Synthesis of Model Super H-Shaped Block Copolymers

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Introduction. Block copolymers are materials of great technological importance,[1] finding application as thermoplastic elastomers, as compatibilizers for polymer blends, in the modification of surface and interfacial properties, etc. Most of our fundamental understanding has been gained by the study of well-defined and nearly monodisperse linear diblock and, to a lesser extent, triblock copolymers. Very little is known about the influence of the chain architecture on properties. In previous papers the synthesis of model miktoarm (from the Greek word *μικτός* meaning mixed) stars of A_2B,[2] A_2B_2,[3] ABC,[4] and ABCD[3] types has been described. Our synthetic approach involves the controlled reaction of monofunctional living macroanions with trichloro- and tetrachlorosilane.

In this paper α,ω-difunctional macroanions and tetrachlorosilane have been used to prepare a new class of block copolymers, i.e., the super H-shaped block copolymers of the B_3AB_3 type, where B is polyisoprene-1,4 (PI-1,4) or polystyrene (PS) and A is PS or PI-3,4 (see Chart 1).

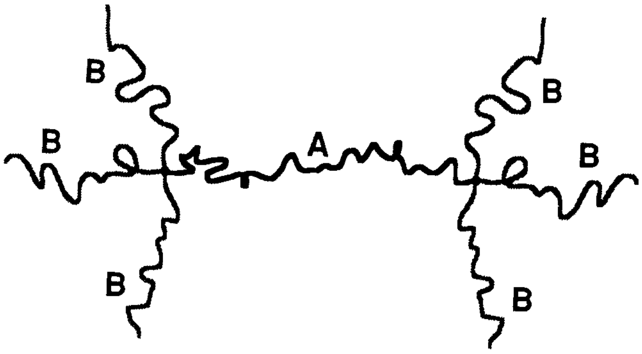
The name H-shaped polymers has been given, by Roovers, to the regular PS combs with two branches prepared from difunctional initiator and methyltrichlorosilane, but by using a different synthetic strategy.[5] By analogy we give the name super H-shaped to the comb polymers with two tetrafunctional branch sites. These materials can also be considered as bridged star polymers.

Experimental Section. The purification of isoprene (Fluka), styrene (Merck), and benzene to the standards required for anionic polymerization has been described elsewhere.[6] Naphthalene was purified by triple sublimation on the vacuum line and was then dissolved under vacuum in benzene and subdivided into ampules. Tetrachlorosilane was fractionally distilled on the vacuum line and was subdivided into tubes without the addition of solvent. Tetrahydrofuran (THF; Merck p.a.) was stirred overnight over CaH_2, distilled on the vacuum line to a sodium mirror, and left for 24 h. This procedure was repeated until no degradation of the Na mirror was observed. Then it was distilled to a flask containing sodium metal and benzophenone and left until the characteristic deep purple color developed. Finally, THF was treated with polystyryl sodium, prepared by the reaction of styrene with a sodium mirror, and transferred into ampules. A middle fraction was taken each time.

The fractionation of the copolymers was carried out by adding methanol to the polymer solution (~0.5% w/v) in benzene at room temperature. It was performed until no precursor or undesirable products were shown to be present by size-exclusion chromatography (SEC).

Size-exclusion chromatography (SEC; THF, 30 °C), low-angle laser light scattering (LALLS; THF, 25 °C), laser differential refractometry (THF, 25 °C), membrane osmometry (MO; toluene, 30 °C), vapor pressure osmometry (VPO; toluene, 50 °C), and ^1H- and ^{13}C-NMR ($CDCl_3$, 30 °C) measurements were performed following procedures published previously.[3,4] Typical examples of LALLS and MO plots are given in Figure 3. The polyisoprenes analyzed by ^1H and ^{13}C NMR were found to have the following microstructure: for the PI connector 61 wt % 3,4, 13 wt % 1,2, and 26 wt % 1,4; for the PI arm, 10 wt % 3,4, 70 wt % *cis*-1,4, and 20 wt % *trans*-1,4. The lower 1,4 content for the PI connector is due to the presence of THF.

