

Synthesis of amphiphilic triarm star block copolymers

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Received: 3 November 1997/Revised version: 1 December 1997/Accepted: 2 December 1997

Summary

We describe the synthesis and the characterization of amphiphilic triarm star block copolymers based on polystyrene, poly(methyl methacrylate), poly(ϵ caprolactone), poly(L lactide) and poly(ethylene oxide) blocks.

This synthesis has been achieved by a new route consisting in 2 successive initiation steps on a core molecule (a 1,1 diphenyl ethylene derivative bearing a protected hydroxy function) located at the end of a first block.

Some results on adsorption onto TiO_2 and micellization studies are given. Preliminary results on solid state indicate an increase of the miscibility of the different incompatible blocks.

Introduction

In addition to linear ABC triblock copolymers, the synthesis of starblock copolymers with sequences of different natures has been one of the challenges in anionic polymerization for the last few years. This type of copolymers is commonly called heteroarm, miktoarm and triarm starblock copolymers. Two strategies have been developed for the synthesis of such heteroarm starblock polymers.

The first one is based on a macromonomer technique : a living anionic polymer of the first monomer is coupled with a macromonomer of the second monomer; the anionic polymerization of the third monomer is then started from the active site to form the third arm. The synthesis of polystyrene - *arm* - poly(dimethylsiloxane) - *arm* - poly(*tert* - butyl methacrylate), polystyrene - *arm* - polybutadiene - *arm* - poly(methyl methacrylate) and polystyrene - *arm* - poly(ethylene oxide) - *arm* - poly(*tert*-butyl methacrylate) triarm star copolymers have been reported by Fujimoto et al (1), Stadler et al (2) and Quirk et al (3), respectively. In this way, it is possible to introduce many types of structure however there are some difficulties. It needs a completely functionalized macromonomer, a perfect control of the stoichiometry of the reaction between the living polymer and the macromonomer (the course of the reaction must be monitored by SEC) and there is some limitation in the molecular weight of the macromonomer. Until now, the molecular weight of the macromonomer does not exceed 33 000.

The second strategy, developed by Hadjichristidis et al (4), consists in subsequent reactions of a multifunctional chlorosilane with the active chain ends of different living polymers. Starbranched ternary and quaternary polymers of the ABC, A_2B_2 and ABCD types, based on polystyrene, polybutadiene, polyisoprene or poly(4-methylstyrene) have been obtained (5, 6). If coupling with the first polymer chain is correctly achieved, the

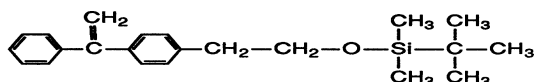
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reaction time of the addition of the other arms increases regularly and reaches two months for the coupling with the fourth sequence. Moreover, fractionation is required to remove the excess of nonlinked polymer chains. In this way, only polystyrene derivatives, polybutadiene and polyisoprene blocks can be directly linked to the chlorosilane core.

In order to avoid reaction between polymeric species, often problematic, we developed a new route (7) consisting of two successive initiation steps on a core molecule located at the end of a first block. This core molecule is a 1,1 diphenylethylene derivative bearing a protected hydroxy function (abbreviation : DPE protected). Initiation of the second monomer through the 1,1 diphenyl carbanion leads to a diblock copolymer of A and B, containing this core molecule in its centre. After deprotection and purification of the diblock copolymer, the central function is activated to initiate the polymerization of the third monomer C. For our purpose, three essential requirements have to be satisfied by the core molecule:

- (i) a quantitative reaction with living carbanionic chain ends without oligomerization;
- (ii) the ability to initiate anionic polymerization of other monomers;
- (iii) the presence of a function protected against strong bases.

1,1-diphenylethylene fulfills requirements (i) and (ii). For requirement (iii), we need a protected function towards anionic conditions which is able after deprotection to become an anionic initiator. To achieve these conditions, we have chosen a hydroxy function protected by a *tert*-butyldimethylsilyl group (8, 9). The formula of the used derivative is :



After deprotection, this hydroxy function can be used for the ring opening polymerization of many monomers such as ethylene oxide, ϵ caprolactone and lactides leading to a wide range of blocks, but this strategy is not suitable for the synthesis of stars copolymers as PS-PB-PMMA or PS-PB-PI.

