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NOVEL STYRENE-BUTADIENE BLOCK COPOLYMERS BY SEQUENTIAL AND STATISTICAL COPOLYMERIZATION OF CORRESPONDING MACROMONOMERS

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Abstract: This paper concerns the synthesis of two different structures of styrene-butadiene block copolymers that were respectively obtained *via* sequential and statistical ring-opening metathesis copolymerization of norbornene-terminated polystyrene (PS) and polybutadiene (PB) macromonomers. The stimulus for preparing such styrene-butadiene copolymers originates from the observation that phase-separated morphologies in block copolymers not only depend on the respective size of the blocks and the interaction parameter (χ), but also on the topological constraints introduced in the copolymer structure. From the differential scanning calorimetry study that was carried, it can be inferred that the two types of copolymers -prepared by sequential and statistical copolymerization of PS and PB macromonomers respectively- exhibit quite different phase separation behaviors, indicating that they develop distinct equilibrium domain morphologies.

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INTRODUCTION

Block copolymers have been the subject of widespread interest and intense research after it was discovered that they segregate into domains of microscopic scale. While binary blends of two incompatible polymers tend to separate on a macroscopic scale, block copolymers develop microphase-separated morphologies due to the covalent junction between the two alien blocks (Ref. 1,2). A description of the morphology -spheres, hexagonally-packed cylinders, lamellae- that forms in linear block copolymers as a function of composition and the processing conditions has been proposed. If other types of topological constraints are introduced in block copolymers in addition to the permanent link between blocks, the resulting equilibrium domain morphologies are likely to further change. For instance, styrene-isoprene star-block copolymers of 35/65 % (w/w) composition are known to develop an ordered bicontinuous double-diamond morphology (Ref. 3), whereas linear block copolymers of same type and equivalent composition form a structure corresponding to hexagonally- packed cylinders. Other kinds of topological constraints than those produced by the central core in a star structure constituted of blocky arms could be envisioned, upon diversifying the molecular arrangement of the two alien blocks and building novel architectures.

Polymacromonomers are a class of branched polymers that are more compact than star molecules ; they are therefore likely to develop original phase-separated morphologies, because of the peculiar entropic constraints associated with this kind of topology. Polymacromonomers are obtained by polymerization of macromonomers and their main characteristic is an axisymmetric distribution of branching points around the central backbone contour. Provided macromonomers are end-fitted with a terminal norbornene unsaturation, they have been shown in many instances to undergo a truly "living" ring-opening metathesis polymerization (ROMP) with a Schrock-type complex as initiator. By this pathway, norbornene-ended macromonomers of polystyrene (PS) (Ref. 4), poly(ethylene oxide) (PEO) (Ref. 5), (PEO-b-PS) (Ref. 6) diblock copolymer have been polymerized with conversions close to unity and well-defined molecular structures.

In the present paper, we shall be concerned with the synthesis of two types of PS/PB based block copolymers that were respectively obtained by statistical and sequential copolymerization of corresponding PS and PB macromonomers. In these comb-shaped copolymers, the two types of grafts are not linked by a permanent junction point as in linear block copolymers or *via* a central core as in star block copolymers, but they are connected through a same polynorbornene backbone. It would be interesting to see how the interplay of configurational entropy and enthalpic contributions affect the phase separation in these (Norbornene-PS)$_m$-b-(Norbornene-PB)$_n$ and (Norbornene-PS)$_m$-co-(Norbornene-PB)$_n$ copolymers.

Before describing the preparation of these PS/PB copolymers of original topology, we shall first report on the synthesis of α- and ω-norbornenyl PB macromonomers and on their subsequent homopolymerization by ring-opening metathesis. The third part of this article will be devoted to a differential scanning calorimetry (DSC) characterization of the different PS/PB copolymers synthesized. This DSC study which was augmented by a dynamic mechanical analysis (DMA) of some samples is preliminary to the mesophase characterization we intend to perform by electron microscopy. If DSC or DMA are by no means suitable for the investigation of the morphologies that form in copolymers, they can well serve as a tool to detect whether a copolymer system retains a disordered homogeneous phase or exhibits a microphase separation. In that event two or more transitions characterized by as many glass transition temperatures could be seen in DSC thermogram whereas a homogeneous system would only give one transition.

