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Synthesis, Characterization, and Properties of Stars Consisting of Many Polyisobutylene Arms Radiating from a Core of Condensed Cyclosiloxanes[†]

Naoki Omura[‡] and Joseph P. Kennedy*

The Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

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ABSTRACT: Novel stars of many polyisobutylene(PIB) arms radiating from a core of condensed methylcyclosiloxanes are described. The synthesis involves hydrosilation of allyl-terminated PIB prearms by small methylcyclosiloxanes (e.g., D_4^H, D_6^H) and competitive moisture-mediated core−core coupling. The effect of conditions (e.g., time, temperature, stoichiometry, nature and molecular weight of prearms, and size of methylcyclosiloxane) on synthesis was investigated. The processes can be controlled and well-defined 21−28 arm stars have been perpared. Microstructures were characterized by various techniques. The intrinsic viscosities of stars are much lower than those of linear PIBs of the same molecular weight over the 30−100 °C range. Branching coefficients depend on the number of arms. Hydrodynamic volumes of stars and combs (polysiloxane backbone carrying PIB branches) are similar, indicating that both assume radial conformations. The stars are resistant to strong acids and bases indicating that resistant PIB coronas protect acid- and base-vulnerable cores. The temperature resistance of stars is similar to that of PIB.

Introduction

In the course of our investigations of novel potentially useful star polymers,[1−6] we became interested in the synthesis of stars comprising of many (>6) polyisobutylene (PIB) arms emanating from a core of multicondensed cyclosiloxanes. Recent work from this laboratory has demonstrated the first synthesis of well-defined stars with close to 6 PIB arms by hydrosilation of ω-allyl-terminated PIB (PIB-allyl) with methylcyclosilanes carrying 6 SiH groups (D_6^H).[1] During these investigations we have also observed that in the presence of traces of water in the hydrosilation charges a certain quantity of stars with a much higher number of arms than the expected 6 also arose.[1] The formation of these "higher order" stars was explained by core−core coupling,[2−4] a process which was corroborated by direct experiments.[1]

Since the number of common methylcyclosiloxanes with multiple SiH functions is quite limited (only two such cyclosiloxanes are commercially available, D_4^H and D_5^H), the preparation of the target multiarm stars by hydrosilation of PIB-allyl by a specific methylcyclosiloxane appeared to be cumbersome. Also, we have found[1] that steric compression severely limits the quantitative hydrosilation of multiple neighboring SiH groups.

It occurred to us that these difficulties could be avoided and the target multiarm stars could be prepared by exploiting our chance observation of core−core coupling, in other words by making multiarm stars by *designed* core−core coupling of small methylcyclosiloxanes (e.g., D_4^H, D_6^H) carrying a number of PIB substituents in the presence of moisture under hydrosilation conditions. Thus, our synthesis challenge shifted to finding conditions under which the hydrosilation of PIB-allyl with inexpensive common cyclosiloxanes and core−core coupling would occur *simultaneously* so that first-order stars would condense to higher order multiarm stars.

Scheme 1 helps one to visualize the synthetic strategy envisioned. The first step is hydrosilation of PIB-allyl by methylcyclosiloxane. Generic formula **A** signifies common methylcyclosiloxanes, D_4^H, D_5^H, etc., with multiple SiH functions; for simplicity **A** shows only three such units. Unless steric compression intervenes, the first step, hydrosilation, is known to proceed with very high efficiency to give **B** (a structure we call a first-order or primary star). Importantly, **B** carries some unreacted SiH groups. The extent of hydrosilation can be controlled (e.g., by controlling the [SiH]/[C=C] ratio, temperature, and catalyst concentration) such that a certain number of SiH groups would survive. In the presence of water (and depending on conditions), in addition to the hydrosilation of PIB-allyl some of the residual SiH functions will be converted to Si−OH groups (see formula **C**)[7,8] which in turn will rapidly self-condense ($2\mathrm{Si{-}OH} \rightarrow \mathrm{Si{-}O{-}Si} + H_2O$) or will react with Si−H ($\mathrm{Si{-}OH} + \mathrm{SiH} \rightarrow \mathrm{Si{-}O{-}Si} + H_2$)[9,10] to form **D** by core−core coupling. Depending on reaction conditions, these processes (i.e., hydrosilation *and* various core−core couplings) proceed *simultaneously and competitively* at various rates until the reactive functions (PIB-allyl, SiH, Si−OH) are consumed or become inactive due to steric hindrance. The outcome of these reactions will be **E**, the sought higher order multiarm star comprising of many PIB arms emanating from a complex core of condensed methylcyclosiloxanes (in **E** the circles indicate methylcycolsiloxanes carrying the PIB arms (long wiggly lines) as well as unreacted −H or −OH groups). In view of the large number of high molecular weight PIB arms (and low molecular weight methylcyclosiloxane rings) the relative proportion of the condensed core relative to the overall structure is negligible (see later).

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* Corresponding author.

[†] Eigth in a series of publications on "Multi-Arm Star Polysiobutylenes". Part 7: Majoros, I.; Marsalko, T. M; Kennedy, J. P. *Polym. Bull.* **1997**, *38*, 15.

[‡] Permanent address: Silicone-Electronics Materials Research Center, Shin-Etsu Chemical Co., Ltd., 1-10 Hitomi Matsuida Usui Gunma, Japan 379-02.

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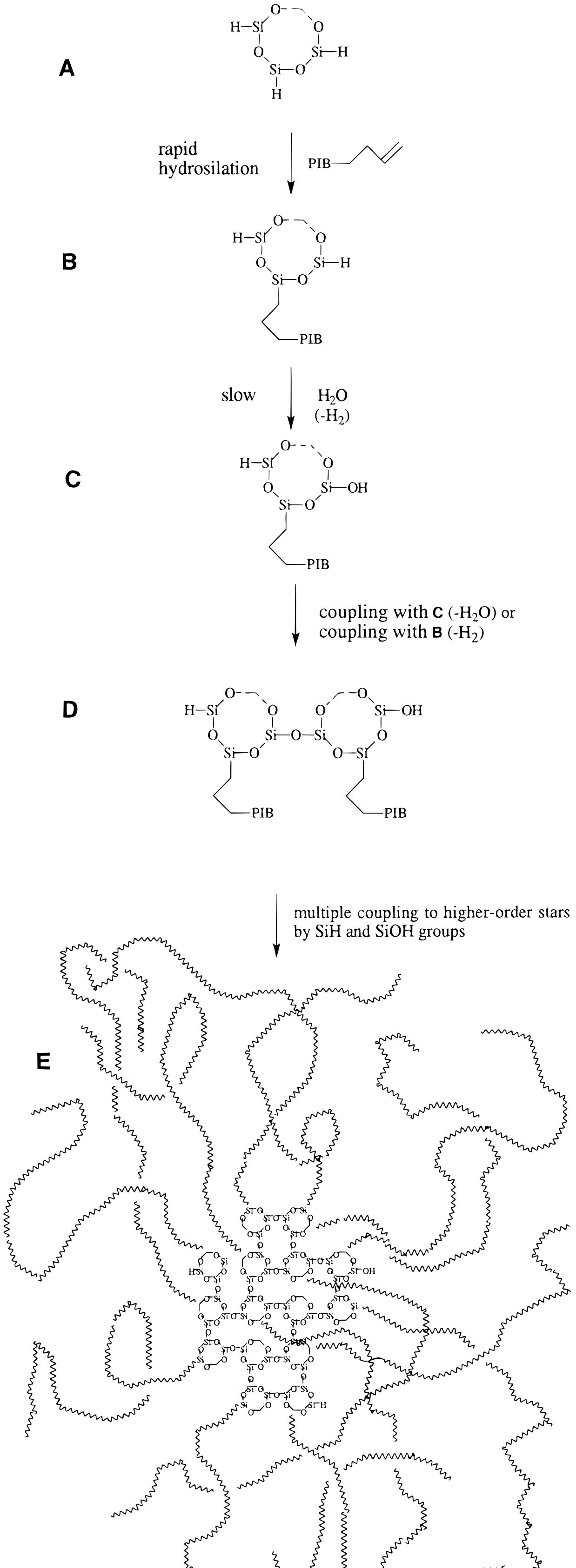
Scheme 1. Synthesis Strategy (See Text)



The condensation of the small rings to give rise to the final core may proceed in a variety of manners, the precise route of which would be extremely difficult to discern. The mechanism may start by 2**C** → **D**, or **B** + **C** → **D**, and would become increasingly complex after the **D** stage. Condensations **D** → **E** would be largely governed by statistics; they bear a certain resemblance to star formation by linking of living species, both anionic and cationic.[2,11,12] It is known that the postulated condensations are accelerated in the presence of hydrosilation catalysts.[13] Also, water affects the competitive reactions, and traces or subanalytical amounts of moisture are present even in carefully dried charges.

