Synthesis of Model 16-Miktoarm (Vergina[†]) Star Copolymers of the A_8B_8 Type

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Introduction. Very little is known about the influence of chain architecture on the properties of block copolymers. For this reason, the synthesis of miktoarm star (μ-star) copolymers, which are star-shaped molecules having chemically different arms, has recently received much attention.[1−8] By using anionic polymerization and controlled chlorosilane chemistry, we are now able to synthesize a new class of nonlinear block copolymers of styrene and isoprene, the 16-μ star copolymers of the A_8B_8 type (Chart 1). The combined characterization results indicate that these new materials have a high degree of molecular and compositional homogeneity.

Experimental Part. The purification of isoprene (Fluka), styrene (Merck), and benzene to the standards required for anionic polymerization has been described elsewhere.[9] All manipulations were done in vacuo in all-glass vessels, specially designed for the synthesis procedure, washed with *n*-BuLi, and rinsed with solvent. Additions were made through breakseals and removals through heat sealing of constrictions. *sec*-BuLi, prepared in vacuo from *sec*-butyl chloride and a lithium dispersion, was the initiator. $Si\{[CH_2CH_2Si(CH_3)][CH_2CH_2Si(CH_3)Cl_2]_2\}_4$, a chlorosilane with 16 active chlorosilane bonds, named for simplicity $S{-}Cl_{16}$, was the linking agent. $S{-}Cl_{16}$ was prepared by using tetravinylsilane as the initial core molecule, methyldichlorosilane as the propagating units, and vinylmagnesium bromide for the transformation of silicon chloride to the silicon vinyl group.[10] This compound is identical with 2G−Cl in ref 10. Fractionation of the Vergina star copolymer A_8B_8 was performed, in several steps, by adding methanol to the copolymer solution (~0.5 vol %) in a mixture of toluene/hexane (4/1). Fractionation of the intermediate 8-arm star polystyrene, from the linear precursor PS, formed by termination of the small excess of living PS, was carried out with the toluene−methanol pair.

Size exclusion chromatography (SEC, THF, 30 °C) with differential refractive index and UV detectors, membrane osmometry (MO, toluene, 35 °C), low-angle laser light scattering (LALLS, THF, 25 °C), laser differential refractometry (THF, 25 °C), and ^{1}H-NMR ($CDCl_3$, 30 °C) measurements were performed following procedures described elsewhere.[1,2] Typical examples of LALLS and MO plots are given in Figures 1 and 2. The microstructure of PI, as found by NMR, was 70 wt % *cis*-1,4, 20 wt % *trans*-1,4, and 10 wt % 3,4.

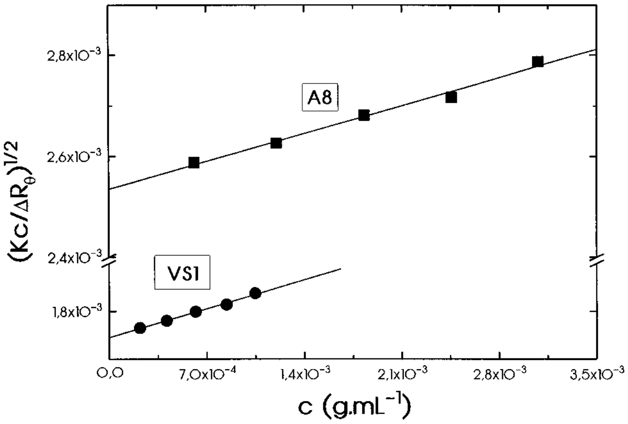
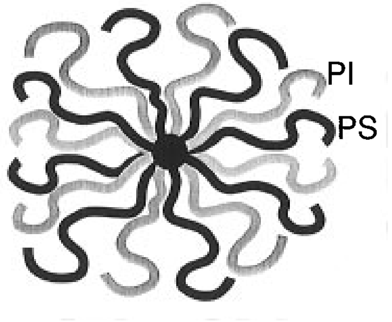


Figure 1. LALLS square-root plot for the 8-arm star PS A8 (■) and the corresponding Vergina star copolymer VS1 (●) in THF at 25 °C (ΔR_θ, excess Rayleigh ratio; K, combination of known optical parameters; c, concentration).

