534 *Macromolecules* **1999,** *32,* 534−536

Synthesis of Model PS(PI)$_5$ and (PI)$_5$PS(PI)$_5$ Nonlinear Block Copolymers of Styrene (S) and Isoprene (I)

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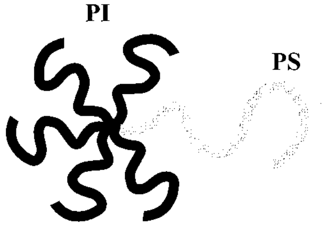
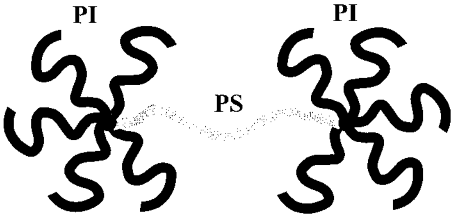
Received September 18, 1998
Revised Manuscript Received November 14, 1998

Chart 1



6-Miktoarm Star Copolymer of the AB$_5$ type



α,ω-Branched Copolymer of the B$_5$AB$_5$ type

Introduction. Well-defined nonlinear block copolymers with trifunctional (AB$_2$: 3-miktoarm star copolymers; B$_2$AB$_2$: H-shaped copolymers)[1,2] and tetrafunctional branch points (AB$_3$: 4-miktoarm star copolymers; B$_3$AB$_3$: super H-shaped copolymers)[3,4] have been synthesized by using anionic polymerization and controlled chlorosilane chemistry. The synthetic approach involves the reaction of the monofunctional (in the case of miktoarm stars) or difunctional living chain A (in the case of H- and super H-shaped) with a large excess of methyltrichlorosilane (bp 66 °C) or tetrachlorosilane (bp 57.6 °C), followed by removal of the excess of silane and reaction of the chlorosilane-capped A chain with the living B chains. The removal of the unused chlorosilane is necessary in order to avoid contamination of the miktoarm star (μ-star) copolymer or of the α,ω-branched copolymer (H- and super H-shaped) by the B$_3$ or B$_4$ star homopolymer.

The above chlorosilanes, due to their low boiling points, can be relatively easily removed from the solution of the chlorosilane-capped A polymer. The solvent, usually benzene, and the chlorosilane are pumped off on a vacuum line until dryness. The remaining product is redissolved in benzene and the solution is pumped again. It has been found[5] that this procedure should be repeated two to three times in order to ensure complete removal of chlorosilane. This procedure cannot be applied in the synthesis of nonlinear block copolymers having more than tetrafunctional branch points because chlorosilanes with more than four chlorine atoms are high boiling liquids or solids.

By using different approaches μ-stars with more than four arms and α,ω-branched copolymers with more than three arms at each chain end have been prepared. Roovers and colleagues[6] have prepared star polymers with one heteroarm and 5−14 homoarms and coined the name “umbrella” polymers. The synthesis uses living anionic polymerization to prepare a short segment of polybutadiene-1,2 (PBd-1,2) at the end of linear polystyrene. The vinyl groups of PBd-1,2 are hydrosilylated with dichloromethylsilane. The “umbrella” polymers are then formed by nucleophilic displacement of the silicon−chlorine with 1,4-PBdLi or (poly-2-vinylpyridine)Li. Stadler and colleagues[7] prepared α,ω-branched copolymers of PS with 7−14 arms of poly(ethylene oxide) at each chain end and gave the name “dumbbell”-shaped grafted block copolymers. The short butadiene-1,2 blocks of a (PBd-1,2)-*b*-PS-*b*-(PBd-1,2) triblock copolymer, with a long styrenic middle block, were modified by hydroboration and oxidation. A multifunctional initiator was obtained by titration of the hydroxyl groups with cumylpotassium, which was used to polymerize ethylene oxide. Finally, Takano et al.[8] prepared star polymers having one poly(2-vinylnaphthalene) arm and about 13 PS arms by coupling polystyrene anions with silylvinyl groups of poly(2-vinylnahthalene-*b*-4-vinylphenyldimethylvinylsilane). Unfortunately, all these methods suffer the disadvantage that the number of arms is difficult to control precisely as in the case of chlorosilane linking agent.

