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Synthesis and characterization of novel well-defined stars consisting of eight polyisobutylene arms emanating from an octa(dimethylsiloxy)octasilsesquioxane core

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ABSTRACT

The synthesis and characterization of novel stars, octa(polyisobutylene-dimethylsiloxy)octasilsesquioxane ($T_8{D}^{PIB}$), consisting of eight polyisobutylene arms emanating from an octa(dimethylsiloxy)octasilsesquioxane ($T_8{D}$) core are described. The synthesis involves: 1) The synthesis of allyl-terminated polyisobutylene (PIB~) prearms, 2) The synthesis of octa(hydrodimethylsiloxy)octasilsesquioxane ($T_8{D}^{H}$) precore and 3) Star formation by hydrosilation of PIB~ with $T_8{D}^{H}$. Conditions for the precision synthesis and characterization of well-defined octa-arm stars are described.

INTRODUCTION

Earlier work [1] has shown that the synthesis of stars (octaisobutylene-octasilsesquioxane, T_8^{PIB}) consisting of eight PIB arms radiating from an octasilsesquioxane (T_8) core by hydrosilation of PIB~ with octahydridooctasilsesquioxane (T_8^{H}) was incomplete even under forcing conditions, and that core-core coupling was a side reaction. We theorized that these problems arose because of steric hindrance around the SiH groups on the T_8^{H}, and that this steric congestion could be eliminated by moving the SiH group one O–SiH bond away from the relatively rigid T_8 skeleton. The formula on the next page shows the structures involved, and computer-generated energetically most favored conformations of T_8^{H} and $T_8{D}^{H}$ (same magnification).

Paper No. VII of the series of "New Polyisobutylene Stars". For paper No. VI see S. Jacob, I. Majoros, and J. P. Kennedy *Macromolecules*, in press.

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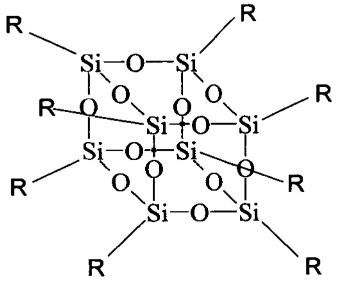
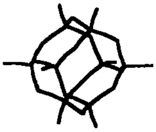
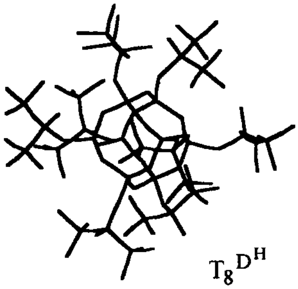




T_8^H



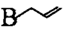
$T_8^{D^H}$

R=	$-H$	$-(CH_2)_3$-PIB	$-O-Si(CH_3)_2-H$	$-O-Si(CH_3)_2-(CH_2)_3$-PIB
	T_8^H	T_8^{PIB}	$T_8^{D^H}$	$T_8^{D^{PIB}}$

The purpose of this communication is to demonstrate the convenient synthesis of well-defined $T_8^{D^{PIB}}$ in the absence of core-core coupling by the use of Karstedt's catalyst within a few hours at room temperature.

EXPERIMENTAL

A. Materials and Syntheses

Materials for and the synthesis of PIB, together with its characterization, have been described [2-7]. Karstedt's catalyst (bis(divinyltetramethyldisiloxane)platinum(0), Pt(DVTMDS)$_x$) (United Chemical Technologies, Inc. (2-3% Pt in xylene, neutral)) and hexachloroplatinic acid monohydrate ($H_2PtCl_6 \cdot H_2O$) (ShinEtsu) were used as received. Toluene, heptane, dimethylformamide, acetone, tetramethylammonium hydroxide (10% aqueous solution), silicic acid, and dimethylchlorosilane (all from Aldrich) were used as received.

