applied standard methods. Scheme 2 depicts the synthetic scheme that was followed to prepare these macromonomers.

Scheme 2

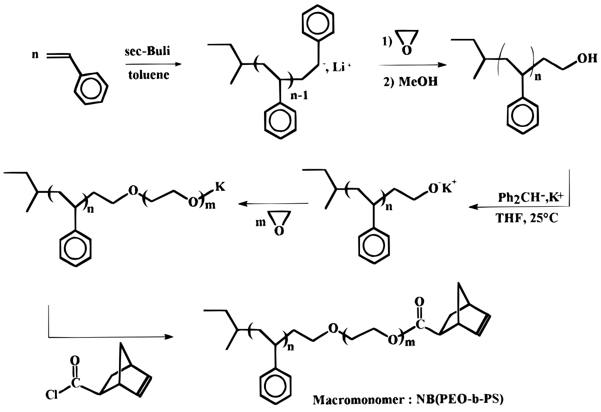


Table 6. Characteristics of [PS-*b*-PEO]−Norbornene Macromonomers

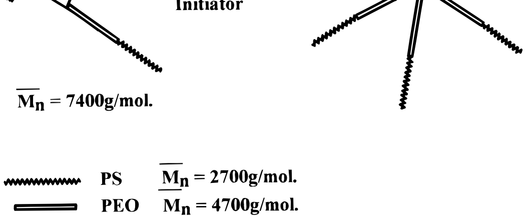
$\overline{M}_{n,PS}$[a] (UV-RI detector) (g/mol)	$\overline{\mathrm{DP}}_{n,PS}$[b] (SEC)	$\overline{\mathrm{DP}}_{n,PEO}$[c] (NMR)	$\overline{M}_{n,calc}$[d] (g/mol)	$\overline{M}_{n,PS\text{-}b\text{-}PEO}$[a] (UV-RI detector) (g/mol)	$\overline{M}_w/\overline{M}_n$
2000	19	129	7874	7700	1.02
2690	26	108	7678	7500	1.02
5660	54	44	7774	7550	1.02

[a] Calibration by PS linear standards. [b] $\overline{\mathrm{DP}}_n$ of ω-hydroxy PS from SEC. [c] $\overline{\mathrm{DP}}_n$ of the PEO block in the [PS-*b*-PEO]−norbornene macromonomer. [d] $\overline{M}_{n,calc} = (104(\overline{\mathrm{DP}}_{n,PS})_{SEC} + 44(\overline{\mathrm{DP}}_{n,PEO})_{NMR}) + 222$.

After polymerization of styrene with *sec*-BuLi as initiator and deactivation of the living PS chains by ethylene oxide, the ω-hydroxyl PS obtained upon precipitation by methanol was deprotonated and used to grow the PEO block. The norbornene unsaturation was subsequently introduced through deactivation of the growing alkoxides by 5-norbornene-2-carbonyl chloride. Three samples of these PS-*b*-PEO−norbornene macromonomers have been prepared with different proportions of the two blocks. These copolymers were analyzed by ^{1}H NMR and SEC (Table 6); from the characteristics pertaining to the PS block and given by SEC, it was easy to deduce the molar mass of the copolymer by ^{1}H NMR.

The good agreement with the values given by the light-scattering detector of the SEC outfit and also the narrow distributions of molar masses confirm that the entire synthetic procedure occurred as expected. The extent of functionalization of these macromonomers was also found to be quantitative.

The ring-opening metathesis polymerization of these macromonomers was as straightforward as in the previous cases.