For the synthesis of the 6μ-star copolymers PS(PI)$_5$ and the α,ω-branched copolymer (PI)$_5$PS(PI)$_5$ we used the hexafunctional chlorosilane 1,2-bis(trichlorosilyl)ethane, which is a solid linking agent (mp ~26 °C). A possible way to remove the excess chlorosilane is to use a selective solvent for the hexachlorosilane and nonsolvent for the PS (e.g., hexane) to precipitate the PS and filter off the solution with the excess chlorosilane. Keeping in mind that the procedure should be carried out under vacuum and repeated many times, one can realize that is almost impossible to perform it. The other possibility is to use stoichiometric amounts of living polymer and chlorosilane. We adopted the latter method to prepare the 6μ-star copolymer PS(PI)$_5$ and the α,ω-branched copolymer (PI)$_5$PS(PI)$_5$ (Chart 1). The synthesis and the molecular characterization results of these novel architectures are presented in this communication.

Experimental Part. The purification of the monomers (isoprene, styrene), the solvents (benzene, tetrahydrofuran (THF)), and the terminating agent methanol, to the high standards required for anionic polymerization, has been described in detail elsewhere.[9] *sec*-BuLi, prepared from *sec*-BuCl and a lithium dispersion, was the initiator for the preparation of monolithium macromolecules, whereas the hydrocarbon soluble dilithium initiator 1,3-bis(1-phenyl-3-methylpentyllithium)benzene (DLi) was used for the synthesis of the difunctional PS. Details of the preparation of the DLi are given in a previous publication.[10] The linking agent 1,2-bis(trichlorosilyl)ethane (Petrarch), named for simplicity S-Cl$_6$, was purified according to a procedure given elsewhere.[11] The pure material was diluted in *n*-hexane and subdivided into ampules with break-seals. The silicon−chlorine bond concentration was determined by acid−

10.1021/ma9814797 CCC: $18.00

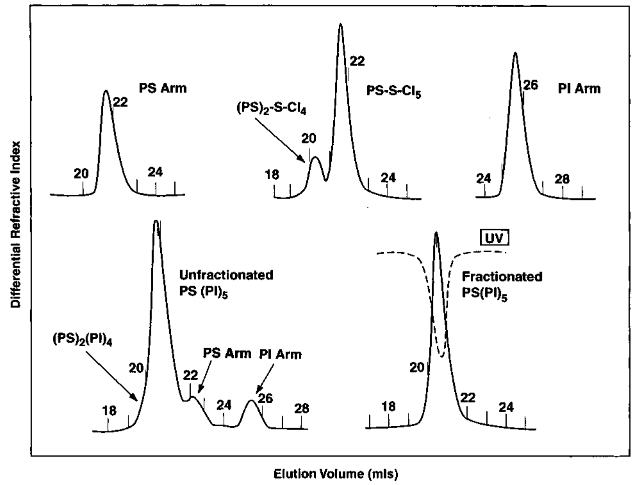


Figure 1. SEC traces taken during the different stages of the synthesis of the 6μ-star copolymer PS(PI)$_5$-1.

base titration. All manipulations were performed, under high vacuum, in glass reactors. Addition of the reagents was made through break-seals, and removal of aliquots for characterization, by heat-sealing of the constrictions. All reactors were previously washed with benzene solution of *n*-BuLi followed by rinsing with benzene, which was the solvent for all polymerizations and linking reactions. The living polymers were prepared in classic reactors, while the linking reactions were performed in reactors similar to those given in previous paper.[5]

The fractionation was carried out by adding methanol to a solution (0.5−1 wt %) of the final product in a mixture of toluene/*n*-hexane (1/1 by volume). It was repeated until no undesirable products were shown to be present by size exclusion chromatography (SEC).

SEC (THF, 30 °C) with differential refractive index and UV detector, membrane osmometry (MO, toluene, 35 °C), vapor pressure osmometry (VPO, toluene, 50 °C), and NMR (CDCl$_3$, 30 °C) measurements were performed following procedures described in details elsewhere.[5] In all cases the correlation factor was better than 0.99. The microstructure of PI, as found by NMR, was 71 wt % *cis*-1,4, 20 wt % *trans*-1,4, and 9 wt % 3,4.

Results and Discussion. The basic reactions used for the synthesis of the 6μ-star copolymers PS(PI)$_5$ are the following:

$$\mathrm{St} + sec\text{-}\mathrm{BuLi} \xrightarrow{\text{benzene, 25 °C}} \mathrm{PSLi}$$

$$\mathrm{PSLi} + \mathrm{S\text{-}Cl_6} \xrightarrow{\text{benzene, 25 °C}} \mathrm{PS\text{-}S\text{-}Cl_5} + \mathrm{LiCl}$$

$$\mathrm{Is} + sec\text{-}\mathrm{BuLi} \xrightarrow{\text{benzene, 25 °C}} \mathrm{PILi}$$

$$\mathrm{PS\text{-}S\text{-}Cl_5} + \text{excess PILi} \xrightarrow{\text{benzene, 25 °C}} \mathrm{PS(PI)_5} + 5\mathrm{LiCl}$$

where St is styrene, S-Cl$_6$ is 1,2-bis(trichlorosilyl)ethane, Is is isoprene, PS is polystyrene, and PI is polyisoprene.

