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Synthesis of three-arm star block copolymers

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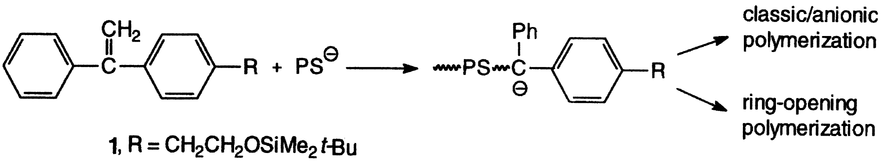
SUMMARY: We describe the synthesis and characterization of three-arm star block copolymers based on polystyrene, poly(ethylene oxide), poly(ε-caprolactone), poly(methyl methacrylate), poly(*tert*-butyl methacrylate) and poly(L-lactide) blocks. The copolymers were obtained by a route consisting of two successive initiation steps on functional macroinitiator. Some results on micellization and crystallization are given. They indicate an increase in the miscibility of different incompatible blocks.

Introduction

An important thrust in modern macromolecular chemistry is to construct complex architectures such as dendrimers, self-organized polymers or multiarm star block copolymers.

Two strategies have been developed for the synthesis of such multiarm (also called heteroarm or miktoarm) star block copolymers. The first one[1)] consists in sucessive reactions of a multifunctional chlorosilane with active chain ends of different living polymers. The other strategy is based on the macromonomer technique: a living anionic polymer of the first monomer is coupled with a non-homopolymerizable macromonomer of the second monomer; the anionic polymerization of the third monomer is then started from the active site to form the third arm. 1,1-Diphenylethene[2-4)] or 1,3-bis(2-phenylethyn-1-yl)benzene (MDDPE)[5)] was used as a non-homopolymerizable macromonomer.

In order to avoid reactions between polymeric species involved in these two strategies, often problematic, we developed a new route[6,7)] with two successive initiation steps on a bifunctional macroinitiator, obtained by end-capping of polystyrene-potassium (or polystyrene-lithium) by the 1,1-diphenylethene derivative **1**, R = $CH_2CH_2OSiMe_2t$-Bu (Scheme 1).



Scheme 1

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The carbanion initiates the "classic" anionic polymerization of methacrylic monomers, methyl (MMA) or *tert*-butyl (*t*-BuMA) methacrylate, ethylene oxide (EO) and ε-caprolactone (CL). After deprotection, the hydroxy function initiates a ring-opening polymerization (ROP) of EO and CL through an alcoholate or of L-lactide (LL) through an alkoxide.

This leads to well defined three-arm star block copolymers of high molecular weight (up to 260 000, polydispersity around 1.2) without any measurable amounts of homopolymers or diblock copolymers.

Results and discussion

Synthesis and characterization of 3-*star*-[polystyrene; poly(ethylene oxide); poly(ε-caprolactone], 3-*star*-[polystyrene; poly(methyl methacrylate); poly(ethylene oxide)] and 3-*star*-[polystyrene; poly(ethylene oxide); poly(L-lactide)] have been described[6,7]. These amphiphilic copolymers contain one hydrophilic block (PEO). In order to introduce a second one, we have used easily hydrolysable *tert*-butyl methacrylate.

First, we have therefore synthesized the bifunctional macroinitiator (in THF at -60 °C, with Li as counterion) and then initiated the polymerization of *tert*-butyl methacrylate. After removing the silyl protecting group, (diphenylmethyl)potassium is added in order to obtain alcoholate which initiates the EO polymerization. In all cases, we obtained a mixture of the expected star polymer and the original diblock PS – P*t*-BuMA.