$T_8^{D^H}$ was synthesized by modifying literature procedures [8-10]: Tetramethylammonium silicate (TMASi) was prepared by reaction of tetramethylammonium hydroxide (348 mL of a 10% aqueous solution) and silicic acid (22.8 g). The mixture was stirred at room temperature for 21 hrs and heated to 60 °C for 17 hrs. The colorless solution was concentrated (Rotovap) and crystallized at ~ 4 °C. The product, a white solid, was filtered, washed with acetone and dried in vacuum for two days (78.9 g, yield > 98 %).

TMASi (8.27 g) was added to a stirred solution of dimethylchlorosilane (176 mL), heptane (176 mL), and dimethylformamide (352 mL). After 1 hr of stirring the mixture was cooled to 0 °C for 30 min, and hydrolyzed by adding droppwise ~ 1 L cold (~ 2 °C) distilled water to complete the formation of the siloxane. The mixture was removed from the ice bath and stirred until room temperature was attained. The organic layer was separated, washed with water until neutral, concentrated by Rotovap, and placed in a freezer for crystallization. The product was collected (2.93 g, yield 83 %) and recrystallized from acetone. The final product was as a white solid. ^1H NMR (C_6H_6): Lit. δ 4.97 (septet, SiH), 0.17 (d, $SiCH_3$); Obs. δ 4.97 (septet, SiH), 0.17 (d, $SiCH_3$).

A representative synthesis of T_8D^{PIB} (new compound) was carried out as follows (see Scheme 1): To PIB (~ 2·10^{-4} mol) dissolved in toluene (30 mL) and stirred for 1 hr in the presence of catalyst (15 μL of Karstedt's catalyst or 20 μL of $H_2PtCl_6{\cdot}H_2O$) was added T_8D^H (~ 0.015 - 0.02 g) in toluene (10 mL). The temperature was ambient in experiments carried out with Karstedt's catalyst and at 76 °C with $H_2PtCl_6{\cdot}H_2O$. Samples were withdrawn at 0.25, 0.5, 2, 4, 24, 48, 96, and 144 hrs, quenched with methanol, washed with methanol and water, and dried in vacuum for a minimum of 48 hrs [1].

B. Characterization

Molecular weight determination by triple detector (RI, UV, LLS) has been described [11-13]. Molecular weights, terminal allyl functions of PIB and the structure of T_8D^H have been characterized by ^1H NMR spectroscopy, as described in references 1,5,7,11-15.

RESULTS AND DISCUSSION

Scheme 1 outlines the steps leading to T_8D^{PIB} . Table 1 shows representative synthesis conditions and results, and Figures 1-4 summarize select SEC traces.

Scheme 1.

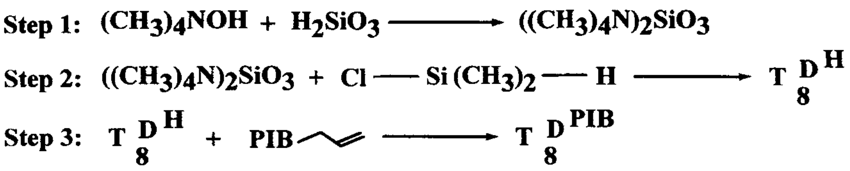


Table 1. Experimental Conditions and Results

	PIB				T_8D^H		[C=C]/[SiH]	Catayst*	$\bar{N}_{w,Arm}$**	Figure
	g	·10^{-4} mol	M_n, g/mol	$\bar{M}_w/\bar{M}_n$	g	·10^{-5} mol				
1	1.7136	1.976	8,700	1.19	0.0153	1.50	1.65	H	CC	1
2	2.9988	1.973	15,200	1.20	0.0155	1.50	1.64	H	CC	
3	1.8712	2.039	9,200	1.15	0.0236	2.32	1.10	K	CC	2
4	3.5771	2.056	17,400	1.17	0.0238	2.34	1.10	K	CC	
5	1.7138	1.977	8,700	1.19	0.0152	1.49	1.66	K	8	4
6	3.0030	1.976	15,200	1.20	0.0151	1.48	1.67	K	8	4
		1-Octadecene								
7	0.0399	1.58	252.5	1.00	0.0201	1.97	1.00	K	CC	3