Chart 1



Results and Discussion. The basic reactions used for the synthesis of the Vergina star copolymers are schematically the following:

$$\text{St} + sec\text{-BuLi} \xrightarrow[C_6H_6]{25\ °C} \text{PSLi}$$

$$8\text{PSLi} + \text{S}{-}\text{Cl}_{16} \xrightarrow[C_6H_6]{25\ °C} (\text{PS})_8{-}\text{S}{-}\text{Cl}_8 + 8\text{LiCl}$$

$$\text{Is} + sec\text{-BuLi} \xrightarrow[C_6H_6]{25\ °C} \text{PILi}$$

$$(\text{PS})_8{-}\text{S}{-}\text{Cl}_8 + \text{excess PILi} \xrightarrow[C_6H_6]{25\ °C} \underset{\text{Vergina star copolymer}}{(\text{PS})_8{-}\text{S}{-}(\text{PI})_8} + 8\text{LiCl} + \text{PILi}\downarrow$$

where St is styrene, Is isoprene, PS polystyrene, and PI polyisoprene.

The PSLi and PILi were prepared in classical secondary reactors. The main reactor used for the linking reaction was similar to the one discribed by Iatrou and Hadjichristidis.[1] The appropriate amount of PSLi in benzene was added to a benzene solution of $S{-}Cl_{16}$, in order to incorporate only 8 arms of PS. The progress of the linking reaction was monitored by removing samples from the reactor and analyzing them by SEC, LALLS, or MO. Depending on the PSLi molecular weight, the formation of the 8-arm star PS was completed in 2−3 weeks. Even in the cases where a small excess of PSLi (~5 wt %) was used, only 8 chlorines were replaced by PS. A small sample of the 8-arm star linking agent $(PS)_8{-}S{-}Cl_8$ was removed from the reac-

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[†] From the similarity to the 16-rayed star, discovered by Professor M. Andronikos of the University of Thessaloniki, in the ancient tomb of the Greek King Phillipos of Macedonia in Vergina, a place in Northern Greece close to Thessaloniki.

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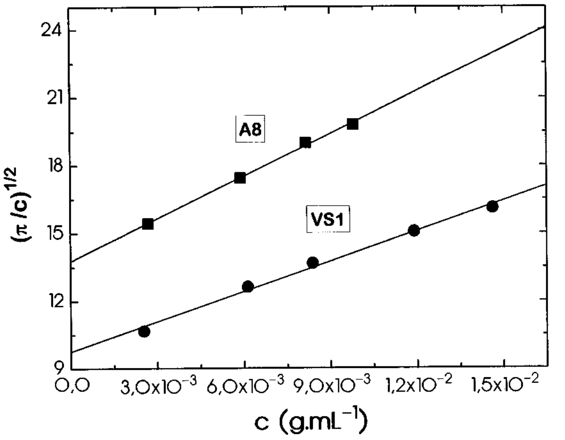

Figure 2. MO square-root plot for the 8-arm star PS A8 (■) and the corresponding Vergina star copolymer VS1 (●) in toluene at 35 °C (π, osmotic pressure; c, concentration).

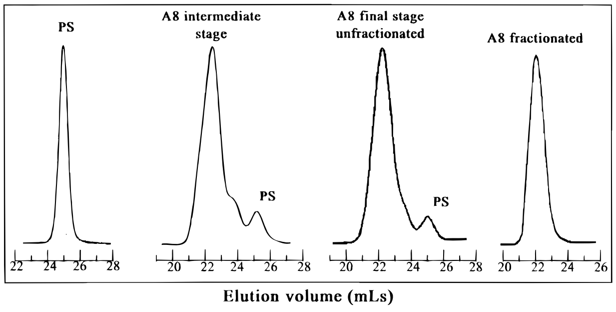

Figure 3. SEC chromatograms of the polystyrene precursor PS and the 8-arm star PS A8 of VS1 after 1 week (intermediate stage) and 3 weeks (final stage) before and after fractionation.

tor for characterization, after elimination of the excess or terminated PS, by fractionation. Finally, an excess of PILi (~30 wt %) was added to the reactor. The progress of the linking reaction was monitored by SEC. Depending on the molecular weight of the already incorporated PS and of the PILi, the Vergina star copolymers were formed after 3−4 weeks. The synthesis of the 16-μ star copolymer of the A_8B_8 type relies on (a) the inability of the sterically hindered styryl anions to react with both chlorines of each peripheral silicon atom of the $S{-}Cl_{16}$ and (b) the ability of the less sterically hindered isoprenyl anions to react completely with the remaining chlorosilane bonds.