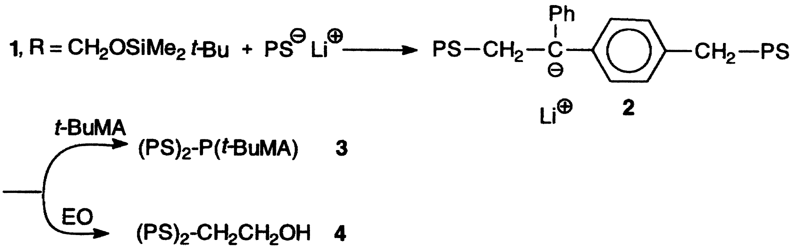
This partial initiation of EO polymerization is not caused by steric problems: the alcoholate formed is accessible since the corresponding Sn alkoxide initiates the L-lactide polymerization[8]. Starting from a diblock with M_n 29 000, PS 17 400, P*t*-BuMA 11 600 and polydispersity 1.15, we obtain 3-*star*-[polystyrene; poly(*tert*-butyl methacrylate); poly(L-lactide)] having M_n 39 300 and polydispersity 1.20, without any measurable amount of the original diblock copolymer.

This partial initiation of the EO polymerization is probably due to the possibility of an intramolecular transesterification between the starting alcoholate (less reactive for EO initiation than the growing PEO chain[9]) and the *tert*-butyl ester group since we recover the original diblock copolymer without measurable modification.

As this way is not suitable for the synthesis of stars containing simultaneously PEO and P*t*-BuMA blocks, we synthesized a PEO macromonomer with a 1,1-diphenylethene extremity in order to use the macromonomer strategy. As the reaction between **1**, R = CH_2CH_2Cl and living PEO leads mainly to elimination[10], we synthesized **1**, R = $CH_2O(CH_2CH_2O)_nCH_3$ by coupling living PEO and a new 1,1-diphenylethene derivative, **1**, R = CH_2Cl. Reaction of polystyrene-lithium, with the macromonomer in THF at -60 °C, followed by addition of *t*-BuMA does not lead to the expected star, 3-*star*-[polystyrene; poly(ethylene oxide); poly(*tert*-butyl methacrylate)] but to a mixture of 3-*star*-[polystyrene; polystyrene; poly(*tert*-butyl methacrylate)] (A_2B star) and PEO. A study of the first stage of this reaction shows elimination of $^{-}O(CH_2{-}CH_2{-}O)_n{-}CH_3$ and a double addition of PS^{-} on the 1,1-diphenylethene derivative. One carbanion remains which can initiate the *t*-BuMA polymerization.

The same reaction (in THF at -60 °C) is also observed with the silyl derivative **1**, R = CH_2OSiMe_2*t*-Bu either with *s*-BuLi or polystyrene-lithium. The reaction between **1**, R = CH_2OSiMe_2*t*-Bu and *s*-BuLi permits to characterize the final product (NMR and MS) and thus to propose a mechanism$^{8)}$ for this 1,6-elimination and the second addition of carbanion. A similar 1,6-elimination was already reported for some styrene derivatives$^{11)}$.

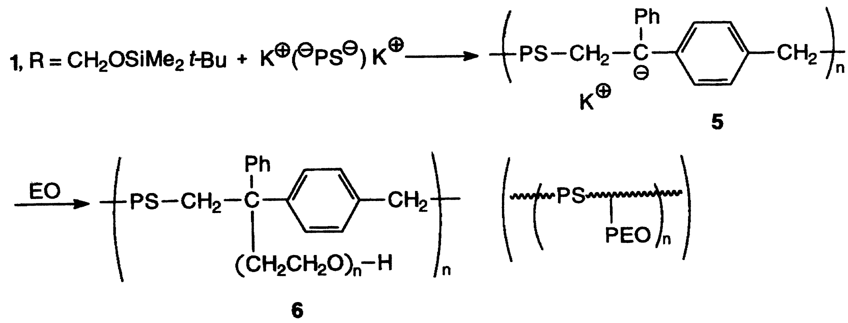
New complex architectures can be obtained by reaction of living polystyrene with **1**, R = CH_2OSiMe_2*t*-Bu (see Scheme 2 and Table 1). **2** with lithium counter-ion can initiate the polymerization of *t*-BuMA leading to a A_2B star **3** or to a polystyrene functionalized in the middle of the chain, **4**.



Scheme 2

This addition-elimination reaction on **1**, R = CH_2OSiMe_2*t*-Bu does not depend on the nature of the counter-ion. The same behavior was also observed with potassium (see Scheme 3 and Table 1).