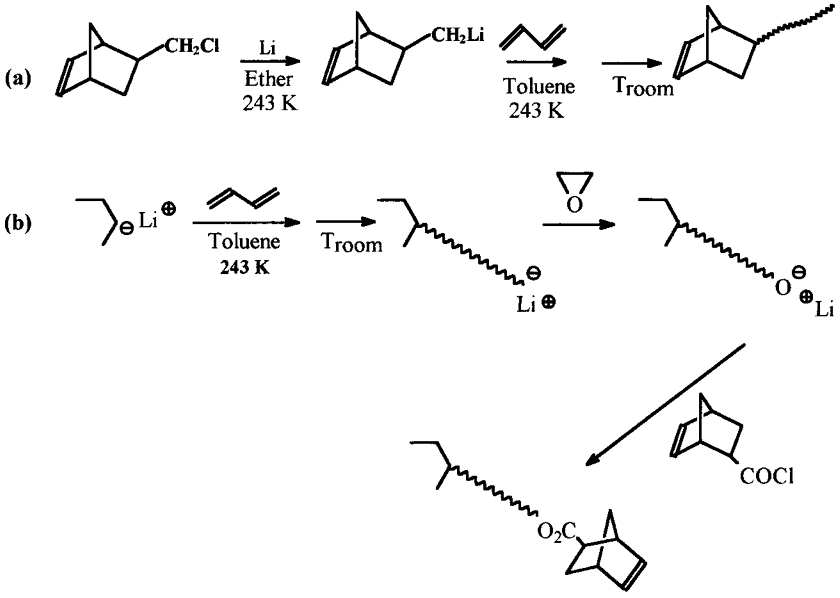
RESULTS AND DISCUSSION

I) Synthesis of α- and ω-norbornenyl polybutadiene macromonomers by anionic polymerization

As "living" polymerizations are the best suited techniques to obtain macromonomers that exhibit high functionalization yield and polydispersity indexes close to unity, we chose to synthesize macromonomers of PB *via* anionic processes.

Two pathways have been explored : the first one is based on the use of an unsaturated anionic initiator, 5-lithiomethyl bicyclo[2.2.1] hept-2-ene [scheme 1(a)] and the second one implies the deactivation of growing polybutadienyl anions by 5-carbonyl chloride bicyclo [2.2.1] hept-2-ene [scheme 1 (b)]. These syntheses have been reported previously (Ref. 7).

The macromonomers synthesized by these two routes exhibit different 1,2-vinyl contents. Route (a) -corresponding to α-norbornenyl macromonomers- affords samples with up to 56% of 1,2-vinyl content because it involves the use of ether. Route (b) -ω-norbornenyl macromonomers- is the best adapted for the synthesis of PB macromonomers with low 1,2-vinyl content.

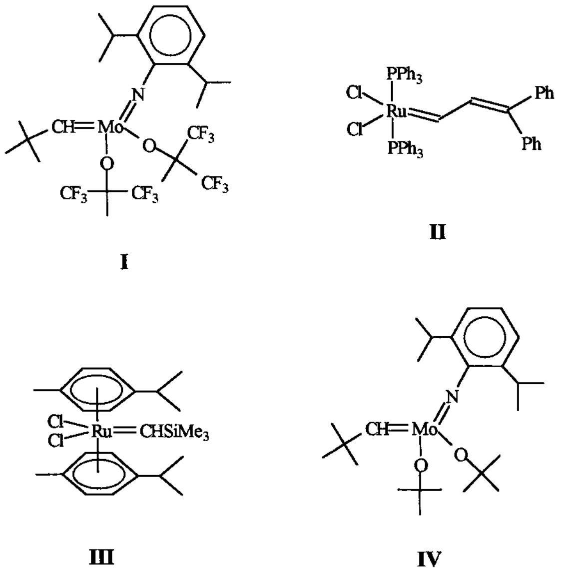


Scheme 1. Synthesis of (a) α-norbornenyl and (b) ω-norbornenyl PB macromonomers

II) Homopolymerization of α- and ω-norbornenyl PB macromonomers

The ROMP of α- and ω-norbornenyl PB macromonomers has been attempted with four alkylidenic initiators (scheme 2) as discussed in a recent paper (Ref. 7).