In this article, we complete the synthesis and the characterization of PS arm PEO arm PCL copolymers : Polystyrene-arm-Poly(ethylene oxide)-arm-Poly(ϵ caprolactone) and we extend this strategy to the synthesis of PS arm PMMA arm PEO copolymers : Polystyrene-arm-Poly(methyl methacrylate)-arm-Poly(ethylene oxide) and PS arm PEO arm PLL copolymers : Polystyrene-arm-Poly(ethylene oxide)-arm-Poly(L lactide)

The basic interest of these triarm star block copolymers lies in the fact that 3 blocks of different nature (chemical structure and amorphous or crystalline state) are linked at a same point. This probably involves new solid state organizations, different of those yet known for linear di and triblocks. Another interesting side of these copolymers is their amphiphilic nature.

Some preliminary results on solid state properties and on solution properties (micellization and adsorption) are given in order to point out the effect of the star structure on copolymer properties.

Experimental

Anionic polymerization was carried out in a flamed glass reactor under nitrogen atmosphere. Styrene, ethylene oxide and ϵ -caprolactone were first stirred over sodium, butyllithium and calcium hydride, respectively, and then distilled under reduced pressure just before polymerization. Methylmethacrylate was first stirred over calcium hydride, distilled then

treated by a solution of triethyl aluminium and finally distilled into the glass reactor just before polymerization. L lactide was dried by dissolution in dry toluene followed by an azeotropic distillation.

1-(4-(2-*tert*-Butyldimethylsiloxy)ethyl)phenyl-1-phenylethylene was synthesized according to a procedure described in the literature (10).

Size exclusion chromatography was carried out in THF (1 ml/min) at 25°C using a Waters 150C liquid chromatograph equipped with three Lichrogel columns (Merck) (PS 400, PS 40, PS 10) and a refractive index detector coupled with a UV detector. Size exclusion chromatography was calibrated with PS standards. ¹H NMR spectra were recorded on a 250 MHz spectrometer (Bruker AC 250) using CDCl₃ as a solvent.

Results and Discussion

Synthesis of Diblock Copolymers

Two series of diblock copolymers containing a 1,1 diphenyl derivative bearing a protected hydroxy function were synthesized.

Aliquots of the polymeric solution were taken after each stage for characterizations.

1. PS -(DPE protected)- PEO

Styrene is polymerized at -78°C in tetrahydrofuran using cumylpotassium as an initiator. After one hour, the core molecule (1-[4-(2-*tert*-butyldimethylsiloxy)ethyl]phenyl-1-phenylethylene) is added to the living chain ends and the typical red colour of the polystyryl anion changes to the deeply dark-red colour of the living diphenylethylene derivative. Twenty minutes later, ethylene oxide is distilled into the reactor at -40°C. After five minutes, the red colour has disappeared and the solution becomes slightly viscous. Then, the reactor is left for three days at room temperature in order to complete the polymerization of the second monomer.

The polymerization is then terminated by addition of dry benzyl chloride, to avoid the formation of a hydroxy chain end that would be active in the subsequent anionic polymerization. The diblock copolymer is precipitated into methanol or cyclohexane depending on whether the main sequence is polystyrene or poly(ethylene oxide), respectively.

2. PS -(DPE protected)-PMMA

After end capping of the living PS by the core molecule, MMA is added into the reactor at -78°C to the solution which turns immediately to yellow. After 20 minutes, the polymerization is then terminated by addition of methanol and precipitated into a mixture of methanol/water (80/20, v/v).

3. Deprotection of the hydroxy function

Deprotection of the core molecule will generate the hydroxy function needed for the polymerization of the third monomer. Thus the silyl protecting group is removed by reaction with three equivalents of tetrabutylammonium fluoride in dry tetrahydrofuran under nitrogen at 70°C for 12 h (11). One equivalent of ammonium chloride is then added to generate the hydroxy function from the tetrabutylammonium salt. The solution is filtered to remove insoluble *tert*-butyldimethylsilyl fluoride. The polymer is then isolated by precipitation and purified by several reprecipitation cycles to remove traces of salts and organic substances. After rigorous purifications, ¹H NMR analysis shows quantitative yield for the deprotection reaction.