* H = $H_2PtCl_6{\cdot}H_2O$, K = Karstedt's catalyst

** CC = core-core coupling

Figure 1 compares RI and LLS eluograms of star formation as a function of time, in the presence of $H_2PtCl_6{\cdot}H_2O$ catalyst at [C=C]/[SiH] = 1.65. The chromatograms clearly show the disappearence of the precore within 0.25 hr and the slow formation of stars by the apparence of peaks at ~ 31.8 min. The LLS traces indicate the formation (0.25 hr) of various higher-order coupled stars (peaks at 25-32 min). The relative proportion of stars increases with time, nonetheless 60 - 70 % PIB remains even after 144 hrs. Comparing the RI and LLS data, detecteble amounts of stars are formed in 2 hrs. The high molecular weight coupled side-products are most likely due to the presence of moisture in the charge [1,12,16]. Evidently this catalyst is not selective and is sensitive to the presence of traces of moisture. Essentially identical results were obtained with PIB of $\overline{M}_n$ = 15,200 g/mol.

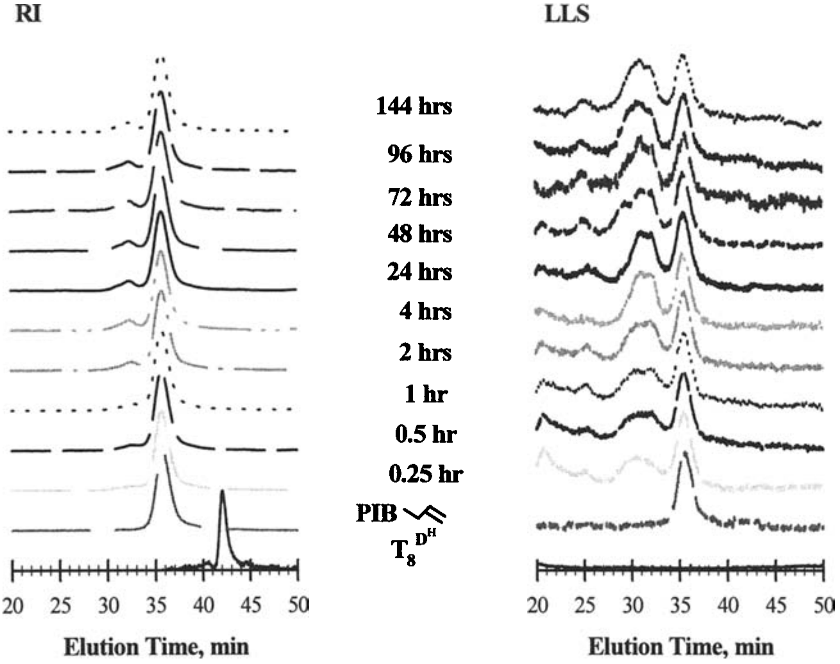


Figure 1. RI- and LLS (90°)-SEC eluograms of T_8D^{PIB} star formation of PIB with T_8D^H by the use of $H_2PtCl_6{\cdot}H_2O$ ($\overline{M}_n$ = 8,700 g/mol, [C=C]/[SiH] = 1.65)

Figure 2 shows the results of experiments carried out by the use of Karstedt's catalyst at [C=C]/[SiH] = 1.1. The precore is consumed within 0.25 hr (the RI peak at ~ 42 min dissappears regardless of the PIB molecular weight) and detectable amounts of stars are formed. The LLS traces do not show the formation of high molecular weight species (as with $H_2PtCl_6{\cdot}H_2O$). Multimodal RI and LLS peaks at ~ 31.5 min appear later, suggesting the formation of various stars. The multiplicity of the peaks decreases by the use of higher molecular weight PIB⌒⫽ (not shown). The formation of high molecular weight stars is clear indication of core-core coupling [12, 16]. Since [C=C]/[SiH] was ~1.1, it is assumed, that core-core coupling will occur when about one SiH/core still remains. At this point competition between core-core coupling and hydrosilation of the last, the 8th, PIB arm progresses. With increasing arm molecular weight core-core coupling is suppressed [12, 16] because the arms of the star encumber the remaining -SiH site.