It appeared that propagating species resulting from both initiators I and III present a too high reactivity towards C=C double bonds, reacting indiscriminately with both cyclic (norbornenyl) and acyclic 1,2-vinyl unsaturations of the PB macromonomer. In the latter case, the metathesis process resulted in the degradation of the PB macromonomer. In contrast, the complex II that is known to be of much lower reactivity than I and III only polymerized the ester-free norbornenyl PB macromonomers [scheme 1(a)], giving sluggishly rather low conversions.



Scheme 2. Complexes used in the homopolymerization of norbornenyl PB macromonomers

The only initiator that was found suitable for the ROMP of PB was the complex IV. More selective than the fluorinated Schrock complex (I), this initiator allowed the polymerization to an almost complete conversion (95 %) for PB macromonomers with low vinyl content and to an encouraging 68% conversion for macromonomers with higher vinyl content.

In fact, the factor that appears to play a crucial role on the conversion of macromonomers is the ratio (n) of the concentration of vinylic unsaturations to that of the norbornene units. Indeed, the conversion of PB macromonomers exhibiting a same molar mass were found to depend on their vinyl content ; the highest conversions being obtained for the lowest values of n (table 1). Eventhough the bicyclic norbornene unsaturations exhibit a far higher reactivity toward carbenic species than 1,2-vinyl unsaturations, the presence of the latters in a greater proportion gives little chances for the terminal norbornene to polymerize to completion. As the rate constant of the ring-opening process (k_{nor}) is undoubtedly significantly higher than that of transfer to 1,2-unsaturations, the propagation is certainly favored at the early stages of reaction. But the decrease in the concentration of norbornene with conversion entails a second phase during which the rates of propagation and transfer tend to become comparable. Upon metathesis with 1,2-unsaturations, the growing metalla-alkylidenic species are likely to evolve into metalla-methylidenes : as the latter species are of rather high reactivity, the side reactions with acylic double bonds that were undetected during the first stage are likely to occur in this second phase, limiting the conversion to moderate values.

Table 1. Characteristics of PB polymacromonomers ($\overline{DP}_n = 10$) obtained from PB macromonomers of almost same molar mass but different vinyl content (polymerization time : 1h)

$\overline{M}^{a)}_{n,macro.}$ (%1,2) SEC g/mol.	n$^{b)}$	conversion$^{c)}$ %	$\overline{M}n^{d)}$ targeted g/mol.	$\overline{M}_n^{e)}$ LS g/mol.	$\overline{M}w/\overline{M}n$ SEC
4700 (13)	11	88	41300	33400	1.29
4700 (56)	49	67	31500	27400	1.54
8200 (13)	20	80	65600	53400	1.54
8400 (28)	43	68	57100	45000	2.16

a) molar mass of macromonomer with its 1,2- vinyl content (%)

b) ratio of the concentration of 1,2-vinyl double bonds to that of norbornenyl unsaturations

c) conversion obtained by deconvolution of the peaks due to PB macromonomer and to polymacromonomer in SEC eluograms

d) $\overline{M}_{n\ targeted} = \overline{M}_{n\ macro} \times \overline{DP}_n \times$ conversion

e) molar masses obtained from SEC equipped with a laser light scattering (LS) detector

Experiments were carried out with macromonomers of low vinyl content to investigate the influence of the $\overline{DP}_n$ targeted on the conversion ; the results obtained showed that conversion can rise to quite high values regardless of the amount of initiator used (table 2).