Motivation for our objective was enhanced insight into the synthesis and structure/property relationships of unique stars and the efficient simple preparation of designed new materials with a unique combination of properties for potential applications such as rheology modifying additives in motor oils, coatings, and paints, etc.[14,15]

This paper describes our synthetic studies culminating in the convenient preparation of the target higher order stars, **E** in Scheme 1, microstructure characterization by a battery of techniques, and a study of viscosity/temperature profiles, and acid–base and thermal resistance of select higher order stars. We have learned to control not only the size of the core but also, more importantly, the number of arms, which ultimately controls rheological properties.

Experimental Section

Materials and Abbreviations. Cyclopentane (anhydrous, Aldrich) was dried by refluxing over lithium aluminum hydride powder for 3 h. 1-Pentene (95%, Aldrich) was used as received. A mixture of D_n^H (designated X-92–154, where n = 5, 6, 7, 8, 9, etc., a side product of the manufacture of D_4^H by hydrolysis of dichloromethylsilane), the α,ω-bis(trimethyl)poly(methyl hydrogen siloxane) with an average degree of polymerization of 38 (MD_{38}^HM), and the H_2PtCl_6 catalyst solution (0.5 wt % Pt in toluene) were received courtesy of Shin-Etsu Chemical Co., Ltd.

Stars are abbreviated by a combination of two symbols, the first of which indicates the number average molecular weight (M_n) of the arms, and the second the number of arms (N_n); for example, 9K-4.4 designates a star having 4.4 PIB arms, each arm with $M_n = 9000$.

Preparation of Starting Materials. (a) Core Precursors. The preparation of hexamethylcyclohexasiloxane, D_6^H, has been described.[1,16] Dodecamethylcyclododecasiloxane, D_{12}^H, was obtained by fractional distillation of X-92-154 by using a spinning band column (Nester/Faust, 75 theoretical plates) under reduced pressure. The fraction at bp 120 °C/0.25 mmHg was collected; yield 1.4 g (0.15%). According to GC analysis this fraction consisted of 87.3% D_{12}^H, 3.1% D_{11}^H, and 8.6% D_{13}^H. The product was stored over CaH_2. ^1H NMR spectroscopy (200 MHz, $CDCl_3$) showed $\delta = 0.19$ (s, 3H in Si-CH_3), 4.80 (s, 1H in Si-H). Fractional distillation of X-92-154 also yielded D_6^H(7.4%), D_7^H-(2.4%), D_8^H(1.0%), D_9^H(0.68%), D_{10}^H(0.32%), D_{11}^H(0.36%). Figure 1shows new information in regard to boiling points as a function of the number of Si atoms in D_n^H.

(b) PIB Prearms. α-*tert*-Butyl-ω-allyl-PIBs (PIB-allyl) were prepared by a two-step one-pot method: First, chlorine-terminated PIB (PIB-Cl) was obtained by using the 2-chloro-2,4,4-trimethylpentane /$TiCl_4$/N,N-dimethylacetamide system.[17] The living polymers were quenched by a 10-fold (PIB2 in Table 1), 20-fold (PIB3), and 50-fold (PIB4) excess of allyltrimethylsilane.[18] α-*tert*-Butyl-ω-isopropenyl-PIBs (PIB-methallyl) were

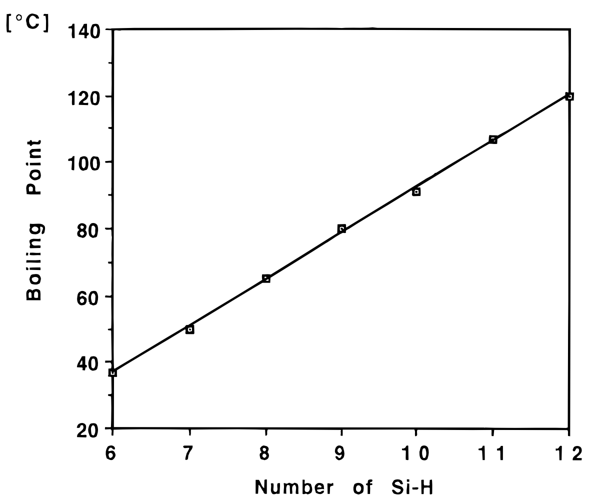


Figure 1. Boiling points of compounds of the homologous series D_n^{H}, where n=6 to 12 (at 0.25mmHg).

Table 1. Characterization of PIB Prearms

		M_n			
PIB	end group	GPC	NMR	M_w/M_n	F_n[a]
1	isopropenyl	3900	3722	1.06	1.05
2	allyl	9300	9300	1.18	1.00
3	allyl	16700	16200	1.13	1.03
4	allyl	31700	35000	1.16	0.91

[a] Number average end group functionality by GPC/^{1}H NMR data.

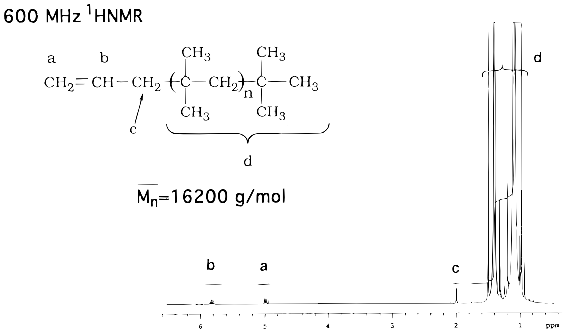


Figure 2. ^{1}H-NMR (600 MHz) spectrum of PIB-allyl and assignments.

obtained by dehydrochlorination of PIB-Cl.[19] The products were characterized by ^{1}H-NMR spectroscopy (200 MHz for PIB-methallyl and 600 MHz fo PIB-allyl) and GPC, details of which have been described.[1,20]

Procedures. (a) PIB Prearms and Calculation of Number of Arms of Stars. Number, and weight average molecular weights (M_n, M_w) and dispersities (M_w/M_n) of linear PIB prearms (PIB-allyl) were determined by GPC. Details of the methodology have been described.[1] The products were further characterized by ^{1}H NMR spectroscopy by the use of a 200 or 600 MHz Varian Gemini spectrometer and standard 5 mm tubes at ambient temperature with 19 mg of the sample/mL of $CDCl_3$. In the 600 MHz NMR, 32 FIDs were collected with a 3.0 s acquisition time for a 3.3 μs pulse width. Figure 2 shows a representative 600 MHz spectrum of a PIB-allyl (M_n = 12 600) together with assignments. The structure of PIB-methallyl prearms were characterized by 200 MHz ^{1}H NMR spectroscopy with 2052 FIDs. The procedures have been described.[1]

The number average end group functionality F_n was calculated by (A) determining M_n by GPC(RI), (B) quantitating the allyl groups (i.e., the protons associated with the $CH_2{=}CH{-}CH_2{-}$ group at $\delta = 5.8$ (proton b in Figure 2), $\delta = 5.0$ (proton a) and $\delta = 2.0$ (proton c)) relative to the total amount of PIB protons in the ($\delta = 0.8{-}1.7$ range (proton d)), and dividing A/B. Table 1 summarizes the structural characteristics of the PIB prearms prepared and used.