The excess of PILi was neutralized by methanol, and the synthesis raw product was submitted to repeated fractionation until no other peaks except the Vergina star copolymer were observed in the SEC chromatograms. An example of the evolution of the synthetic procedure, as monitored by SEC, is shown in Figures 3 and 4. The characteristics of the precursors PS and PI, of the intermediate 8-arm star polystyrenes $(PS)_8{-}S{-}Cl_8$, after neutralization with methanol, and the Vergina star copolymers are given in Table 1. The narrow molecular and compositional distribution found by SEC (DRI, UV) and the good agreement between the M_w values determined by LALLS and the calculated ones from $(M_w)_{VS} = 8(M_w)_{PS} + 8(M_w)_{PI}$ indicate a high molecular and compositional homogeneity. In addition, in the case of VS1, where MO measurements were possible, the values of M_n confirm the model character of the prepared Vergina star copolymers. This fact is also supported by (a) the good agreement between the PS content of the VS copolymers, calculated from the M_w of the precursors and that found by NMR and UV and (b) the good agreement between the specific refractive index increment dn/dc values found experimentally and the values calculated from the equation $(dn/dc)_{VS} = x(dn/dc)_{PS} + (1 - x)(dn/dc)_{PI}$, 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) and 0.131 mL g^{-1}(PI). The small differences are within the limits of the acceptable errors.

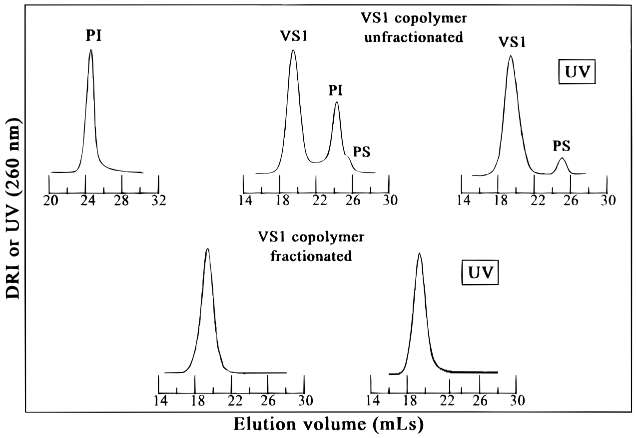

Figure 4. SEC chromatograms of the polyisoprene precursor PI and the unfractionated and fractionated Vergina star copolymer VS1. At 260 nm, only the PS is visible by the UV detector.

Table 1. Molecular Characteristics of the Precursors Polystyrene (PS) and Polyisoprene (PI), the Intermediate 8-Arm Star PS (A8), and the Vergina Star Copolymers (VS) of the A_8B_8 Type

	VS1	VS2	VS3
PS arm, $M_w{}^a$ ($M_n{}^b$) × 10^{-4}	2.09 (2.00)	4.36	4.36
PS arm, $(M_w/M_n)^c$	1.06	1.03	1.03
A8, $M_w{}^a$ ($M_n{}^b$) × 10^{-4}	16.1 (15.5)	34.6	34.6
A8, $(M_w/M_n)^c$	1.06	1.05	1.05
PS arms, $DB_w{}^d$ ($DB_n{}^e$)	7.7 (7.8)	7.9	7.9
PI arm, $M_w{}^a$ ($M_n{}^b$) × 10^{-4}	2.02 (1.92)	4.82	7.12
PI arm, $(M_w/M_n)^c$	1.06	1.07	1.05
VS, $M_w{}^a$ ($M_n{}^b$) × 10^{-4}	33.0 (31.4)	71.0	89.4
VS, $M_w{}^f$ ($M_n{}^g$) × 10^{-4}	32.9 (30.9)	73.4	91.8
VS, $(M_w/M_n)^c$	1.07	1.05	1.05
PI arms, $DB_w{}^d$ ($DB_n{}^e$)	8.4 (8.3)	7.6	7.7
wt % PS (SEC/UV)	47	50	40
wt % PS (^{1}H-NMR)	48	49	41
wt % PS (dn/dc)^h	54 (0.162)	51 (0.160)	37 (0.152)
wt % PS^f (PS^g)	49 (49)	49	39

[a] LALLS in THF at 25 °C. [b] Membrane osmometry in toluene at 35 °C. [c] SEC in THF at 30 °C. [d] Weight-average degree of branching. [e] Number-average degree of branching. [f] Calculated from precursor M_ws. [g] Calculated from precursor M_ns. [h] Laser differential refractometry in THF at 25 °C, dn/dc in mL g^{-1}.

In conclusion, the combined characterization results indicate that Vergina star copolymers of the A_8B_8 type, having a high degree of molecular and compositional homogeneity, can be synthesized by using anionic polymerization and controlled chlorosilane chemistry. In forthcoming papers, the microphase separation,[11] the order−disorder transition,[12] the solution properties in toluene, cyclohexane, and dioxane, and the association behavior in decane[13] will be reported.

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