Chart 1. Super-H Block Copolymer of the B_3AB_3 Type



Results and Discussion. The basic reactions used for the synthesis of the super H-shaped copolymers of the B_3AB_3 type are schematically the following:

$$\text{naphthalene} + \text{Na} \rightarrow \text{sodium naphthalenide (I)}$$

$$\text{St (or Is)} + \text{I} \rightarrow \text{NaPSNa (or NaPINa) (II)}$$

$$\text{II} + \text{excess } SiCl_4 \rightarrow Cl_3SiPSSiCl_3 \text{ (or } Cl_3SiPISiCl_3\text{) (III)}$$

$$\text{III} + \text{excess PILi (or PSLi)} \rightarrow (PI)_3PS(PI)_3 \text{ [or } (PS)_3PI(PS)_3\text{]}$$

where St is styrene and Is is isoprene.

Preparation of the Difunctional Initiator and the Connector. The living difunctional polymers were prepared in all-glass vessels provided with break-seals for the addition of THF and reagents and constrictions for removal of products, following the procedure described by Roovers and Toporowski.[7] The final concentration of the disodium initiator never exceeded 0.03 g/mL, due to solubility reasons.

The living difunctional polymers were maintained for 1-2 h at 20 °C and were then left to react with the linking agent. The preparation of the initiator and the connector, along with the addition of $SiCl_4$, was performed within 10 h, in order to avoid side reactions.[8,9]

Linking Reaction of the Living Connector with the Tetrachlorosilane. The apparatus used for the addition of the dilute solution of the living difunctional polymers to the large excess of the linking agent is similar to the one described by Iatrou and Hadjichristidis.[3,4] The ratio of Si-Cl/C-Li was always higher than ~2000. The excess tetrachlorosilane was removed under vacuum line conditions.

In all cases, the SEC chromatogram of the hexafunctional macromolecular linking agent was almost indistinguishable from the parent material. A typical example is given in Figure 1. The small peak that appears on the high molecular weight side and represents about the 2% of the product is due to the coupled material $Cl_3Si(PS)ClSiCl(PS)SiCl_3$. In order to reduce this product in the case where PI was the connector, the disodium connector was capped with three to four styrene units on both ends, before the reaction with $SiCl_4$. In all cases three to four

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Table 1. Molecular Characteristics of the Super H-Shaped Block Copolymers

sample	$M_n \times 10^{-4}$ connector[a]	$M_n \times 10^{-4}$ arm[a]	$M_n \times 10^{-4}$ SH[a]	$A_2{}^a \times 10^4$ (mL mol g^{-2})	M_w SH[b] $\times 10^{-4}$	$A_2{}^b \times 10^4$ (mL mol g^{-2})	M_w/M_n[c]	dn/dc[e] (mL g^{-1})
$(PS)_3PI(PS)_3$ (SH-1)	2.19	0.4[d]	4.56	2.8	4.62	2.3	1.08	0.145
$(PI)_3PS(PI)_3$ (SH-2)	10.9	1.61	20.9	6.3	22.5	5.5	1.08	0.160
$(PI)_3PS(PI)_3$ (SH-3)	10.9	2.94	29.0	5.9	30.8	5.5	1.07	0.152

[a] Membrane osmometry in toluene at 37 °C. [b] LALLS in THF at 25 °C. [c] SEC in THF at 30 °C. [d] Vapor pressure osmometry in toluene at 50 °C. [e] Laser differential refractometry in THF at 25 °C. [f] 51 wt % PS (SH-1); 52 wt % PS (SH-2); 37 wt % PS (SH-3) by NMR.

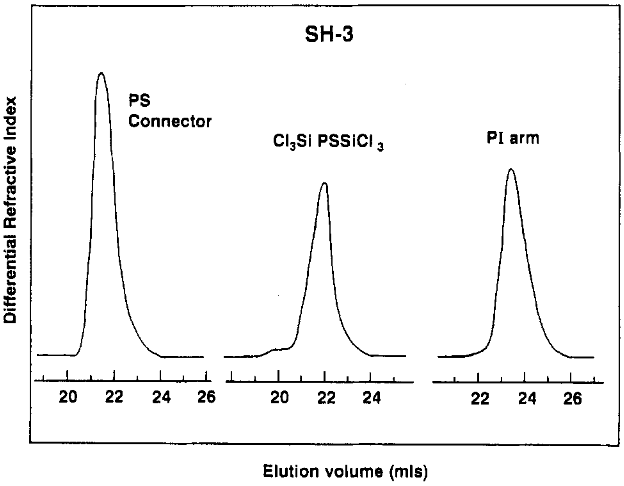

Figure 1. SEC chromatograms of the PS connector, the α,ω-hexachlorosilane-capped PS, and the PI arm.