Reaction of difunctional polystyrene-potassium with **1**, R = CH_2OSiMe_2*t*-Bu in THF at -60 °C proceeds as a step polymerization and leads to a polyanion **5** ($n \approx 7$) which initiates the polymerization of EO. Finally, a model of graft copolymer PS-*g*-PEO **6** is obtained.



Scheme 3

Table 1: Characteristics of star block copolymers and intermediates

Product	PS-Li	2	3	4	K-PS-K	5	6
M_n [a)]	5 500	12 300	16 700	12 300	3 000	20 000	96 000
Polydispersity [b)]	1.16	1.20	1.20	1.20	1.15	1.9	2.0

[a)] Using ^{1}H NMR and M_n (SEC) of the PS precursor; [b)] by SEC

Properties of star block copolymers

We will describe now some results on solid-state and solution properties in order to point out the effect of the star structure on copolymer properties.

Solid- state properties

We have studied the structure and the dynamics of structure formation in a star containing two crystallizable polymers, 3-*star*-[polystyrene; poly(ethylene oxide); poly(ε-caprolactone)] [12)]. The main conclusions are:

- Both blocks can crystallize in the stars provided that their length ratio is below 3, in contrast to the homologous diblocks[13)].

- The reduction in the equilibrium melting temperature in the stars is caused primarily by the amorphous PS block. The star structure further reduces the $T_m{}^0$ but to a smaller extent.

Different superstructures were formed (spherulites/axialites) depending on the type of crystallizable block (PEO/PCL). The nucleation sites of the two superstructures were entirely independent suggesting a heterogeneous distribution of star molecules with PEO or PCL crystals. This heterogeneous distribution implies the existence of a kind of macrophase separation between unlike crystals.

From the growth rates of the superstructures, the fold surface Gibbs energies were obtained indicating a neat PEO crystal and mixing of the amorphous PS block within the PCL crystal. This conclusion was supported by the results of the atomic force microscopy in thin films which have indicated the formation of perforated PCL crystals.

Micellization

It is well known that amphiphilic block copolymers like PS-*b*-PEO form micelles in water. The core of the micelle is the collapsed PS and the chains stretched in water are PEO. In the case of micellization of stars in water, we have a new situation: there are two hydrophobic blocks, PS and PMMA. In order to obtain micelles, these two incompatible blocks must be confined in the core of a micelle.

Dynamic light scattering studies demonstrate the formation of micelles especially for high PEO contents10). For example, the micellization of the 3-*star*-[polystyrene; poly(methyl methacrylate); poly(ethylene oxide)] containing 66 % of PEO (M_n 19 000, DP_{PS} 40, DP_{PMMA} 26 and DP_{PEO} 289) leads to the formation of micelles with a hydrodynamic radius $R_H = 16 \pm 2$ nm.

An empirical relationship between the size of each block and the R_H of the micelle was established for PEO-PS diblock copolymers14):

$$R_H\,(\mathrm{nm}) = 0.98\,DP_{PS}^{0.75} \,.\, DP_{PEO}^{-0.17} + 0.76\,DP_{PS}^{-0.53} \,.\, DP_{PEO}^{0.74}$$

Using this relationship, we are able to calculate the size of micelles obtained from a hypothetic PS-PEO diblock having as a whole the same hydrophilic and hydrophobic blocks as our three-arm star, e.g., with DP_{PEO} 289 and $DP_{"PS"}$ 66, the sum of DP_{PS} 40 and DP_{PMMA} 26. We obtain $R_H = 14$ nm, which is very close to 16 nm, the experimental value for the three-arm star micelles. This means that in our three-arm stars, the PMMA block acts as the PS block in chemical contribution to the size of the micelle.

In two cases, it appears that star structure implies an increase in miscibility between the incompatible blocks.

Conclusion

We have described a route to three-arm star block copolymers through a bifunctional macroinitiator and showed the potential of this strategy for the synthesis of star copolymers. The main effect of the star structure is an increase in the miscibility of different incompatible blocks.

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