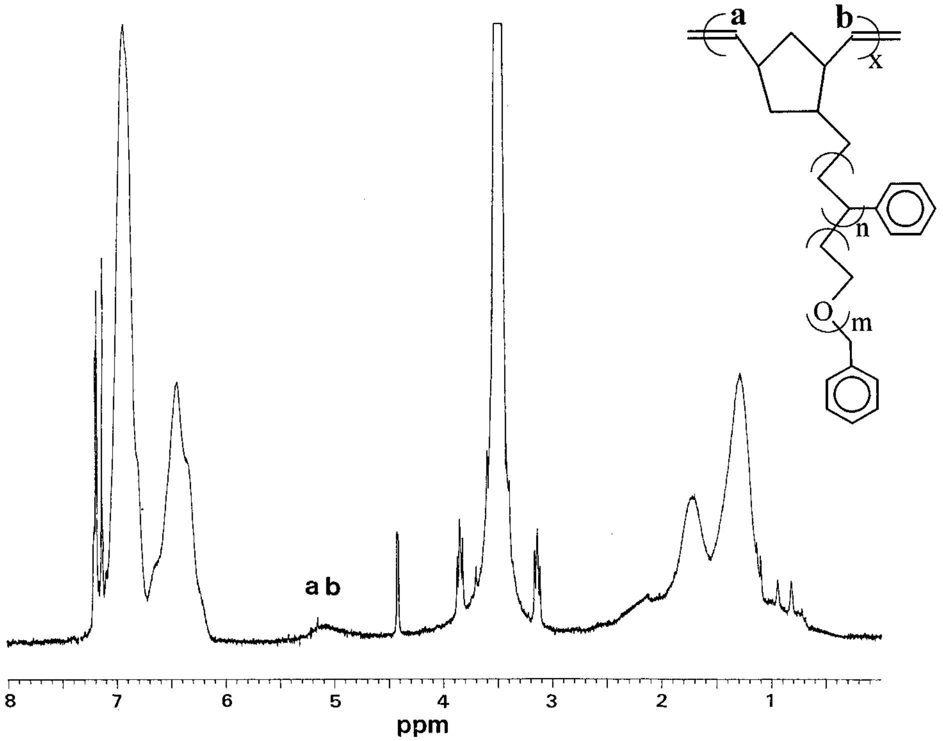


Figure 4. ^{1}H NMR spectrum of the polymacromonomer obtained from the homopolymerization of the α-norbornenyl−PS macromonomer.

Table 7. Characteristics of Poly([PS-*b*-PEO]−Norbornene) Obtained from a [PS-*b*-PEO]−Norbornene Macromonomer of 7400 g/mol

[macromonomer]/[initiator]	conversion (%)	$\overline{M}_n$ (targeted) (g/mol)	$\overline{M}_n$ (LS detector) (g/mol)	$\overline{M}_w/\overline{M}_n$ (LS detector)
5	100	37 000	52 200	1.15
10	100	81 400	91 700	1.10

The same sample of macromonomer was subjected to ROMP; two experiments corresponding to two $\overline{DP}_n$'s have been carried out. As seen in Table 7, all the macromonomer has effectively participated in the polymerization process, and again it is worth stressing the excellent agreement between targeted and measured values of molar masses. These results convince us that quite similar polymerization yields would have been obtained with the two other macromonomers of the same family. Even though these polymacromonomers could not be readily used as associative thickeners because of the too large size of the PS block, our command of the macromonomer technique is precise enough to enable us to vary the size of each block and the $\overline{DP}_n$ of the PM at will.

Conclusion

The discovery that highly strained cyclic olefins such as norbornene can be polymerized under "living" conditions *via* ring-opening metathesis has paved the way to the progressive utilization of the latter mechanism in macromolecular engineering.

The polymerization of macromonomers, which is known for its poor yields when mediated by classical chain addition processes, is straightforward whenever it proceeds *via* "living" ring-opening metathesis. Miscellaneous macromonomers have indeed been polymerized to complete conversion in the presence of appropriate initiators of metathesis reactions.

The objective of the present study is to demonstrate that ROMP can also be applied to copolymerize either sequentially or statistically two macromonomers of different chemical nature or homopolymerize macromonomers that are themselves block copolymers.

Amphiphilic architectures of totally unprecedented topologies have been constructed by the macromonomer technique: Janus-type structures can be derived by sequential copolymerization of PS and PEO macromonomers, whereas branched assemblies that could serve as unimolecular micelles or associative thickeners become accessible by ROMP of PS-*b*-PEO-based macromonomers.