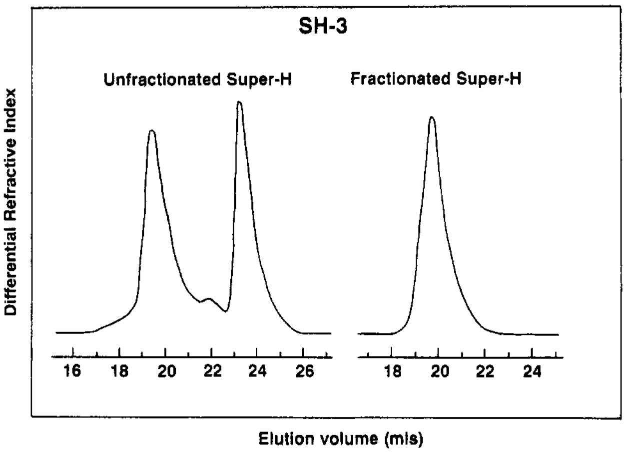

Figure 2. SEC chromatograms of the SH-3 prior to and after five fractionations.

units of Bd were added to the living arm in order to facilitate the linking reaction with the connector. The SEC chromatogram of the raw product is shown in Figure 2 along with the chromatogram of the fractionated polymer.

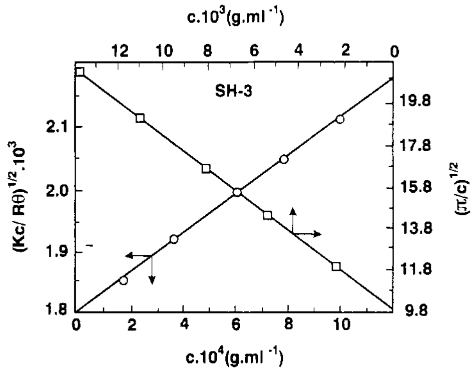

Figure 3. MO square-root plot (○) in toluene at 37 °C and LALLS square-root plot (□) for the SH-3 in THF at 25 °C (ΔR_θ, excess Rayleigh ratio; k, combination of known optical parameters; c, concentration).

The characteristics of the precursors (connector and branches) and the fractionated super-H's are given in Table 1. The good agreement between the values found by osmometry and the calculated one from $(M_n)_{SH} = (M_n)_{con} + 6(M_n)_{br}$, indicates the high degree of homogeneity in molecular weight and composition of the super H-shaped copolymers prepared. This fact is also supported by (a) the good agreement between the PS content of the SH polymers calculated from the M_n of the connector and the arms [52% (SH-1), 53% (SH-2), 38% (SH-3)] and that found by NMR (Table 1) and (b) the good agreement between the specific refractive index increment dn/dc values found experimentally (Table 1) and the calculated ones [0.147 mL·g^{-1} (SH-1), 0.161 mL·g^{-1} (SH-2), 0.152 mL·g^{-1} (SH-3)] from the equation $(dn/dc)_{SH} = x(dn/dc)_{PS} + (1 - x)(dn/dc)_{PI}$ where x is the PS content in % w/w. The following dn/dc values, found experimentally for the precursors in THF at 25 °C, were used: 0.188 mL·g^{-1} (PS), 0.178 mL·g^{-1} (PS, M_W = 4000), 0.131 mL·g^{-1} (PI-1,4), 0.115 mL·g^{-1} (PI-3,4).

In conclusion, the combined characterization results indicate that super H-shaped block copolymers of the B_3-AB_3 type having a high degree of molecular and compositional homogeneity can be synthesized by using a difunctional initiator and tetrachlorosilane as linking agent and following the same approach as in the case of miktoarm stars.

This synthetic strategy can be also used for the synthesis of other super H-shaped and H homopolymer or block copolymers for example: $[(PS)(PI)_2](PS)[(PI)_2(PS)]$, $[(PS)(PI)(PBd)](PS)[(PS)(PI)(PBd)]$, $[(PS)(PI)](PS)$-$[(PS)(PI)]$, $(PI)_3(dPI)(PI)_3$, $(dPI)_3(PI)(dPI)_3$, $(PI)_3$(PS-b-PI-b-PS)$(PI)_3$, etc.

Two forthcoming papers will describe the microphase separation of the prepared super H-shaped block copolymers[10] and the synthesis and dynamic properties of the super H-shaped PI having deuterium in the connector or in the branches.[11]

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References and Notes

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