The M_n, M_w and M_w/M_n of stars were obtained by a GPC instrument equipped with an on-line refractive index (RI) and laser light scattering (LLS) detector (Minidawn, Dawn F. Wyatt Technology Co.) in conjunction with an Optilab Instrument (also of Wyatt Technology) which provided d*n*/d*c* values. The data were evaluated by Astra 4.0 software (Wyatt Technology). Details of the procedure have been described.[2,3,5] M_n was calculated from M_w data obtained by GPC(LLS), and using the Astra 4.0 software. For the calculation of the number of arms (N_n) of higher order stars, the M_n of the core was considered negligible relative to that of the sum of the arms. (A simple calculation illustrates the basis for this simplification. We have found empirically (see later) that higher order stars can be readily obtained by the use of a $[SiH]/[C{=}C] = 4$ stoichiometry, in other words with $[D_6^H]/[C{=}C] = 6/4 = 1.5$ mol. Thus, e.g., a 30 arms star will contain a core of 20 condensed D_6 rings (mol wt = 360) representing for the core a total of $M_{n,core} = 7200$ (i.e., 20 × 360). With PIB prearms of, e.g., $M_n = 9300$ or $M_n = 16\,200$ (see later, Tables 3−5) the total M_n of the coronas will be 279 000 or 486 000, respectively. Thus the experimental error due to the above simplification will be a negligible 2.6 or 1.5%, respectively.

Preliminary Investigations: Kinetics of Star Formation. Representative procedures to monitor star formation were as follows.

(a) First-Order (or Primary) Stars. To a homogeneous solution of PIB-allyl (162 mg, 0.0174 mmol, of $M_n = 9300$), and D_6^H (1.04 mg, 0.00289 mmol, in ca. 1 mL dry cyclopentane) were added CaH_2 (~10 mg) and H_2PtCl_6 (3.6 μL in toluene). The system was agitated and distributed to five dry sample vials (8 mL), the cyclopentane was removed by vacuum, and the sample vials were placed in a N_2-blanketed desiccator containing $CaCl_2$. After 1.5, 3, 6, 24, and 168 h at room temperature, an excess (~1.0 mL) of 1-pentene was added to the active charges to quench the reactions. The samples were immediately analyzed by GPC(LLS) as to extent of conversion, molecular weight, and dispersity. Core−core coupling was absent after 9 days, indicating that the THF was reasonably dry.

Conversions were determined by correlating the GPC-(RI) peak area of the star to that of unreacted PIB-allyl and correcting with the appropriate d*n*/d*c* values($(dn/dc)_{9K\text{-}4.4} = 0.118$, $(dn/dc)_{PIB}$, $M_{n=9300} = 0.118$).

(b) Higher Order Stars. The above procedure was used except the concentration of D_6^H was (4.18 mg, 0.0116 mmol).

Synthesis of Star Polymers. (a) First-Order (Primary) Star 9K-4.4. To a homogeneous solution of PIB-allyl (4942 mg, 0.532 mmol, $M_n = 9300$ and D_6^H (39.9 mg, 0.111 mmol) in ~20 mL dry cyclopentane were added H_2PtCl_6 (114 μL in toluene) and CaH_2 (~50 mg). The charge was placed in a petri dish, and the cyclopentane was removed by vacuum. The system was placed in a N_2 filled desiccator containing $CaCl_2$ for 10 days at room temperature. After this period an excess (~10 mL) of 1-pentene was added to the charge to quench the reaction, and the system was filtered to remove the CaH_2 drying agent. After being purified by perticipating with hexane/acetone to remove the Pt catalyst, the product was dried in a vacuum oven (60 °C for 3 days) and analyzed for conversion, molecular weight and dispersity by GPC(LLS).

(b) Higher Order Star 16K-22. To a homogeneous solution of PIB-allyl (4875 mg, 0.301 mmol, M_n = 16 200), $D_6{}^H$ (72.3 mg, 0.201 mmol), and ~10 mL of dry cyclopentane was added H_2PtCl_6 (114 μL toluene solution). The charge was placed in a 100 mL flask, and the cyclopentane was removed by evacuation. The flask was capped and placed in a heating oven at 120 °C for 2 weeks. After this period the reaction was terminated by the introduction of an excess (~10 mL) of 1-pentene; the product was dissolved in ~30 mL of hexane and precipitated in an excess of acetone. After filtration, the product was vacuum dried (60 °C, 3 days) and analyzed as to conversion, molecular weight, and dispersity by GPC(LLS).

(c) Comb-Shaped Polymer 16K-24C. To a homogeneous solution of PIB-allyl (5341 mg, 0.330 mmol, M_n = 16 200), $MD_{38}{}^HM$ (38.4 mg, 0.0157 mmol), and ~ 10 mL of dry cyclopentane was added H_2PtCl_6 (123 μL of a toluene solution). The charge was placed in a petri dish, and the cyclopentane was removed by vacuum. The system was placed in a N_2-filled desiccator containing $CaCl_2$ for 2 weeks at room temperature. After this period, an excess (~10 mL) of 1-pentene was added to the charge to quench the reaction, and the system was filtered to remove the CaH_2 drying agent. The product was dried in a vacuum oven (60 °C for 3 days) and analyzed by GPC (LLS) as to conversion, molecular weight, and dispersity.

^{1}H NMR Study of First-Order Stars. Star polymers (19 mg/mL of $CDCl_3$) were characterized by ^{1}H NMR spectroscopy by the use of a 600 MHz Varian Gemini spectrometer, standard 5 mm tubes, and $CDCl_3$ at ambient temperature (see conditions used for prearms). Stars (prior to quenching with 1-pentene) were characterized without purification (no precipitation) to avoid hydrolysis of SiH groups. Peak assignments: δ = 0.0−0.2 (Si−CH_3), 0.4−0.5 (Si−CH_2CH$_2$CH$_2$−PIB), 0.8−1.7 (PIB protons), 4.7(Si−H). The Si−CH_3 peak is split into two peaks. The peak at δ = 0.00−0.12 is due to CH_3−Si−CH$_2$−CH$_2$−CH$_2$−PIB, and that at δ = 0.12−0.20 is due to CH_3−Si−H. The peak integrals yielded the following quantities (normalized to 1 mol of PIB)

$$\mathrm{Si{-}CH_3} = \frac{\mathbf{I}_{0.0-0.2}}{3}\frac{\mathrm{H\ in\ PIB}}{\mathbf{I}_{0.8-1.7}}$$

where $\mathbf{I}_{0.0-0.2}$ is the resonance integral for Si−CH$_3$ protons in the d = 0.0−0.2 range, and $\mathbf{I}_{0.8-1.7}$ is that for all PIB protons and H in PIB is the number of protons of PIB.

$$\mathrm{core\ content} = \frac{\mathrm{Si{-}CH_3} \times 60.1}{\mathrm{PIB}_{M_n} + \mathrm{Si{-}CH_3} \times 60.1}$$

$$\mathrm{remaining\ SiH\ in\ core} = \mathbf{I}_{4.7}\frac{\mathrm{H\ in\ PIB}}{\mathbf{I}_{0.8-1.7}}$$

$$\mathrm{consumed\ SiH} = \frac{\mathbf{I}_{0.4-0.5}}{2}\frac{\mathrm{H\ in\ PIB}}{\mathbf{I}_{0.8-1.7}}$$

$$N_{\mathrm{n,NMR}} = N_{\mathrm{SiH}}\frac{\mathrm{consumed\ SiH}}{\mathrm{Si{-}CH_3}}$$

N_{SiH} is the number of SiH group per core. Since the Si−OH resonance cannot be separated from the broad resonance, the total moles of hydrolized SiH (Si−OH) and condensed core (Si−O−Si) are calculated as follows:

$$\mathrm{SiH\ converted\ to\ Si{-}OH\ or\ Si{-}O{-}Si} = \mathrm{Si{-}CH_3} - \mathrm{consumed\ SiH} - \mathrm{remaining\ SiH}$$

Viscometry. Star polymers were contaminated by unreacted PIB prearms (PIB-allyl content 7−20%); therefore, their intrinsic viscosities were corrected as follows:[21]

$$[\eta]_{\mathrm{star}} = ([\eta]_{\mathrm{expt}} - \omega_{\mathrm{arm}}[\eta]_{\mathrm{arm}})/\omega_{\mathrm{star}}$$

ω_{arm} and ω_{star} are the weights of the arm and the star polymer, respectively. The $[\eta]_{\mathrm{arm}}$ values were obtained by measuring the intrinsic viscosities of six different PIBs in the range M_w = 11 000−377 000 at six temperatures in the 30−100 °C range and calculating the Mark−Houwink constants, **K** and a, from these data.

