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Synthesis of Well-Defined Star Block Copolymers Using 1,1-Diphenylethylene Chemistry

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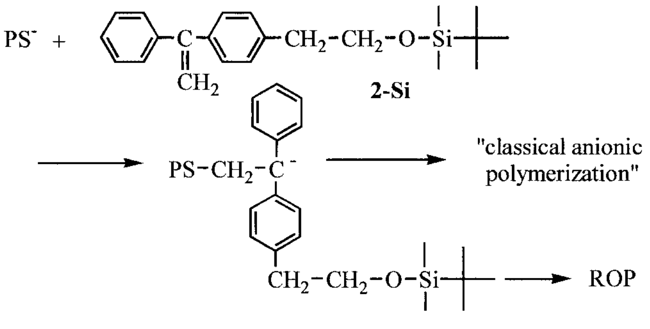
Summary: We described the use of 1,1 diphenylethylene derivatives in the synthesis of well-defined star block copolymers. Classical end-capping of polystyryl carbanion with $-CH_2CH_2OTBDMSi$ derivative gives a heterobifunctional macroinitiator leading to ABC star block copolymers through successive anionic and ring opening polymerizations (ROP) or anionic and atom transfer radical (ATRP) polymerizations. An unexpected reaction between polystyryl carbanion and $-CH_2OTBDMSi$ derivative, strongly depending on the medium polarity, opens an easy way to either A_2B or A_3B star block copolymers.

Introduction

At the present time, the only strategy leading to A_2B, A_3B and ABC star block copolymers is the selective step-by-step coupling reaction on trichloromethylsilane and tetrachlorosilane. A_2B[1-4], A_3B[5] and ABC[6] were so obtained. Besides these coupling reactions, the other main access to star block copolymers with complex and well-defined architectures uses the chemistry of 1,1 diphenylethylene derivatives through non-homopolymerizable macromonomer[7-9] or heterobifunctional macroinitiator[10,11] ways. This heterobifunctional macroinitiator, that we have recently developped, was obtained by end-capping a polystyryl K (or Li) by **2-Si** derivative (scheme 1).

Scheme 1: ABC star block copolymers using a heterobifunctional macroinitiator



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The resulting carbanion initiated a classical anionic polymerization and the hydroxy function, obtained after deprotection, was used to initiate a ROP.

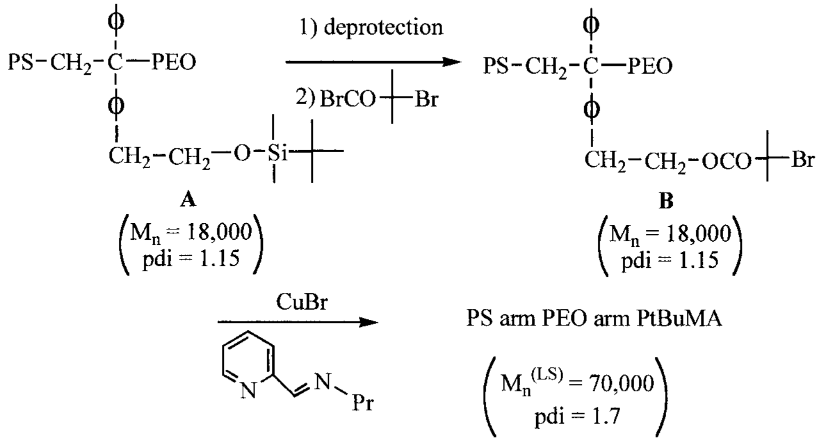
In this paper, we described the use of two 1,1 diphenylethylene derivatives in order to obtain various well-defined star block copolymers.

Results and discussion

The main advantage of the heterobifunctional macroinitiator way is to avoid polymer coupling but one limitation is the presence of side reactions as mentionned in the synthesis of PS arm PtBuMA arm PEO star block copolymer.[12] Starting from **2-Si**, we have polymerized tBuMA through a classical anionic way, leading to a PS-b-PtBuMA intermediate. After deprotection, we have initiated the ROP of ethylene oxide. We have obtained a mixture of the expected star block copolymer and the previous diblock copolymer, resulting from an intramolecular transesterification on a tBu ester group.

In order to obtain a pure and well-defined product, we have used an alternative strategy allowing to polymerize tBuMA in the last step (scheme 2).