Experimental Part

Materials. 5-(Hydroxymethyl)bicyclo[2.2.1]hept-2-ene (NBCH$_2$OH) (Aldrich, purity 98%), benzyl bromide (Aldrich, purity 98%) and *sec*-butyllithium (Janssen Chemica, 1.3 M in cyclohexane/hexane) were used as received. Styrene was distilled over CaH$_2$ and stirred over CaH$_2$ for 24 h before being cryodistilled. Ethylene oxide (Fluka, purity 99.8%) was stirred over sodium at −30 °C for 3 h and cryodistilled. (Diphenylmethyl)potassium (Ph$_2$CHK) in tetrahydrofurane (THF) solution and 5-norbornene-2-carbonyl chloride were synthesized according to well-established procedures. Dioxane, THF, benzene, toluene, and tetramethylethylenediamine (TMEDA) were distilled from sodium−benzophenone. Methanol was stirred over MgSO$_4$ and distilled just prior to its use.

The Schrock complex Mo(NAr)(OC(CH$_3$)(CF$_3$)$_2$)$_2$(CHtBu) used as initiator was obtained according to literature methods.[19]

The carbanionic norbornene-based initiator, 5-(lithiomethyl)-bicyclo[2.2.1]hept-2-ene, and the polystyrene−norbornene macromonomers[12] and poly(ethylene oxide)−norbornene macromonomers[13] were prepared according to recipes recently reported.

Methods. All reagents were stored and used under inert atmosphere. All anionic polymerizations were performed under a slight nitrogen overpressure using a tight reactor equipped with a nitrogen inlet, magnetic stirring, a sampling device, and burets meant to introduce solvent, initiator, monomers, and deactivator. Ring-opening metathesis polymerizations were carried out in a glovebox under moisture-free conditions. NMR spectra were obtained using a Brucker

AC200 spectrometer. NMR spectra of macromonomers and those of the corresponding polymacromonomers are essentially the same except that the signals due to the ethylenic protons are shifted from $\delta = 5.6-6.3$ ppm for the macromonomer to $\delta = 5-5.5$ ppm for the polymacromonomer (Figure 4).

The size exclusion chromatography equipment consisted of a JASCO HPLC pump type 880-PU, TOSOHAAS TSK gel columns, a Varian refractive index detector, and a JASCO 875 UV/VIS absorption detector, THF being the mobile phase. The columns were calibrated with polystyrene or poly(ethylene oxide) standards. The actual molar masses of the copolymer samples were calculated from the response of the multiangle laser light-scattering detector that (Wyatt Technology) was connected to the size exclusion chromatographer. Provided the differential refractive index increment (d*n*/d*c*) is precisely known, the Multiangle Laser Light Scattering (MALLS) detector that measures the scattering intensity of the eluting polymer gives access to the true value of the mass average molar mass ($\overline{M}_w$) upon summation of the mass corresponding to each slice. The determination of the number average molar mass of the branched polymer using this equipment tended to be less accurate. SEC being sensitive to the hydrodynamic volumes of the species, two macromolecules of different molar mass but similar radii of gyration could be eluted at the same volume. The curve giving the distribution of molar masses is therefore narrowed. The $\overline{M}_n$ values deduced from this distribution curve and the overall $\overline{M}_w$ values drawn from light scattering are overestimated. It is therefore not astonishing to obtain polydispersity indices lower than 1.1 by this technique.