The branching coefficients were calculated by

$$g^* = \left|\frac{[\eta]_{\mathrm{star}}}{[\eta]_{\mathrm{linear}}}\right|^{T,M_w}_{\mathrm{tol}}$$

Determination of Acid and Base Resistance. Into a 20 mL vial were charged star polymer (20 mg) in 1 mL of xylene (if desired) and concentrated or 50% sulfuric acid (4 mL); the vial was sealed and placed in a heating oven at 70° for 3 days, 1 week, and 3 weeks. Mixing was provided by heat convection. Subsequently, the vial was opened and the charge was diluted by 3 mL of n-hexane. The organic layer was separated and washed with water several times until neutral. The volatiles were removed in vacuum, and the product was analyzed by GPC(LLS), specifically, to determine the M_n(by Astra software) and the amount of star remaining relative to the peak characteristic of PIB.

Base resistance was examined as follows: Into a 20 mL vial were charged star polymer (20 mg) in 1 mL of xylene and t-BuOK (50 mg). The vial was sealed and placed in a heating oven at 70 °C for 1 day, 3 days, 1 week, and 2 weeks. Subsequently, the vial was opened and the remaining t-BuOK was removed by filtration. The volatiles were removed in vacuum, and the product was analyzed by GPC(LLS), specifically, to determine the M_n (by Astra software) and the amount of star remaining relative to the peak characteristic of PIB.

Simultaneously, control experiments were also carried out under similar conditions with decamethylcyclosiloxane (D_5) in the presence of n-nonane as internal standard, to ascertain the quantitative hydrolysis of a cyclosilane similar to that of the core.

Base resistance was also tested under more aggressive condition as follows. Into a 100 mL one-neck flask were placed star 9K-4.4 (120 mg), ethanol (6.0 g), tetrahydrofuran (12.5 g), and t-BuOK (0.2 g), and the solution was refluxed for 1 week. After filtration, the volatiles were removed by vacuum, and the polymer was analyzed by GPC to ascertain the disappearance of the star and the survival of the PIB arms.

Thermal Stability. The heat stabilities of primary and higher order stars (5−10 mg samples), together with appropriate linear PIB and siloxane controls, were

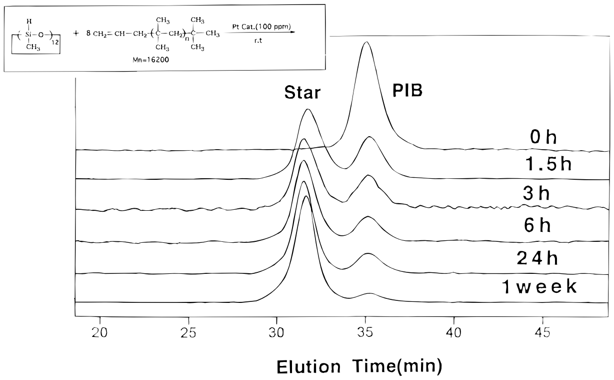


Figure 3. Representative series of GPC(RI) traces of primary star formation (the inset shows synthesis details).

Table 2. Kinetics of Primary Star Formation ([SiH]/[C=C] = 1.5, Room Temprature)

time,[a] h	Convn,[b] %	experimental data[c] N_n	$M_n \times 10^3$	M_w/M_n	calculated values $N_{n,calc}$	$M_{n,calc} \times 10^3$
1.5	64	5.6	91	1.26	5.1	84
3.0	69	6.1	99	1.25	5.5	90
6.0	80	6.6	108	1.25	6.4	104
24	81	7.1	115	1.26	6.5	105
168	92	8.2	133	1.27	7.4	120

[a] Reaction quenched by 1-pentene. [b] By RI. [c] Calculated from LLS data.

studied by using a DuPont thermogravimetric analyzer (Model 951 and a Model 9900 computer) in air by heating to 600 °C at 10 °C/min. The temperatures at 5, 10, 20, and 30% weight loss were determined.

Computer Simulation of Core Structures. The structure of cores was simulated by using the MSI Insight II, Version 3.00, program.[22–24] A 300-step minimization was performed on the initial structure until a convergence of 0.10 kcal/mol was reached. Then a 1500 fs molecular dynamics calculation was run followed by a 500-step final minimization to 0.001 kcal/mol convergence.

Results and Discussion

Orienting Studies. (a) Optimization of Primary Star Formation. The first phase of this research was directed toward an exploration or reaction conditions leading to the efficient synthesis of primary stars. Specifically, kinetic experimentation was carried out to gain insight into the various effects (e.g., nature and molecular weight of PIB prearms, size of cyclosiloxane core, and reagent stoichiometry) on conversions and number of arms.

Figure 3 and Table 2 summarize the results of a representative kinetic study of hydrosilation of PIB-allyl by D_{12}^H at [SiH]/[C=C] = 1.5.

Table 2 shows the data obtained by GPC(LLS) and, in the last two colums, N_n and M_n calculated from conversions by

$$N_{n,calc} = \frac{\mathbf{N}\mathrm{SiH}}{[\mathrm{SiH}]/[\mathrm{C{=}C}]} \times \text{conversion}$$

$$M_{n,calc.} = N_n(M_n \text{ of prearms}) + M_n \text{ of siloxane core}$$

Comparison of experimental and calculated N_n's are in satisfactory agreement. (This agreement also indicates that the dn/dc values were accurate.) The fact that the experimental N_n data are somewhat higher than calculated values suggests minor core–core coupling.

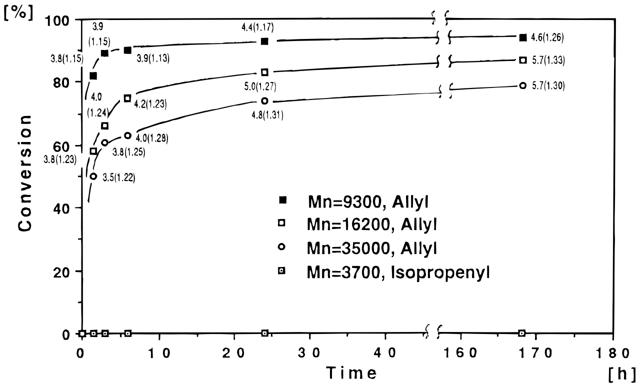


Figure 4. Relative rate of hydrosilation using ω-allyl- and ω-isopropenyl-PIB prearms of different molecular weights in conjunction with D_6^H. ([SiH]/[C=C] = 1.5, room temperature.) The numbers adjacent to the experimental points indicate N_n (the number of PIB arms); the numbers in parentheses are M_w/M_n values.

As shown by the family of GPC(RI) traces, the peak associated with the PIB prearms (~35 min) gradually decreases whereas that signaling the star (~32 min) increases and its shape narrows. After 1 week the conversion to star is almost quantitative (~92%), and the narrowness of the peak (M_w/M_n = 1.27) suggests the formation of a well-defined primary star. Significantly, the M_ns' and the number of arms N_n increase monotonically, and N_n reaches the theoretical value of 8 (considering [SiH]/[C=C] = 1.5).

A series of experiments were carried out by the use of different prearms (PIB-allyl and PIB-methallyl) and different prearm molecular weights (see Table 1). Figure 4 summarizes experimental conditions and results. As expected, primary star formation is fastest with the lowest molecular weight PIB-allyl; however, somewhat unexpectedly, star formation was absent with PIB-methallyl even though its M_n was quite low. Evidently, steric compression by CH_3 greatly retards star formation by hydrosilation. Similar effects have also been observed earlier.[1] The dispersity of all the stars was quite narrow (M_w/M_n = 1.1–1.3), showing a slight but persistent broadening with time; this phenomenon may be due to the onset of core–core coupling. The theoretical N_n ($N_{n,theor}$) in these experiments is 4.0, however, the data show a continuous increase with time. The N_n obtained with the higher molecular weight PIB prearm exceeded $N_{n,theor}$ due to competing core–core coupling.

Figure 5 summarizes the results of three series of experiments in which the [SiH]/[C=C] ratio was varied. Fastest conversion to star was obtained by the use of [SiH]/[C=C] = 1.5, however, product dispersity was relatively broad (M_w/M_n = 1.26) and N_n=4.6. These data indicate minor core–core coupling. Evidently remaining SiH groups react with H_2O and lead to condensation. With [SiH]/[C=C] = 1.0, the dispersity was narrow (M_w/M_n = 1.14), but conversion reached only ~80%.