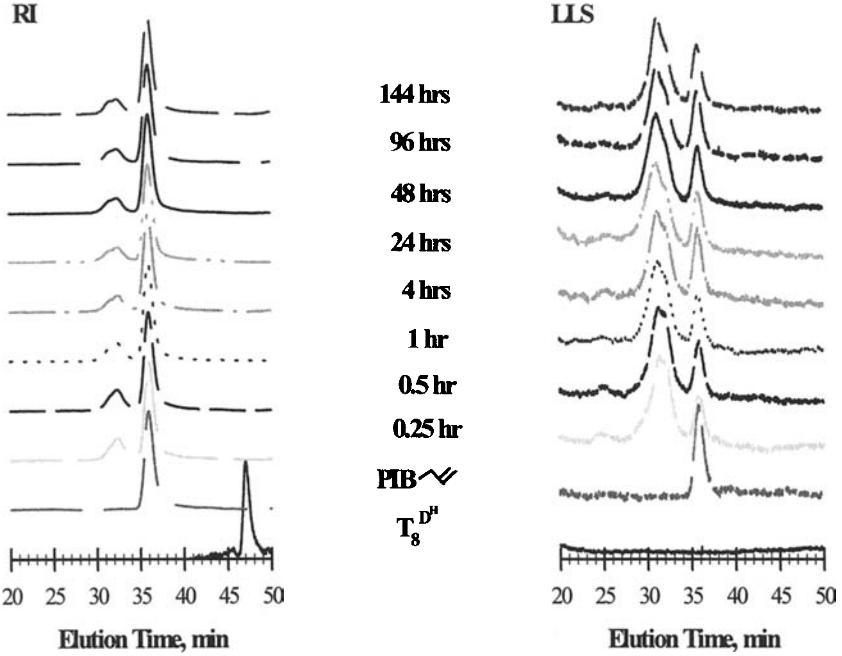
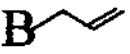


Figure 2. RI- and LLS (90°)-SEC eluograms of T_8D^{PIB} star formation of PIB⌒⫽ with T_8D^H by the use of Karstedt's catalyst ($\overline{M}_n$ = 9,200 g/mol, [C=C]/[SiH] = 1.1)

Core-core coupling was further investigated by hydrosilating 1-octadecene with Karstedt's catalyst at [C=C]/[SiH] = 1.00. As shown in Figure 3 the precore disappears and star is formed in 2 hrs (new peak at ~ 39 min), and the RI traces indicate core-core coupling after 2 hrs. According to the literature [1, 12, 16] and the above results, star-star (or core-core) coupling occurs preferentially in the presence of low molecular weight arms, low (here close to unity) [C=C]/[SiH], and extended reaction times. The type of catalyst is also important: Karstedt's catalyst seem to give faster and cleaner reactions than the conventional $H_2PtCl_6{\cdot}H_2O$ catalyst. To avoid the presence of higher-order stars and to produce uniform PIB stars the rate of hydrosylation of the prearm should be fast relative to the that of core-core coupling (side reaction).