Synthesis of [PEO-*b*-PS]−Norbornene Macromonomers. In a typical reaction, styrene (8 mL, 7×10^{-2} mol) and TMEDA (0.9 mL, 6×10^{-3} mol) were dissolved in 100 mL of benzene at 15 °C. The initiator solution of 5-(lithiomethyl)-bicyclo[2.2.1]hept-2-ene (10 mL, 3.3×10^{-3} mol) was added at once. The reaction medium was then heated to 25 °C for 3 h. The living polystyryl carbanions were then transformed into lithium alkoxides by addition of 1 mL (20×10^{-3} mol) of ethylene oxide, the ω-hydroxyl PS macromonomer being recovered upon addition of an excess of methanol and two successive precipitations by this solvent. Three successive freeze-drying processes of the PS precursor were carried out from dioxane solution prior to the growth of the PEO block. The PS macromonomer (4 g, 1.74×10^{-3} mol) was then dissolved in 150 mL of THF and its hydroxyl chain end deprotoned using Ph_2CHK (3.06 mL, 1.74×10^{-3} mol). This deprotonation step was considered to be complete as soon as the reaction mixture retained the red-orange color characteristic of Ph_2CHK in slight excess. The solution was then cooled to −30 °C, and 7 mL (0.14 mol) of ethylene oxide was added. The solution was allowed to rise to room temperature overnight. Deactivation of the reaction medium was performed by addition of 2 mL of benzyl bromide. The KBr salt formed was removed by filtration over Celite. Precipitation of the copolymer sample was performed by using a mixture of ethanol/pentane (1/10) at −30 °C. After three successive freeze-drying processes in dioxane, the PEO-*b*-PS−norbornene macromonomer was ready to undergo ROMP.

Synthesis of [PS-*b*-PEO]−Norbornene Macromonomer. In a typical synthesis, 60 mL (0.57 mol) of styrene was dissolved in 250 mL of toluene and cooled to −30 °C. A 16 mL solution of *sec*-butyllithium (20.8×10^{-3} mol) was added. After 5 min of stirring, the solution was heated to room temperature for 3 h. Then, the solution was cooled to −30 °C, and 2 mL of ethylene oxide (40×10^{-3} mol) was added, followed by the introduction of 3 mL (75×10^{-3} mol) of methanol.

For the growth of the PEO block, a similar procedure to that previously described was applied. In this case the polymerization was terminated with 15 g of 5-norbornene-2 carbonyl chloride (97×10^{-3} mol). The KCl salt formed was filtered over Celite. Two successive freeze-drying processes from dioxane solution were necessary before undertaking the ring-opening metathesis polymerization of these macromonomers.

Homopolymerization of PS-*b*-PEO Block Macromonomers. In a typical polymerization, 11 mg (15.6 μmol) of the fluorinated Schrock initiator was dissolved in 2 mL of toluene. PS-*b*-PEO−norbornene macromonomer ($\overline{M}_n = 5400$ g/mol) (500 mg, 925 μmol) was dissolved in 8 mL of toluene and slowly added to the initiator solution under stirring. Deactivation of the reaction medium was performed after about 1 h of polymerization by addition of 0.1 mL of benzaldehyde. Precipitation in pentane yielded the pure polymacromonomers.

Sequential Copolymerization of PS and PEO Macromonomers. In a typical polymerization, 12 mg (17 μmol) of the same Schrock initiator was dissolved in 2 mL of toluene. PS macromonomer ($\overline{M}_n = 2800$ g/mol) (500 mg, 178.6 μmol) was dissolved in 8 mL of toluene and added to the initiator solution under stirring. After 30 min, an aliquot was sampled out from the reaction medium just before the addition of the 130 mg (86.7 μmol) of PEO macromonomer ($\overline{M}_n = 1500$ g/mol) in solution in 1 mL of toluene. After about 4 h, the carbenic species were quenched by benzaldehyde. Precipitation in pentane yielded the pure polymacromonomer.

Statistical Copolymerization of PS and PEO Macromonomers. In a typical synthesis, 10 mg (14. 2 μmol) of the same Schrock initiator was dissolved in 2 mL of toluene. PS−norbornene macromonomers ($\overline{M}_n = 2800$ g/mol) (199 mg, 71 μmol) and 400 mg (148 μmol) of PEO−norbornene macromonomers ($\overline{M}_n = 2700$ g/mol) were dissolved in 8 mL of toluene and slowly introduced to the initiator solution under stirring. After 1 h, benzaldehyde was added to the medium. Precipitation in pentane yielded the pure polymacromonomer.

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