The stoichiometric amount of PSLi was added dropwise under continuous stirring to the chlorosilane solution (benzene ~10 vol %) in order to avoid the replacement of more than one chlorine by the PS. Despite the precautions taken, a local excess of living PSLi over the linking agent cannot be avoided, thus leading to the formation of the two arms product (PS)$_2$-S-Cl$_4$ (~10%, Figure 1). Nevertheless, the almost exclusive formation of the monoarm species indicates that the addition of a second arm, which is a polymer−polymer reaction, is severely retarded. The unreacted S-Cl$_6$ leading to 6-arm star PI, covered by the other peaks of the final product, is completely eliminated by fractionation (Figure 1). The addition of the PSLi into the chlorosilane solution was performed within 1 day. After the formation of PS-S-Cl$_5$, excess PILi was added, and the mixture was allowed to react for 3 weeks. The excess PILi was neutralized by methanol, and the final product was submitted to fractionation. A typical example of the evolution of the synthesis, as monitored by SEC, is shown in Figure 1. The peak at the lower elution volume side of the main peak corresponds to the (PS)$_2$(PI)$_4$ μ-star (Figure 1), resulting from the (PS)$_2$-S-Cl$_4$. The characteristics of the precursors and the final fractionated 6μ-stars are given in Table 1.

The narrow distribution of the DRI and UV peaks (Figure 1) and the good agreement between the calculated values of $M_{\mathrm{n}\mu} = M_{\mathrm{nPS}} + 5M_{\mathrm{nPI}}$ and the determined by MO (Table 1) indicate a high degree of homogeneity in molecular weight and composition. This fact is also supported by the good agreement between the PS content found by NMR/UV and that calculated from the M_n of the PS arm and the final product.

The synthesis of the α,ω-branched copolymer (PI)$_5$PS-(PI)$_5$ was performed according to the following basic reactions:

$$\mathrm{Is} + sec\text{-}\mathrm{BuLi} \xrightarrow{\text{benzene, 25 °C}} \mathrm{PILi}$$

$$\mathrm{S\text{-}Cl_6} + \mathrm{PILi}\ (\sim 10\%\ \text{excess}) \xrightarrow{\text{benzene, 25 °C}} \mathrm{(PI)_5\text{-}S\text{-}Cl} + 5\mathrm{LiCl}$$

$$\mathrm{St} + \mathrm{DLi} \xrightarrow{\text{benzene, 25 °C}} \mathrm{LiPSLi}$$

$$\mathrm{LiPSLi} + \text{excess}\ \mathrm{(PI)_5\text{-}SCl} \xrightarrow{\text{benzene, THF (3\%), 25 °C}} \mathrm{(PI)_5PS(PI)_5} + 2\mathrm{LiCl}$$

where DLi is 1,3-bis(1-phenyl-3-methylpentylidene−lithium)benzene.

The initial step of the synthesis involved the reaction of a small excess (~10%) of living PILi (solution ~ 5 vol % in benzene) over the stoichiometric amount of the chlorosilane solution (PILi:S-Cl$_6$ = 5.1:1). The excess PILi is necessary in order to ensure the formation of the desired product (PI)$_5$-S-Cl. The formation of the six-arm product will not interfere in the subsequent steps of the synthesis because this byproduct is unreactive and can be separated by fractionation after the completion of the synthesis. The formation of (PI)$_5$-S-Cl was allowed to proceed for 1 week. The PS connector part was prepared using the difunctional initiator 1,3-bis(1-phenyl-3-methylpentyllithium)benzene (DLi). From the SEC traces (Figure 2a) it is obvious that a small amount of monofunctional species (with half of the molecular weight of the connector) is also present. This monofunctional PS coming from the monofunctional initiator present in DLi leads to the formation of PS(PI)$_5$ μ-star, which was eliminated by fractionation (Figure 2b). It is clear that even after 5 weeks the coupling reaction was not complete (Figure 2b), maybe due to steric hindrance. After repeated fractionations the pure product was isolated and characterized. The results are given in Table 1.