This cheerful result obtained for the homopolymerization of ω-norbornenyl PB macromonomers (Ref. 7) prompted us to attempt both the sequential and the statistical copolymerization of these latter macromonomers with α-norbornenyl PS macromonomers.

Table 2. Polymerization of PB macromonomer of different $\overline{DP}_n$' s

$\overline{M}^{a)}_{n,macro.}$ (%1,2) SEC g/mol.	$n^{b)}$	$\overline{DP}n$ targeted	conversion$^{c)}$ %	$\overline{M}_n{}^{d)}$ targeted g/mol.	$\overline{M}n^{e)}$ LS g/mol.
1800 (14)	5	10	95	17100	28000
		25	95	42750	42900
		50	96	86400	84600
4700 (13)	11	10	88	41300	33400
6900 (12)	15	10	81	55900	58900
		25	85	147000	111000
8200(13)	20	10	80	65600	53400
		25	85	174000	165000

a, b, c, d, e : same as in table 1

III) Copolymerization of ω-norbornenyl PB macromonomers with α-norbornenyl PS macromonomers

The data pertaining to the two PB and PS macromonomers that were used in the copolymerizations are given in table 3. Only PB macromonomers exhibiting a small value of n were copolymerized with macromonomers of PS of about the same molar mass, so as to limit the occurrence of transfer reactions in accordance with the results previously commented on.

Table 3. Characteristics of ω-norbornenyl PB and α-norbornenyl PS macromonomers.

Macromonomer	$\overline{M}_{n,macro.}$ targeted g/mol.	$\overline{M}_{n,macro.}$ a) SEC g/mol.	$\overline{M}_w / \overline{M}_n$ SEC	$\overline{M}_n$ ^1H NMR g/mol.
PB	1800 (13)[b] (5)[c]	2160	1.05	2200
PS	1800	1620	1.16	1500

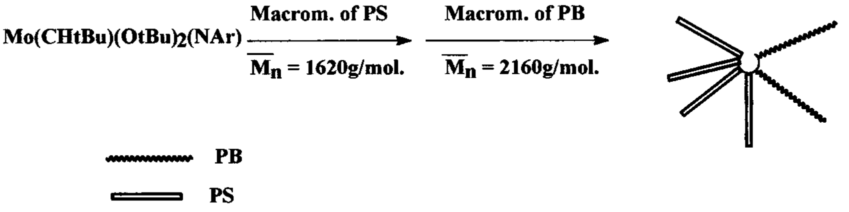
a) calibration by PS linear standards for PS macromonomers and PB linear standards for PB macromonomers

b) percent of 1,2-vinyl content of PB macromonomer determined by ^1H NMR

c) ratio (n) of the concentration of 1,2-vinyl double bonds to that of norbornenyl unsaturations measured by ^1H NMR

III-1) Sequential copolymerization of PS and PB macromonomers

Three copolymers were synthesized by sequential ROMP of PS and PB norbornene-ended macromonomers (table 4). These copolymacromonomers were prepared as illustrated in scheme 3.



Scheme 3. Sequential copolymerization of PS and PB macromonomers

PS macromonomer in toluene solution was first added to the toluene solution containing the Schrock complex. The polymerization of the macromonomer was complete within 30 minutes. The PB macromonomer in toluene solution was then added to the living PS polymacromonomer. After complete conversion of the second macromonomer (2h), a small amount of benzaldehyde was introduced in the reaction medium so as to deactivate the growing carbenes in a Wittig-type reaction. Analyses of the medium aliquot by SEC, prior to the introduction of PB macromonomer and after polymerization of the latter, shows that conversions of both macromonomers came close to unity, regardless of the PS/PB ratio used (table 4).

Table 4. Characteristics of $(\text{N-PB})_n$-b-$(\text{N-PS})_m$ block copolymacromonomers from SEC equipped with a light-scattering detector.