Synthesis of star block copolymers

For the synthesis of PS arm PEO arm PCL and PS arm PMMA arm PEO, the diblock copolymer containing a hydroxy function at the junction of the 2 blocks is introduced in the reactor and thoroughly dried by several cycles of dissolution in dried tetrahydrofuran and removal of the solvent under high vacuum. Dried and degassed solvent (THF) is condensed on this purified material in the reactor at -78°C . The solution temperature is then increased to 40°C to complete the dissolution especially for copolymers of high poly(ethylene oxide) content.

The anionic activation - which consists in transforming the hydroxy function into an alcoholate in order to initiate the anionic ring-opening polymerization of EO and CL - is achieved by addition of diphenylmethyl sodium dissolved in THF on the diblock copolymer solution.

1. PS and PEO arm PCL

ϵ caprolactone is added at room temperature to the solution which turns immediately to yellow. The polymerization is short stopped with ethanol after a few minutes to avoid oligomer formation by backbiting reaction (12). The star copolymer is then precipitated into cyclohexane. Nevertheless, we observed the formation of cyclic ϵ caprolactone oligomers, size exclusion chromatography (SEC) patterns showing a broadening in the low molecular weight region.

2. PS arm PMMA arm PEO

Ethylene oxide is polymerized in the same way as previously described : cf the synthesis of the diblock PS-DPE protected - PEO. Copolymers are precipitated into a mixture of methanol/water (80/20, v/v) for small contents of poly(ethylene oxide) and diethylether for high PEO contents.

3. PS arm PEO arm PLL

For this synthesis, the ring opening polymerization of L-lactide is initiated in toluene solution by the system $\text{Sn}(\text{octoate})_2$ -hydroxy function beared by the diblock copolymer. Tin octoate is added to the solution of copolymer previously dried by a toluene azeotropic distillation. The ratio $[\text{LL}]/[\text{Sn}]$ is about 1500 and polymerization is run, at 100°C , for 3 days.

Star copolymers are precipitated into heptane. In order to eliminate the small amount of homopolylactide, detected by SEC chromatograms, the crude copolymer is dissolved in chloroform and then precipitated into methanol. After this purification, SEC pattern shows only the star peak.

Characterization

The composition of the copolymer (diblock and star) is determined by proton nuclear magnetic resonance. In all cases, we obtain the superposing of homopolymer spectrums.

The M_n of copolymers (diblock and star) are calculated using ^1H NMR analysis and M_n of the PS precursor determined by SEC. M_w/M_n are estimated from copolymers SEC traces. SEC shows relatively narrow molecular weight distributions for star block copolymers. See, for example, size exclusion chromatography traces reported on fig. 1.

The characteristics of some starblock copolymers are given in table 1, showing the potential of this new strategy for the synthesis of amphiphilic starblock copolymers.

Table 1: Characteristics of triarm star block copolymers

	First block		Second block		Third block		Star	
	M_n	% wt.	M_n	% wt.	M_n	% wt.	M_n	I_p
PS-PEO-PCL	PS		PEO		PCL			
	13 000	5	1 100	0.4	246 000	94.6	260 000	1.47
	33 000	67.9	5 600	11.7	9 900	20.4	48 000	1.22
	4 700	13.2	20 000	56.7	10 700	30.1	35 000	1.27
PS-PMMA-PEO	PS		PMMA		PEO			
	4 000	20.7	2 600	13.4	12 700	65.9	19 000	1.16
	4 000	33.7	2 600	22.1	5 200	44.2	12 000	1.2
	4 000	47.7	2 600	30.8	2 400	21.5	9 000	1.26
PS-PEO-PLL	PS		PEO		PLL			
	35 400	71	5 500	11	9 000	18	50 000	1.11
	4 700	18.4	20 000	78.4	800	3.2	25 500	1.3