Unexpected insight into the details of star formation was obtained by experiments in which the rate of star formation with D_6^H and D_{12}^H was compared. Figure 6 summarizes the results of four series of experiments showing the rates of hydrosilation of PIB-allyl (M_n = 9300) by D_6^H and D_{12}^H at two stoichiometries (i.e., [SiH]/[C=C] = 1.0 and 1.25). Interestingly, D_{12}^H was found

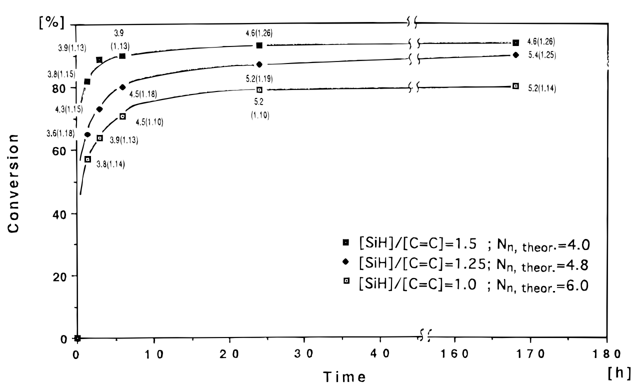


Figure 5. Relative rate of hydrosilation of ω-allyl-PIB prearms by D_6^H at different [SiH]/[C=C] ratios (PIB2 in Table 1, room temperature; for the meaning of numbers adjacent to the experimental points, see Figure 4).

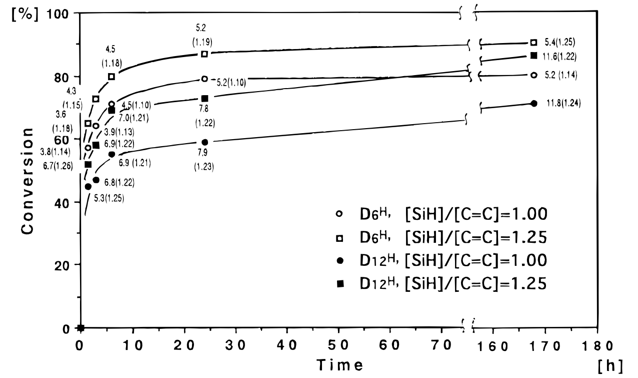


Figure 6. Rate of hydrosilation of ω-allyl-PIB prearms by D_6^H and D_{12}^H at [SiH]/[C=C] = 1.0 and 1.25 (PIB2 in Table 1, room temperature; for the meaning of numbers adjacent to the experimental points, see Figure 4).

Table 3. Interatomic Distances between Si Atoms[a]

D_6^H Å

	Si 1	Si 2	Si 3	Si 4	Si 5	Si-6
Si 1	0.00	3.17	5.20	6.16	5.08	3.12
Si 2		0.00	3.17	5.30	5.55	5.03
Si 3			0.00	3.16	5.18	5.26
Si 4				0.00	3.16	4.61
Si 5					0.00	3.17
Si 6						0.00

D_{12}^H Å

	Si 1	Si 2	Si 3	Si 4	Si 5	Si 6	Si 7	Si 8	Si 9	Si10	Si11	Si12
Si 1	0.00	3.15	4.98	6.98	9.20	9.45	9.42	9.26	7.98	7.06	6.09	3.10
Si 2		0.00	3.16	6.10	8.89	9.23	9.28	9.52	9.26	9.23	8.87	6.11
Si 3			0.00	3.09	6.12	7.05	8.00	9.27	9.41	9.47	9.22	7.05
Si 4				0.00	3.18	5.05	7.08	9.23	9.47	9.41	9.24	7.94
Si 5					0.00	3.14	6.08	8.85	9.21	9.27	9.54	9.28
Si 6						0.00	3.09	6.09	7.05	7.98	9.27	9.41
Si 7							0.00	3.15	5.02	7.03	9.21	9.45
Si 8								0.00	3.14	6.06	8.82	9.17
Si 9									0.00	3.07	6.06	6.99
Si10										0.00	3.14	5.00
Si11											0.00	3.13
Si12												0.00

[a] Numbering of Si atoms in Figures 7 and 8.

to be less reactive initially than D_6^H at both stoichiometires, and the dispersities of the stars obtained with the larger cyclosiloxane were broader than with the smaller ring.

An explanation for this observation was provided by computer-simulated models. Table 3, and Figures 7 and 8 show the results of the simulation. Thus, computer modeling of D_6^H and D_{12}^H indicated that in D_6^H all CH_3– and H– substituents on the Si's are forced toward the outside of the ring so that the SiH groups are readily available to react; in contrast, in the larger loser D_{12}^H some of the SiH groups are initially inside the ring cavity and therefore are less available for hydrosilation. Interestingly, with the D_{12}^H system the number of arms increases relatively rapidly between 30 and 170 h; this phenomenon suggests a change in the core conformation with progressing hydrosilation.

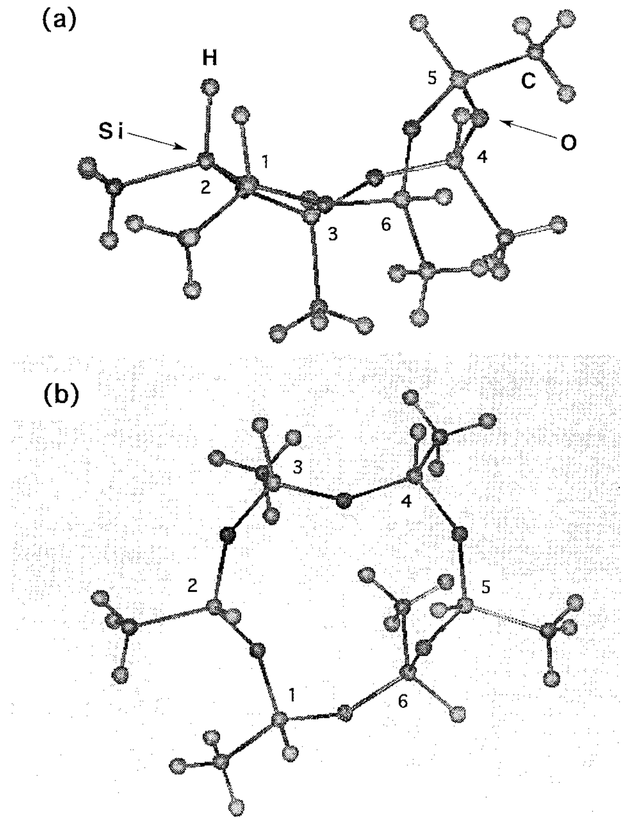


Figure 7. Structure of D_6^H by computer simulation: (a) side view; (b) top view. The numbers indicate Si atoms to facilitate the reading of Table 6.

An examination of interatomic distances between silicone atoms shown in Table 3 substantiates this conclusion. The numbering of the Si atoms is shown in Figure 7 and 8. According to the data, the maximum distance between two silicone atoms in D_6^H (i.e., between Si1 and Si4)is 6.16 Å; on the other hand, in D_{12}^H, the maximum distance (between Si5 and Si11) is 9.54 Å. The distance between Si and H in $Si-CH_3$ is ~2.52 Å. Thus, it would be difficult for D_6^H to assume a conformation in which the H and CH_3 substituents on Si are inside the ring. This means that both H and CH_3 are preferentially outside the ring; i.e., all the SiH groups are available for hydrosilation. In contrast, for D_{12}^H, it is easier to assume conformations in which the H and CH_3 substituents on Si are inside the ring; i.e., some of the SiH moieties are buried and will be less available for hydrosilation during the first phase of hydrosilation (<30 h, see Figure 6).

Analysis of the rate of increase of N_n (see Figure 6) holds further clues as to the reaction mechanism. In the case of D_{12}^H, N_n increases dramatically during the period from 1 day to 1 week (i.e., N_n grows from ~8 to ~12) whereas with D_6^H this effect is close to negligible (N_n ~ 5.2 to ~5.3). The large increase N_n with D_{12}^H indicates the onset of relatively rapid core coupling with D_{12}^H. This process would occur because SiH groups (both outside and inside the ring) can preferentially react with the small highly mobile H_2O molecules leading to core condensation by the processes outlined in Scheme 1. In contrast, in the case of D_6^H, hydrosilation of PIB-allyl is relatively rapid on account of the available unhindered SiH groups, so that the opportunity for core coupling is reduced.