PS/PB/ Initiator	% PB targeted	Conversion %	$\overline{M}_n$ [a] targeted g/mol.	$(\frac{\delta n}{\delta c})$ targeted	$(\frac{\delta n}{\delta c})$ exp.	$\overline{M}_n$ [b] LS g/mol.	$\overline{M}_w / \overline{M}_n$ SEC
25/22.5/1	55	90	89100	0.155	0.149	88200	1.41
10/25/1	77	100	70200	0.145	0.142	68600	1.45
25/10/1	35	100	62100	0.168	0.165	87800	1.32

a) $\overline{M}_{n,\text{targeted}} = 1620.\overline{DP}_{n,PS} + 2160.\overline{DP}_{n,PB}$

b) molar masses obtained from SEC equipped with a LS detector

SEC chromatograms of the final aliquot evidence a marked shift towards shorter elution volume of the peak due to the copolymer and do not exhibit any broadening or shoulder that would be indicative of unexpected deactivation (figure 1). Moreover, analyses by ^{1}H NMR of the resulting copolymers corroborate the initial PS/PB composition.

For the measurement of the actual molar masses of these copolymers, it was resorted to laser light scattering ; their refractive index increment was determined by classical methods and compared with theoretical values (table 4). These latter values were obtained assuming that the refractive index increment varies as a linear function of their composition : $\frac{\delta n}{\delta c} = \omega_{PB}(\frac{\delta n}{\delta c})_{PB} + \omega_{PS}(\frac{\delta n}{\delta c})_{PS}$, where ω_{PB} and ω_{PS} refer to the weight fractions of PB and PS respectively. The good agreement observed between experimental and theoretical refractive index increments, associated with the excellent correspondence between experimental and targeted molar masses suggest that these copolymer samples exhibit little -if any- heterogeneity in composition.

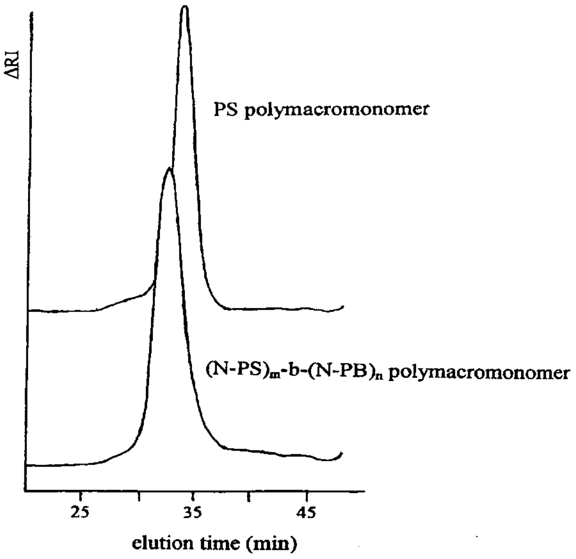
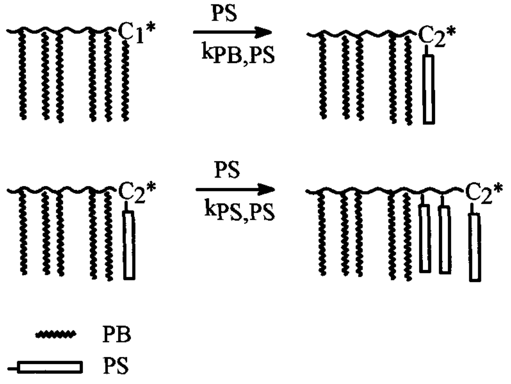


Figure 1. SEC traces of the polymacromonomer obtained from the sequential polymerization of PS-norbornene and PB-norbornene macromonomers.

The order of polymerization of macromonomers appears to be essential for a complete crossover to occur when adding the second type of macromonomers. Indeed, substitution of PB for PS, as first macromonomer polymerized, brought about marked changes. As a matter of fact the sequential addition of PB and then of PS macromonomers resulted in their complete polymerization but the SEC chromatogram of the final compound exhibited a bimodal distribution. The peak corresponding to the first block of PB polymacromonomer has not completely disappeared. It seems that not all carbenic species carried by PB polymacromonomers were able to initiate polymerization of PS macromonomers. Repeated polymerizations did afford the same result.