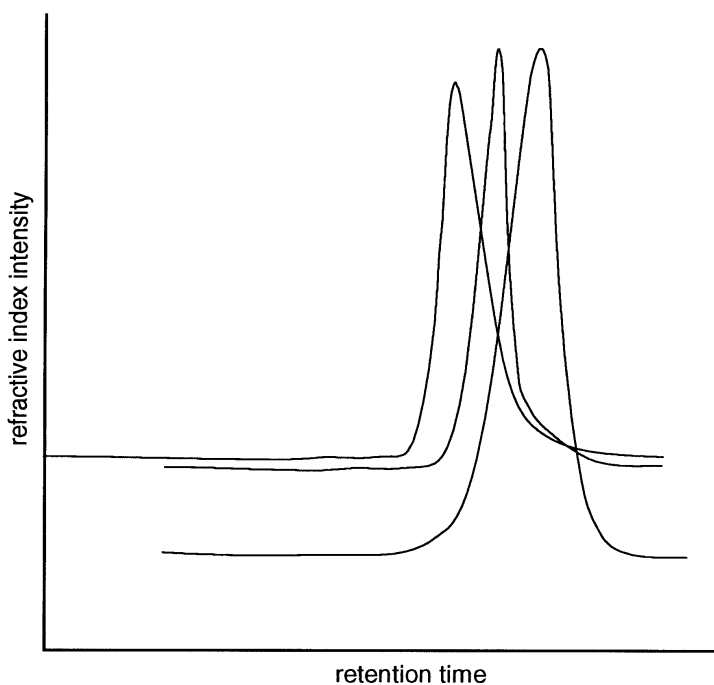


Fig. 1 : Size exclusion chromatography traces of a PS - arm - PEO - arm - PCL triarm star and its precursors from the left to the right:

1) star, $M_n = 48\ 000$, $I_p = 1.22$ 2) PS-b-PEO 3) PS
 RI signal versus retention time in arbitrary units.

Properties : some preliminary results

1. Solid state properties

Concerning morphology of triarm star block copolymers, there is only one report on polystyrene-arm-polyisoprene-arm-polybutadiene which shows only one low T_g as polyisoprene and polybutadiene are well mixed (13).

We have some preliminary results (14, 15) on the solid state organization of the serie PS arm PEO arm PCL containing 2 crystallizable polymers. As known for linear diblocks (16), only the main sequence (with the greatest size) crystallizes. At room temperature we observe a lamellar crystalline structure without apparent microseparation and in the melt there is no mesomorphic structures. This is quite different from linear triblocks with one crystallizable block, as for example Polystyrene-*b*-Polybutadiene-*b*-Poly(ϵ caprolactone), showing a microphase separation (17).

This absence of microseparation in our case suggests that the star structure involves an increase in miscibility between the blocks in the amorphous part.

2. Micellization of PS arm PMMA arm PEO

It is well known that amphiphilic block copolymers, like PS-*b*-PEO, form micelles in water (18). 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.

Preliminary studies by dynamic light scattering demonstrate the formation of micelles especially for high PEO contents (15). For example, the micellization of the star PS-PMMA-PEO containing 65,9 % of PEO ($M_n = 19\ 000$, $N_{PS} = 40$, $N_{PMMA} = 26$ and $N_{PEO} = 289$, where N is the number of units in a block) 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 copolymers (19):

$$R_H \text{ (in nm)} = 0.98 N_{PS}^{0.75} \cdot N_{PEO}^{-0.17} + 0.76 N_{PS}^{-0.53} \cdot N_{PEO}^{0.74}$$

Using this relationship, we are able to calculate the size of micelles obtained from a hypothetic PS-PEO diblock having globally the same hydrophilic and hydrophobic blocks as our triarm star e.g. with $N_{PEO} = 289$ and $N_{PS} = 66$, sum of $N_{PS} = 40$ and $N_{PMMA} = 26$. We work out $R_H = 14$ nm, which is very close to 16 nm obtained experimentally for the triarm star micelles.

It means that in our triarm stars, the PMMA block acts as the PS block in the chemical contribution to the size of the micelle.

Further studies are in progress in order to elucidate one phase or microseparation morphology of the hydrophobic core.

3. Adsorption of PS arm PEO arm PCL onto TiO_2 in toluene solution (20)

As PEO is selectively adsorbed and collapsed on TiO_2 , the solution layer is made of PS and PCL blocks anchored at a same point of the interface liquid-solid. The PCL blocks are close together and stretched into toluene whereas the PS blocks are separated and seem to be relatively unperturbed compared to their conformation as free chains in toluene solution. The adsorbed amount at polymer saturation is significantly lower for the star as compared to a diblock PEO-PS having similar size for each block.

Conclusion

We have described a new route to amphiphilic star block copolymers and showed the potential of this new strategy for the synthesis of star copolymers.

The main result of the preliminary studies on solid state properties is that the star structure of these block copolymers seems to increase the miscibility of the different incompatible blocks in the bulk.

Further studies are in progress in order to elucidate the bulk morphology of these copolymers.

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