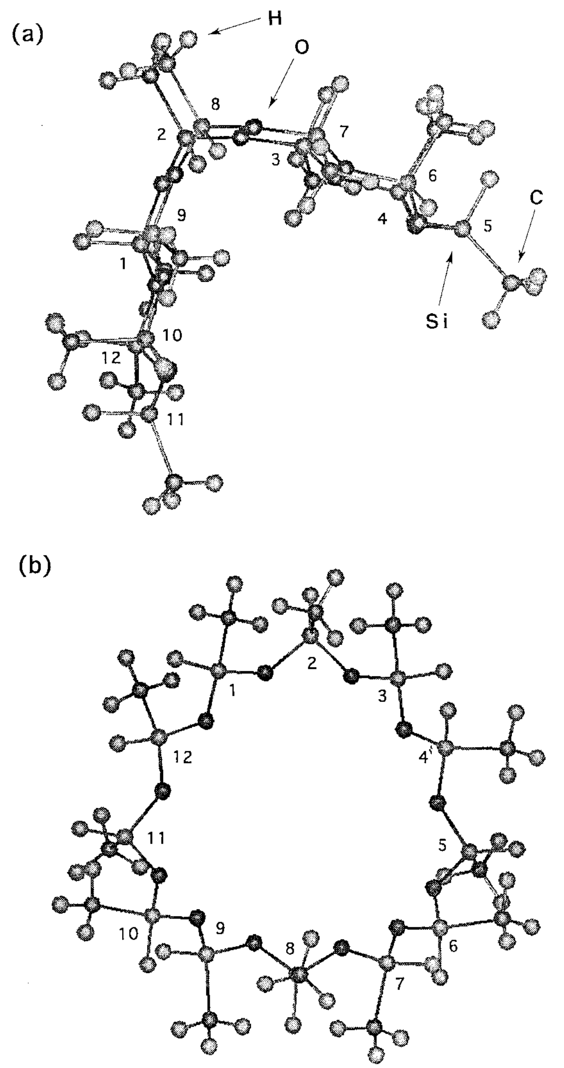


Figure 8. Structure of D_{12}^{H} by computer simulation: (a) side view; (b) top view. The numbers indicate Si atoms to facilitate the reading of Table 6.

(b) Kinetics of Higher Order Star Formation. Higher order stars arise by covalent bond formation between two or more first order (or primary) stars (core–core coupling), and therefore contain a multiplicity of arms emanating from condensed primary stars (see **E** in Scheme 1).

Figure 9 shows evidence for the formation of higher order stars. It summarizes the results of two series of experiments in which PIB-allyl and D_6^H were reacted at room temperature and at 120 °C (the legend gives experimental conditions). According to the GPC(RI) traces collected at various times, at room temperature the peak indicating the PIB prearm (~35 min) decreases steadily, until after 1 week only a very small amount of residual prearm remains, whereas at the same time two new peaks (~34 and ~32 min), appear, most likely indicating the presence of higher order stars. With increasing time, the relative amounts of the two peaks gradually shift toward the higher molecular weight (lower elution time) species, and after 1 week the two major higher order star components are present in approximately the same proportion. In contrast, the events unfold much more rapidly at 120 °C: The PIB prearm disappears more rapidly and the relative quantities of the two major higher order stars (peaks at ~34 and ~32 min) shift in favor of the higher molecular weight species. Similarity of the GPC(RI) traces suggest that 1.5 h at 120 °C is approximately equivalent to 1 day at room temperature. For all practical purposes higher order star formation is essentially complete in 6–24 h.

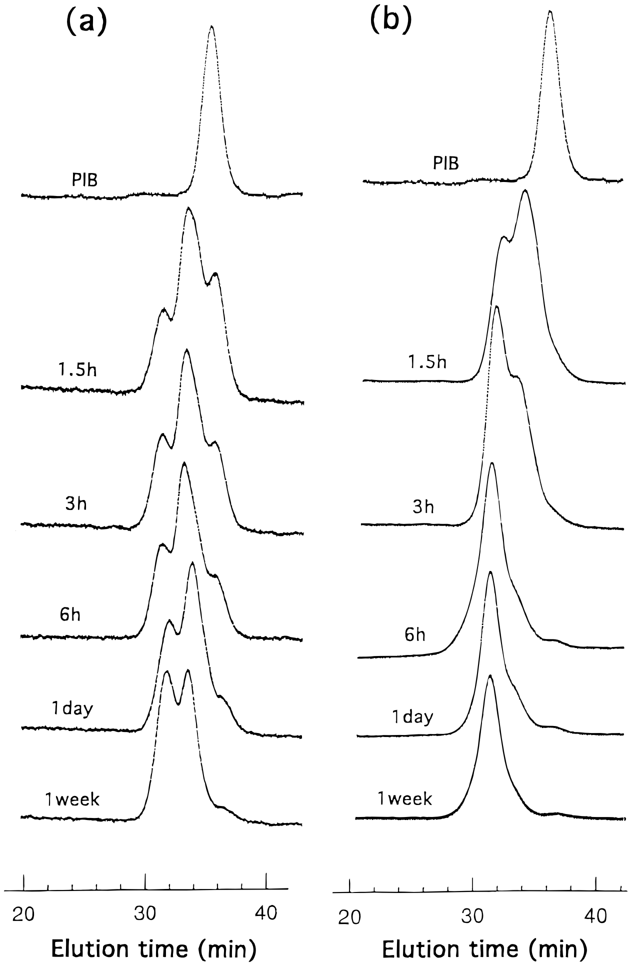


Figure 9. GPC(RI) trace indicating the formation of a higher order star: (a) at room temperature; (b) at 120 °C. Prearm PIB M_n = 9300 (PIB2 in Table 2). Core: $D6^H$, [SiH]/[C=C] = 4.0.)

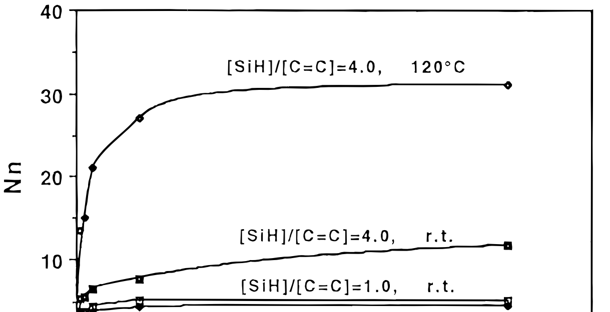


Figure 10. Rate of formation of number of arms (N_n) at various [SiH]/[C=C] ratios and temperatures. Prearm PIB M_n = 9300 (PIB2 in Table 2). Core: $D6^H$.

Figure 10 summarizes the rate of buildup of the number of arms under various experimental conditions. Evidently, higher order star formation is relatively rapid at 120 °C with product formation virtually complete in 1 day.

In sum, according to these kinetic data and other information assembled in this section, well-defined first-

Table 4. Synthesis and Characterization of Star Polymers

	synthesis conditions					star characterization results							
									N_n			methylcyclosiloxane, wt %	
polymer symbol	M_n[a]	siloxane	[SiH]/[C═C]	time, days	T, °C	star,[b] %	M_n[c]	M_w/M_n	LLS	conv.	NMR[d]	expt[d]	theor[e]
						First Order Star							
9K-4.4	9 300	D6^H	1.25	10	*f*	92	41 000	1.08	4.4	4.4	4.0	0.83	0.82
9K-9.0	9 300	D12^H	1.25	10	*f*	89	84 000	1.31	9.0	8.7	8.0	0.76	0.82
16K-4.2	16 200	D6^H	1.25	10	*f*	89	68 000	1.08	4.2	4.3	...	0.46	0.47
16K-8.8	16 200	D12^H	1.25	10	*f*	82	144 000	1.22	8.8	7.9	...	0.46	0.47
33K-4.7	35 000	D6^H	1.25	14	*f*	80	156 000	1.19	4.9	3.9	...	0.22	0.22
						Higher Order Star							
9K-28	9 300	D6^H	4.00	7	120	94	260 000	1.23	28				1.48
16K-21	16 200	D4^H	4.00	14	120	91	344 000	1.39	21				1.48
16K-22	16 200	D6^H	4.00	14	120	93	350 000	1.54	22				1.48
						Comb							
16K-24C	16200	MD38^{H}M	1.81	14	*f*	93	394 000	1.30	24				

[a] By ^{1}H-NMR. [b] From GPC(RI) eluograms(relative areas of star/PIB-allyl prearm). [c] Calculated by Astra software from LLS data. d*n*/d*c* of PIB: 0.118−0.122 mL/g. [d] From 600 MHz ^{1}H NMR, wt % calculated. [e] Calculated from weight of PBI-allyl prearm and siloxanes. [f] Room temperature.

order stars with maximum N_n and narrow dispersity can be prepared with [SiH]/[C═C] = 1.25 at room temperature, whereas higher order stars will preferentially arise by the use of [SiH]/[C═C] = 4.0 at 120 °C. On the basis of this information, we proceeded to the synthesis of desirable higher order stars.