The lower reactivity of the metalla-alkylidenic species carried by the PB polymacromonomer compared to that exhibited by the carbenes borne by the PS chains could be responsible for this behavior : the propagation rate constant ($k_{PS,PS}$) may indeed be higher than the crossover rate constant ($k_{PB,PS}$) (scheme 4).

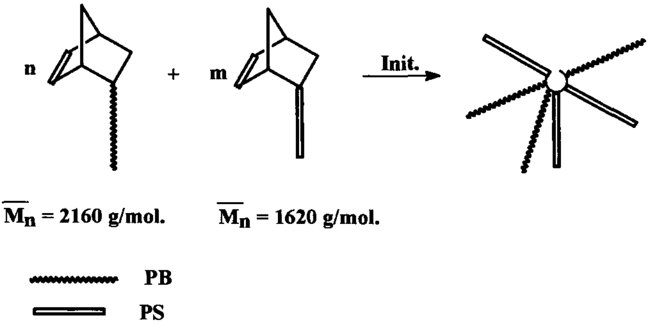


Scheme 4. Block copolymerization of PS macromonomer initiated by PB-based active centers

It is therefore essential to first polymerize the macromonomer of PS before adding the macromonomer of PB in order to obtain (Norbornene-PS)$_m$-b-(Norbornene-PB)$_n$ copolymer of homogeneous composition and non contaminated with homopolymers.

III-2) Statistical copolymerization of PB and PS macromonomers

Three copolymers corresponding to various ratios of PB/PS macromonomers were synthesized by statistical copolymerization (table 5). The two macromonomers were mixed together in toluene and subsequently added to Schrock complex according to scheme 5.



Scheme 5. Statistical copolymerization of PS and PB macromonomers

After 10 minutes of reaction, benzaldehyde was added to the reaction medium to quench active growing species and the copolymer was recovered by precipitation in methanol. In the three cases, complete conversion of both PS and PB macromonomers was achieved as checked by SEC connected to UV and RI detectors. The eluograms exhibit narrow and symmetrical distributions. It was not possible in this series of experiments to conclude whether the copolymerization of the two macromonomers occurred statistically and exhibited a tendency for the formation of blocks.

The polymacromonomer samples were also analyzed by SEC coupled with a laser light scattering. The molar masses obtained were found to be in good agreement with the targeted values.

Table 5. Characteristics of $(N\text{-}PS)_m\text{-co-}(N\text{-}PB)_n$ statistical copolymacromonomers from SEC equipped with a light-scattering detector.

PS/PB/ Initiator	% PB targeted	Conversion %	$\overline{M}_n$ a) targeted g/mol.	$(\frac{\delta n}{\delta c})$ targeted	$(\frac{\delta n}{\delta c})$ exp.	$\overline{M}_n$ b) LS g/mol.	$\overline{M}_w / \overline{M}_n$ SEC
25/25/1	55	99	93500	0.156	0.153	96300	1.61
25/10/1	35	100	62100	0.169	0.169	61000	1.44
10/25/1	77	98	68800	0.149	0.144	57800	1.36

a,b : same as in table 4

IV) DSC characterization of PS/PB block copolymers

Polystyrene and polybutadiene are two moderately incompatible polymers. Their interaction parameter χ is positive (0.1) but rather small so that the two polymers form homogeneous blends as long as their $\overline{DP_n}$'s do not approximately exceed 20 (Ref. 8).

For instance, a homogeneous blend with only one glass transition temperature (T_g) was found upon mixing PS and PB macromonomers of 2000 g/mol. molar mass (table 6). In linear diblock copolymers constituted of PS and PB, a homogenous disordered phase can be found up to polymerization degrees (N) of 100 (Ref. 9). Because of the presence of a permanent junction between the blocks, macrophase separation is prevented and the scale of phase separation is restricted to tens of nanometers domain size. The Leibler theory (Ref. 9) predicts that the disordered-ordered transition occurs roughly in linear symmetrical diblocks (f = 0.5) for $\chi N = 10.5$: PS-b-PB copolymers of symmetrical composition separate into microdomains only above molar masses of 8000 g/mol.