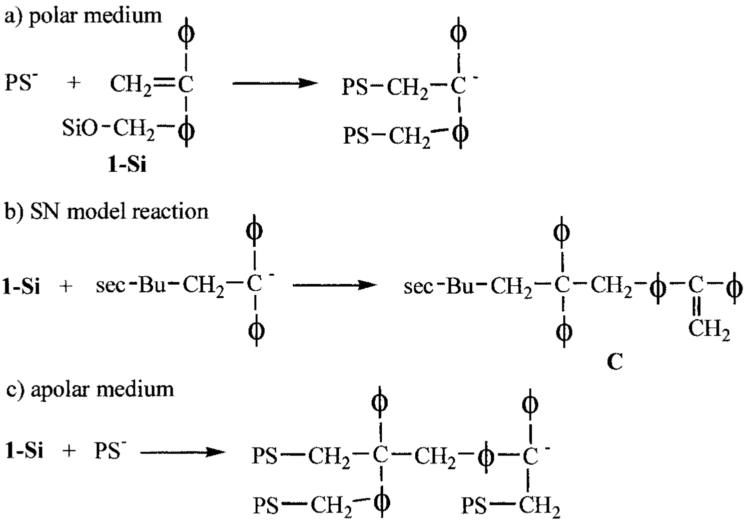
Scheme 2: ABC star block copolymer via anionic polymerization and ATRP



Starting from the heterobifunctional macroinitiator, we have first polymerized EO and desactivated the living alcoolate with benzyl bromide. After deprotection, the PS-b-PEO (**A**) block copolymer was functionalized by reaction of 2-bromo isobutyryl bromide[13] on the hydroxy group, generating an ATRP macroinitiator (**B**). The polymerization of tBuMA was run in toluene at 80°C, using CuBr/pyridylmethanimine[14] as catalyst and has led to the expected star block copolymer with nevertheless a strong increase of the polydispersity index.

We have also synthesized a new 1,1 diphenylethylene derivative (**1-Si**) with only one CH_2 between the oxygen and the phenyl ring.. We have described an unexpected reaction between **1-Si** and PSLi (or K), leading in THF at –50°C to the addition of two PS chains on the diphenylethylenyl carbanion.[15] This reaction allowed the synthesis of A_2B star block copolymer in only two steps (scheme 3a).

Scheme 3: Different reactions between **1-Si** and carbanions



If the same reaction was run in an apolar medium (toluene/THF, v/v = 10/1), we observed a triple addition of the polystyryl carbanion instead of the double obtained in THF.[16] This new reaction implied several diphenylethylene derivatives as the addition of three carbanions on one **1-Si** was impossible. The only hypothesis involved a nucleophilic substitution (SN) on the benzylic carbon of **1-Si**. This hypothesis was checked by running a model reaction (scheme 3b). After one hour at –50°C, we have observed the total disappearance of the siloxy group and the quantitative obtention of **C**.

A second series of model reaction between **1-Si** and secBuLi allowed to propose a mechanism for the reaction of PSLi and **1-Si** in an apolar medium. A series of addition and substitution reactions of two **1-Si** and three PSLi (scheme 3c) has led to a diphenylethylenyl carbanion.

Different medium compositions have been used and the change in multi PS structure occured in the range 20-30% of THF in the solvent mixture. It appeared that the THF content was critical to obtain only one type of structure (double or triple PS chains). Such critical value was also observed in the functionalization reaction of PSLi with CO_2.[17] This peculiar result could be linked to the nature of the ions pairs, which are tight or loose in low or high THF content respectively.[18]

In polar or apolar medium, the 1,1 diphenylethylenyl carbanion bearing two or three PS chains was able to initiate a second polymerization. In table 1, we have reported the characteristics of PS_2PEO and PS_3PEO star block copolymers obtained by this way. When the polymerization was run in toluene with Li as counterion, a phosphazene base ($tBuP_4$)[19] was added just before EO in order to active its polymerization.

Table 1: Characteristics of PS_2PEO and PS_3PEO star block copolymers.

Counter ion	Solvent	PS	Multi PS		Star block copolymer			
		M_n^{RI} (pdi)	M_n^{RI} (pdi)	M_n^{LS}	Struct.	M_n^{RI} (pdi)	M_n^{LS}	M_n d)
K a)	THF	11,200 (1.14)	22,000 (1.25)	24,200	PS_2PEO	40,200 (1.28)	70,200	61,100
Li b)	Toluene /THF	10,300 (1.17)	33,400 (1.20)	35,200	PS_3PEO c)	61,500 (1.40)	200,000	171,900

a) initiator = phenyl isopropyl potassium
b) initiator = sec-BuLi
c) addition of $tBuP_4$ before EO polymerization with $[tBuP_4]/[carbanion]=1.1$
d) determined by both ^1H NMR and SEC analysis

Conclusion

The use of 1,1 diphenylethylene derivatives has led to well-defined star block copolymers through a large range of reactions. Classical end-capping of a living PS chain with derivatives bearing a protected function (such as $-CH_2CH_2TBDMSi$) was suitable to obtain ABC star block copolymer, whereas unexpected reactions on $-CH_2TBDMSi$ and strongly depending on the medium, have opened an easy route to A_2B and A_3B star block copolymers.

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