Synthesis of Star Polymers. Guided by the results of orienting experiments (see above), various star polymers have been synthesized. Table 4 shows synthesis and characterization data for stars and a comb polymer prepared for comparison purposes (see later). The first column shows the product symbol, columns 2−6 concern synthesis conditions, and columns 7−14 list characterization information.

First-order stars made with D$_6^H$ exhibit very narrow dispersities (M_w/M_n = 1.08−1.19), whereas the dispersities of those made with D$_{12}^H$ are somewhat broader (M_w/M_n = 1.2−1.3) most likely because of the onset of core−core coupling caused by the different conformations of SiH groups (see above). The dispersities of higher order stars tend to be broader (M_w/M_n, = 1.23−1.54) although they are still narrower than stars made by linking of living polyisobutylenes with divinylbenzene (1.6−5.1).[4,25]

In regard to the number of arms (N_n) and cyclosiloxane core content (last five columns in Table 4), the agreement between the data obtained by independent methods (see Experimental Section) is quite satisfactory.

^{1}H NMR Characterization of First-Order Star. Direct evidence for the presence of star synthesis was obtained by high-resolution (600 MHz) ^{1}H NMR analysis of unpurified first-order stars.[20,26] Figure 11 shows a representative ^{1}H NMR spectrum of first-order star 9K-4.4 (see Table 4) (a) before and (b) after quenching with 1-pentene. Quantitative analysis (see Experimental Section) yielded the following information (normalized to 1 mol of PIB):

Si−CH$_3$	1.24 mol
SiH consumed	0.82 mol
SiH remaining	0.19 mol
SiH converted to Si−OH or Si−O−Si	0.22 mol

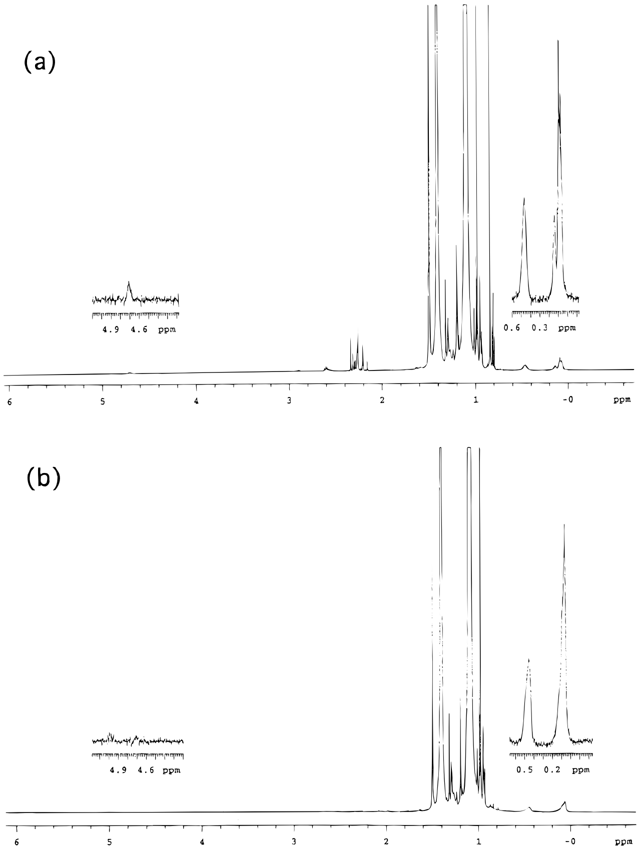


Figure 11. 600 MHz ^{1}H NMR spectrum of Star 9K-4.4 (see Table 4): (a) before quenching with 1-pentene, with unreacted Si−H present; (b) after quenching with 1-pentene, with Si−H absent.

Theoretical N_n values are reasonably close to those obtained by NMR spectroscopy (see the first two rows in Table 4); furthermore, these values are in reasonable agreement with those obtained by GPC(LLS) and calculated from percent conversions. The amount of Si−O−Si units is very low. The amounts of Si−OH and SiH groups were expected to be similar. The "survival" of Si−OH groups in air (presence of moisture) is most likely due to the protection of the PIB corona. The molecular weight of star 9K-9.0 did not change after 4 months of exposure to laboratory air (i.e., absence of core−core coupling).

The N_n values obtained by ^{1}H NMR spectroscopy(see column 12, Table 4) are consistently lower than those obtained from GPC(LLS) and conversions (see columns 10 and 11, Table 4) which may be due to minor core−core coupling.

Viscosity Studies. Since star polymers are of great interest as rheology control agents, we have investigated dilute solution viscosities of select stars. Figure 12 shows intrinsic viscosities of various star polymers

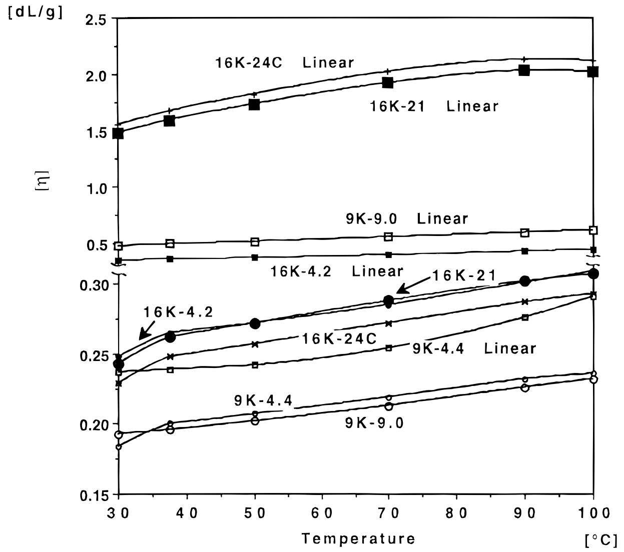


Figure 12. Intrinsic viscosities of linear (calculated) and star polymers as a funciton of tempreature. For example, 16K-21 linear shows the calculated [*h*] correspoding with the star polymer 16K-21 of the same M_w

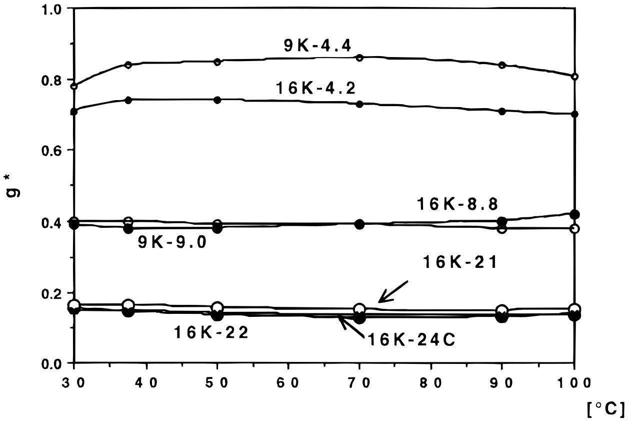


Figure 13. *g** values of star-PIBs as function of temperature.

together with those of linear PIBs (calculated values) in toluene as a function of temperature. Evidently, the intrinsic viscosity of stars is much lower than those of the linear counterparts and is mainly determined by the molecular weight of the arms and much less by the number of arms. Similar observations have been discussed in detail elsewhere.[5,27]

Figure 12 also shows, for comparative purposes, the intrinsic viscosity/temperature profile of a comb polymer. This structure 16K-24C (see last line in Table 4) was assembled by hydrosilating PIB-allyl prearms (M_n = 16 200 g/mol) with $MD_{38}{}^{H}M$. Interestingly, the intrinsic viscosity of this comb polymer is very close to those of stars with similar arm molecular weights. This suggests that the hydrodynamic volume of this comb and those of the stars are similar. We postulate that because of the incompatibility of the linear siloxane backbone and PIB arms, the relatively small backbone is forced into a tight central coil and the structure assumes a radial shape similar to that of a star.