To decrease the formation of higher-order stars and to obtain well-defined "primary stars", the [C=C]/[SiH] ratio was increased to 1.66 (see also Exp 1 and 2 in Table 1). Figure 4 shows the RI and LLS eluograms obtained with PIB prearms of $\overline{M}_n$ = 15,200 g/mol. The core was consumed and detectable amounts of star formed within 0.25 hr. The formation of higher-order stars was suppressed as indicated by the absence of a shoulder at low elution times. The RI peak area (%) does not change within the monitored time frame. The $\overline{N}_{w,Arm} = \left(\overline{M}_{w,Star} - M_{core}\right)/\overline{M}_{w,Arm}$ was calculated [16] and found to be 8 in the final product. Similar results were also obtained with PIB  $\overline{M}_n$ = 8,700 g/mol.

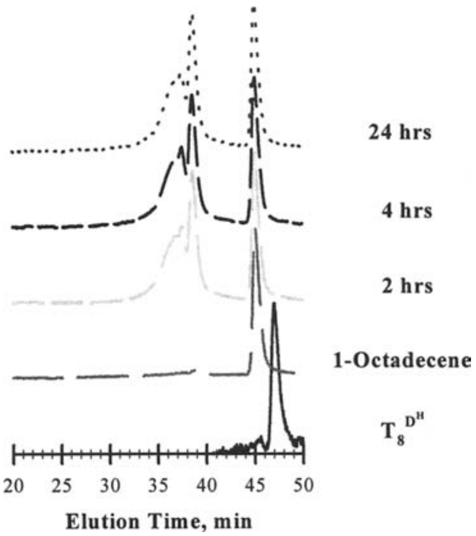


Figure 3. RI-SEC eluograms of star formation of 1-octadecene with $T_8^{D^H}$ by the use of Karstedt's catalyst ([C=C]/[SiH] = 1.00).

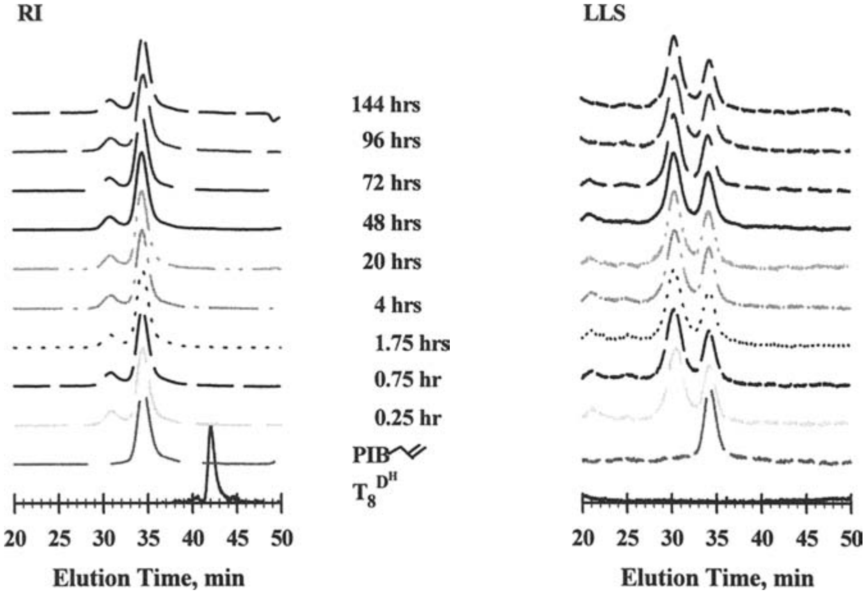


Figure 4. RI- and LLS (90°)-SEC eluograms of T_8D^{PIB} star formation of PIB with T_8D^H by the use of Karstedt's catalyst ($\overline{M}_n$ = 15,200 g/mol, [C=C]/[SiH] = 1.66)

CONCLUSION

Well-defined octa-polyisobutylene-arm radial star polymers with polysiloxane cores can be produced by hydrosilating by PIB with T_8D^H in the presence of the Karstedt's catalyst in a few hrs at room temperature. The conventional hydrosilation catalyst, $H_2PtCl_6 \cdot H_2O$, produces side products by core-core coupling. The rate of hydrosilation is faster than the rate of side reactions by the use of Karstedt's catalyst.

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