Table 1. Molecular Characteristics of the PS(PI)$_5$ and (PI)$_5$PS(PI)$_5$ Nonlinear Block Copolymers

	PS connector or arm		PI arm		final product					
sample	10^{-3} M_n[a]	M_w/M_n[b]	10^{-3} M_n[c]	M_w/M_n[b]	10^{-3} M_n[a]	10^{-3} M_n[d] (calc)	M_w/M_n[b]	% PS[e] (^{1}H NMR)	% PS[f] (UV/SEC)	% PS[g] (calc)
PS(PI)$_5$-1	76	1.02	10.4	1.03	126	128	1.05	63	61	60
PS(PI)$_5$-2	106	1.03	9.7	1.04	152	154.5	1.05	70	67	69
PS(PI)$_5$-3	167.5	1.03	9.7	1.04	218	216	1.05	79	75	77
(PI)$_5$PS(PI)$_5$[h]	118	1.07	7.4	1.04	203	192	1.09	68	68	65

[a] Membrane osmometry in toluene at 35 °C. [b] SEC in THF at 30 °C. [c] Vapor pressure osmometry in toluene at 50 °C. [d] Calculated: $M_{n\mu} = 5M_{nPI} + M_{nPS}$ for the PS(PI)$_5$ and $M_{n\alpha,\omega} = 10M_{nPI} + M_{nPS}$ for the (PI)$_5$PS(PI)$_5$. [e] Weight percent by ^{1}H NMR. [f] SEC–UV (262 nm) in THF at 30 °C. [g] Calculated: $M_{nPS}/M_{n\mu \text{ or } \alpha,\omega}$. [h] The M_n of the intermediate (PI)$_5$S–Cl product (Figure 2a) after neutralization with methanol and fractionation (toluene/methanol) was 39 200 (MO).

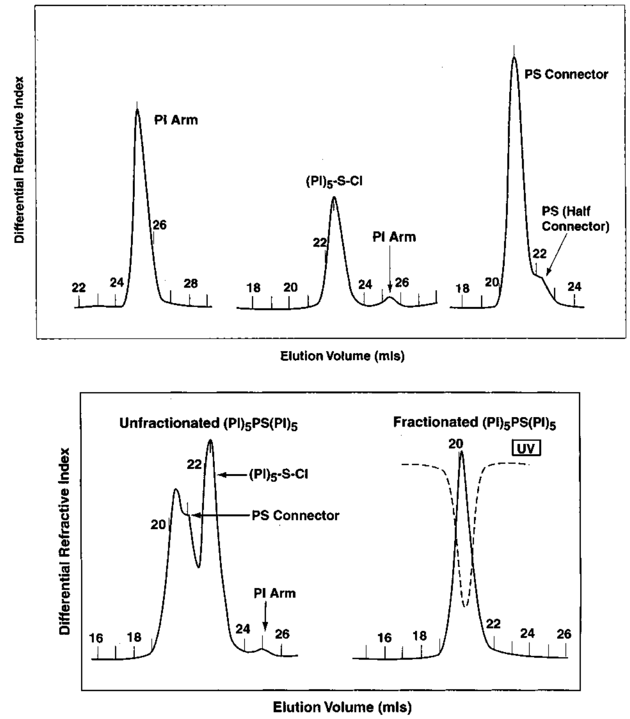


Figure 2. (a, top) SEC traces of the PI arm, the intermediate product (PI)$_5$-S-Cl and the PS connector of the (PI)$_5$PS(PI)$_5$. (b, bottom) SEC traces of the (PI)$_5$PS(PI)$_5$ prior to and after fractionations.

The narrow distribution of the DRI and UV peaks (Figure 2a,b) and the good agreement between the calculated values of $M_{n\alpha,\omega} = M_{nPS} + 10M_{nPI}$ and the one determined by MO (Table 1) indicate a high degree of homogeneity in molecular weight and composition. This fact is also supported by the good agreement between the PS content found by NMR/UV and that calculated from the M_n of the PS arm and the final product.

In conclusion, the combined characterization results indicate that two new architectures of nonlinear block copolymer with hexafunctional branch points PS(PI)$_5$ and (PI)$_5$PS(PI)$_5$ can be synthesized by anionic polymerization and 1,2-bis(trichlorosilyl)ethane as linking agent. By using the same approach, we have prepared α,ω-branched polybutadienes and by hydrogenation the corresponding polyethylenes.[12] The microphase separation of the new nonlinear block copolymers will be studied in a forthcoming paper.

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MA9814797