The DSC characterization and the DMA of such linear diblocks shows that such copolymers produce three mesophases characterized by three different T_g's. In addition to the domains that contain essentially pure polystyrene and polybutadiene an interphase with its own glass transition temperature (58-60°C) apparently develops at the interface between the two blocks.

The situation appears quite similar for PS/PB block copolymers that were prepared by sequential copolymerization of the two macromonomers. A transition (T_g = 100°C) due to the pure PS phase is indeed seen, at least for the sample containing 65 weight percent of PS, as well as that corresponding to pure polybutadiene (T_g = -94°C). A third phase that can be attributed to the interphase region (T_g = 40-60°C) where the two types of macromonomers extensively mix each other also occurs.

As to the copolymers that were obtained by statistical copolymerization of the two macromonomers, only one sample was characterized. The sample containing 70 % of PS and 30 % of PB exhibited only one T_g, in sharp contrast with the behavior observed for copolymers of almost same composition but prepared by sequential polymerization of corresponding macromonomers. This last result shows that each polymacromonomer structure develops peculiar topological constraints that in turn affect the extent and the type of microphase separation occurring. Amazingly, the results of the copolymerization of PS and PB macromonomers appears not different from the copolymers that are obtained by sequential, and statistical copolymerizations of two micromolecular comonomers : blocky systems are generated by sequential polymerization whereas homogeneous disordered phases arise through statistical copolymerization. Unfortunately no thermodynamic rationale that would account for the interplay of the enthalpic contributions and the effects due to configurational entropy or the block sizes in this kind of topologies has been developed yet. However, this preliminary study encourages to carry on this investigation and particularly the characterization of the morphologies formed by electron microscopy.

Table 6. T_g's of different topologies based on PS and PB (determined by DSC)

Structure	PS/PB composition ^{1}H NMR (%w/w)	Molar mass g/mol.	Tg_1 °C	Tg_2 °C	Tg_3 °C
PS macromonomer	100/0	1620$^{a)}$	-	-	75
PB macromonomer	0/100	2160$^{a)}$	-94	-	-
PS/PB macrom.blend	50/50	1620/2160	-	-79	-
PS-b-PB linear	50/50	4400$^{a)}$	-	-68	-
PS polymacromonomer	100/0	41000$^{b)}$	-	-	88
PB polymacromonomer	0/100	61000$^{b)}$	-89	-	-
PS/PB polymacrom. blend	50/50	41000/61000	-90	-	100
PS-b-PB linear	65/35	80000$^{b)}$	-90	58	100
$(N\text{-}PS)_m\text{-}b\text{-}(N\text{-}PB)_n$ polymacrom.	45/55	88200$^{b)}$	-89	60	*
$(N\text{-}PS)_m\text{-}b\text{-}(N\text{-}PB)_n$ polymacrom.	20/80	68600$^{b)}$	-90	40	*
$(N\text{-}PS)_m\text{-}b\text{-}(N\text{-}PB)_n$ polymacrom.	65/35	87800$^{b)}$	-94	58	100
$(N\text{-}PS)_m\text{-}co\text{-}(N\text{-}PB)_n$ polymacrom.	70/30	61000$^{b)}$	-	40	-

a) $\overline{M}_n$ determined from ^{1}H NMR

b) $\overline{M}_n$ determined from SEC equipped with a LS detector

* not detected because of lack of precision

EXPERIMENTAL PART

Materials

Toluene was distilled from sodium-benzophenone. Mo(NAr)(CHtBu)(OtBu)$_2$ was synthesized according to a literature method (Ref. 10).

Methods

All reagents were stored and used under inert atmosphere.

Ring-opening metathesis polymerizations were carried out in a glove box under moisture-free conditions. NMR spectra were recorded 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 detector and a JASCO 875 UV/VIS absorption detector, THF being the mobile phase. The columns were calibrated with polystyrene or polybutadiene standards. The actual molar masses of the copolymer samples were calculated from the response of the multiangle laser light scattering detector (Wyatt Technology) that was connected to SEC.