From intrinsic viscosity data we have calculated branching coefficients *g**, and Figure 13 shows *g** as a function of temperature for the structures listed in Table 4. In accord with the conclusions above, the *g** of the 16K-24C comb is virtually identical to those of two stars of similar arm molecular weight.

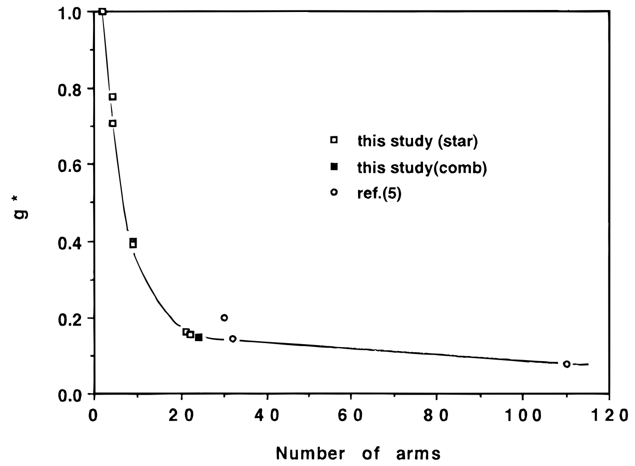


Figure 14. *g** values vs the number of arms.

Figure 14 shows *g** as a function of N_n of stars prepared in this work together with those prepared by linking living polyisobutylenes with dinvinylbenzene.[5] Significantly, all the data can be plotted on a common line, which is strong evidence that all these structures are radial. This conclusion is of significance for the present research: The facts in Figure 14 indicate that the higher order stars are also comprised of coronas of multiple PIB arms emanating from a condensed core.

Acid and Base Resistance. Common cyclosiloxanes are known to be quite vulnerable to acid or base hydrolysis.[28,29] In view of the possible uses of our novel stars (e.g., rheology controlling additives in motor oils exposed to harsh environments), it was of interest to test their resistance toward strong acid and bases. Table 5 shows the results of experiments. D_5 was included as a control to mimic the hydrolytic behavior of a structure similar to the cores of stars. According to the results, 50% H_2SO_4 had practically no effect on representative stars in bulk after heating to 70 °C for 3 weeks. Similar results have also been obtained by the use of *p*-toluenesulfonic acid with hexamethyldisiloxane (M_2). Evidently the acid-resistant PIB corona completely envelops and thus protects the acid-vulnerable core. We theorized that by repeating the experiment in the presence of an acid-resistant solvent (e.g., xylene) that would loosen up the protective corona (e.g., xylene), contact with concentrated H_2SO_4 would be facilitated and degradative hydrolysis would proceed. Indeed, this is what happened, and degradation occurred with star 9K-9.0 having relatively short PIB arms (i.e., smaller corona). Interestingly, however, after the M_n decreased from 84 000 to 36 000, the degradation practically stopped. We speculate that incomplete hydrolysis transformed the relatively large cores to smaller cores and that the smaller cores were protected by the intact PIB arms from further acid attack. Indeed, star 16K-4.2 with the longer PIB arms even under these more forcing conditions degraded only to a limited extent.

Similar experiments were also carried out with *t*-BuOK to test the base resistance of stars. According to the results, D_5 rapidly degraded even at room temperature, whereas the stars, depending on the time and temperature, underwent various extents of lesser degradations.

Under more aggressive conditions in the presence of alcohol, stars were completely decomposed.

Thermal Stability. Table 6 shows thermal stability information for star polymers and various controls in terms of decomposition temperatures at various extents of weight loss. According to these data, the thermal

Table 5. Acid and Base resistance of star polymers[a]

acid	time, days 0	3	7	14	21
D_5 (blank)					
50% H_2SO_4, no solvent					
amount of D_5 degraded, (%)[b]	0	−30	−44	−85	
16K-4.2					
50% H_2SO_4, no solvent					
$M_n \times 10^3$	68	67	63		67
decrease in the amount of star(%)	0	−3	−5		−5
9K-9.0					
50% H_2SO_4, no solvent					
$M_n \times 10^3$	84	82	83		81
decrease in the amount of star, (%)	0	−1	−3		−1
D_5 (Blank)					
conc. H_2SO_4, toluene					
amount of D_5 degraded(%)	0	−100			
16K-4.2					
conc H_2SO_4, xylene					
$M_n \times 10^3$	68	58	58	56	
decrease in the amount of star, %	0	−5	−6	−5	
9K-9.0					
Conc H_2SO_4, Xylene					
$M_n \times 10^3$	84	36	32	30	
decrease in the amount of star, %	0	−1	−2	−3	

base	time, days 0	1	3	7	14
D_5 (blank)					
t-BuOK, toluene,					
amount of D_5 degraded, %[b]	0	−88			
16K-4.2					
t-BuOK, xylene, 70 °C					
$M_n \times 10^3$	68	55	55	46	47
decrease in the amount of star, %	0	−10	−11	−16	−22
9K-9.0					
t-BuOK, xylene, 70 °C					
$M_n \times 10^3$	84	37	35	31	30
decrease in the amount of star, %	0	−7	−7	−8	−13
9K-4.4					
t-BuOK, THF, and MeOH					
$M_n \times 10^3$		not determined			
decrease in the amount of star, %	0			−75	−79

[a] At 70 °C. [b] By GC.

Table 6. Thermal Stability by TGA

polymers	temp, °C 5% wt loss	10% wt loss	20% wt loss	30% wt loss
Linear-PIBs				
PIB $M_n = 3720$	267	292	316	328
PIB $M_n = 9300$	257	275	293	307
PIB $M_n = 145000$	273	285	297	306
Silicones				
KF-96 100CS[a]	331	340	353	364
M^HD80M^{H}[b]306	324	344	365	
First-Order Stars				
9K-4.4	270	282	298	309
9K-9.0	257	270	286	296
16K-4.2	278	296	313	325
16K-8.8	275	290	309	318
33K-4.7	280	292	307	315
Higher Order Star				
16K-22	262	276	295	306

[a] Dimethylpolysiloxane (Shin-Etsu Chemical Co., Ltd.). [b] α,ω-dihydrodimethylsiloxane (degree of polymerization: 80).

stability of the stars reflect those of the PIB arms. This finding is not surprising in view of the large preponderance of the PIB moiety in the stars and the superior heat resistance of polysiloxanes.

Conclusions

The simple and inexpensive synthesis of star polymers consisting of a corona of PIB arms connected to and enveloping a methylcyclosiloxane core has been demonstrated. The arms arise of well-defined narrow dispersity allyl-terminated PIB. The core can be obtained either from a simple cyclosiloxane (D_4^H, D_6^H, or D_{12}^H have been used), in which case so called first-order or primary stars will be formed, or by the condensation of first-order stars to higher order stars, as outlined in Scheme 1. The competitive processes can be controlled by the judicious choice of experimental conditions and first-order or higher order stars can be prepared. The latter product/process is of particular significance for the rapid and convenient synthesis of multiarm stars. The syntheses of 21−28-arm stars have been described. The stars have been characterized by a variety of techniques, and the kinetics of star formation was analyzed.

The intrinsic viscosities and branching coefficients g^* of stars and a comb polymer of similar composition in the 30−100 °C range were studied. The intrinsic viscosities of stars are much lower than those of linear PIB arms of the same molecular weight. The g^* values of stars depend on the number of arms and not on the molecular weight of arms. The hydrodynamic volume of star and comb polymers of similar composition are virtually identical, suggesting that the combs also assume radial conformations in dilute solution. The g^* values as a function of the number of arms of stars prepared in this study and those made by linking living PIB carbocations by dinvinylbenzene follow the same pattern indicating the formation of fundamentally similar structures by both techniques. Stars are much more resistant to concentrated H_2SO_4 and *t*-BuOK than the naked core, suggesting that the PIB corona envelops and thus protects the cores from the attack of these aggressive chemicals. The overall heat resistances of the stars were found to be similar to that of PIB.

This study demonstrates that sometimes a side reaction which when first identified appears to be undesirable[1] can on further reflection become of great utility.

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