Blends, used as references in DSC analyses, were prepared by the dissolution/precipitation method. The DSC and DMA studies were realized with a Perkin Elmer DSC7 calorimeter and a Perkin Elmer DMA7 analyzer respectively equipped with Perkin Elmer TAC 7/DX thermal analysis controllers. Samples were heated at a heating rate of 10°C/min.

PB and PS macromonomer syntheses

These syntheses were performed according to procedures described in previous papers (Ref. 4, 7).

Homopolymerization of norbornene-ended PB macromonomers

14 μmol of catalyst (I, II, IV) was weighed and introduced into a flask containing 2 mL of toluene. $14 \cdot 10^{-5}$ mol. of the macromonomer ($\overline{M}_n = 4700\ \mathrm{g/mol}$) 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 given times of polymerization by addition of 0.1 mL of benzaldehyde. Precipitation by methanol yielded the pure polymacromonomer.

With catalyst III, 0.009 g ($1.5 \cdot 10^{-5}$ mol) of (p-cymene) ruthenium (II) chloride dimer, 0.017 g ($6 \cdot 10^{-5}$mol) of tricyclohexylphosphine and $1.5 \cdot 10^{-4}$ mol of the macromonomer ($\overline{M}_n = 1800\ g/mol$) were dissolved in 5 mL of chlorobenzene. 0.012 g ($10 \cdot 10^{-5}$ mol) of (trimethylsilyl)diazomethane in solution in 5 mL of chlorobenzene was added to the macromonomer solution under stirring. The polymerization medium was heated at 333 K for a few minutes. Deactivation of the medium was performed by addition of 0.1 mL of benzaldehyde.

Sequential copolymerization of PS and PB macromonomers

In a typical experiment, 368 mg ($2.27 \cdot 10^{-4}$ mol.) of PS macromonomer ($\overline{M}_n = 1620\ g/mol$) were first polymerized at room temperature in 10 mL of toluene in the presence of 5 mg ($9.09 \cdot 10^{-6}$ mol.) of the Schrock-type complex. After 30 minutes, 491 mg ($2.27 \cdot 10^{-4}$ mol) of PB macromonomer ($\overline{M}_n = 2160\ g/mol$), dissolved in 2 mL of toluene, were introduced in the reaction medium. After polymerizing PB macromonomer during 2 hours, 0.1 mL of benzaldehyde was added to deactivate the metalla-alkylidenic species. Precipitation in methanol gave rise to the expected block copolymacromonomer.

Statistical copolymerization of PB and PS macromonomers

In a typical experiment, 368 mg ($2.27 \cdot 10^{-4}$ mol.) of PS macromonomer ($\overline{M}_n = 1620\ g/mol$) and 491 mg ($2.27 \cdot 10^{-4}$ mol.) of PB macromonomer ($\overline{M}_n = 2160\ g/mol$) were dissolved together in 8 ml of toluene and then poured into the flask containing the toluene solution of 5 mg ($9.09 \cdot 10^{-6}$ mol.) of the Schrock-type complex. Deactivation of the reaction medium was performed after 10 minutes of polymerization by addition of 0.1 mL of benzaldehyde. The statistical copolymacromonomer was recovered by precipitation in methanol.

PS-b-PB linear diblock copolymer syntheses

Firstly, styrene was anionically polymerized in toluene at room temperature using *sec*-butyllithium as initiator. Subsequently the PB block was grown by polymerization of butadiene initiator by the living polystyryl anions. The expected copolymer was obtained by deactivation of polybutadienyl anions with methanol.

CONCLUSIONS

This paper shows that the ROMP of macromonomers is a powerful tool to assemble chains in unprecedented topologies. Macromonomers of PS and PB were copolymerized sequentially and statistically to complete conversion. These copolymers exhibit quite different phase separation behavior, because the two types of copolymerization reactions induce peculiar topological constraints.

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