Macromolecules **2007,** *40,* 3929−3938 **3929**

Hydrosilylation Reactions of 1,3-Diynes and Bis(silyl hydrides): Model Studies and Polymerizations

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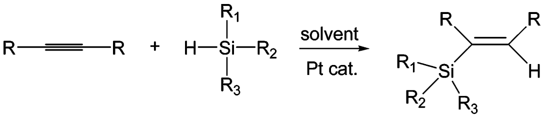
Received November 20, 2006; Revised Manuscript Received March 12, 2007

ABSTRACT: The first examples of polymers made from the bis-hydrosilylation reaction of 1,3-diynes and bis-silylhydrides are reported. These polymers exhibit modest molecular weights and possess a *cis,cis*-2,3-disubstituted-1,3-butadiene structure as determined NMR analysis of model compounds. SEC and MALDI analysis of reaction mixtures suggest that cyclic dimers and higher order oligomers are also formed. Model reactions indicate that very sterically hindered diynes or silyl hydrides give only the 1,3-eneyne mono-addition products.

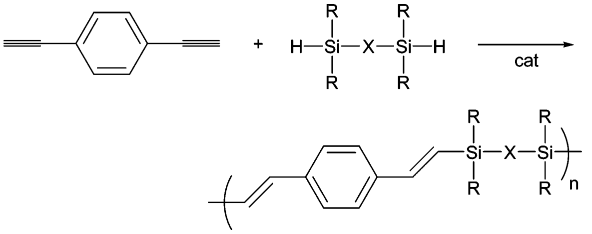
Introduction

The hydrosilylation reaction between alkynes and silylhydrides is a well-established process for the formation of vinyl silane derivatives with a wide variety of substituents being tolerated on both the silane component and the unsaturated organic moiety.[1] Typically, *cis* or *Z* adducts are formed by metal-catalyzed reactions as shown in eq 1, but this can vary depending on the catalyst and reaction conditions.[2]



(1)

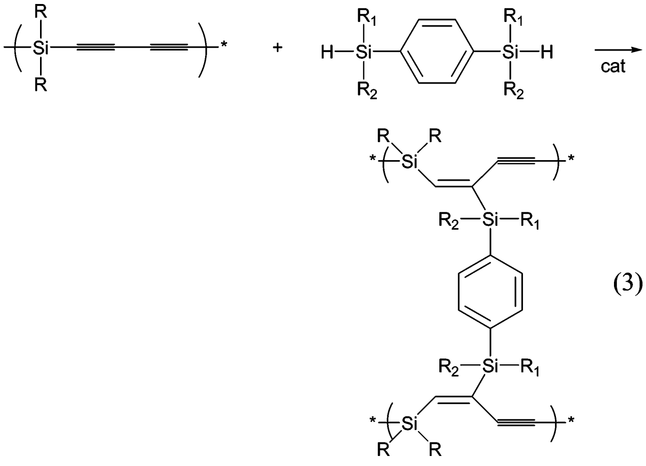
Silylhydrides have been found to react with 1,6-diynes to generate cyclic species[3] and to provide novel fluorescent dyes,[4] and have been exploited in the preparation of polymers as well. α,ω-Diynes containing aromatic spacers have been combined with α,ω- silyl dihydrides (eq 2),[5] or α,α-silyl dihydrides to give phenylenevinylene polymers.[6] Dehydrogenative silylation of acetylenes with ortho-substituted bis(dimethylsilyl)benzene also gave thermally stable polymers.[7] Preceramic polymers were made from α,α-silyl dihydrides and α,α-silyl diacetylenes[8] and photoluminescent carbosilanes were derived from phenylethynylsilanes.[9]



(2)

Cross-linked structures were also obtained through the hydrosilylation reaction of silylhydrides with poly[(silylene)-diethynylenes] (eq 3)[10] and with octakis(hydridosilsesquioxane) and 1,3-diethynylbenzene.[11]

We were interested in examining the properties of polymeric 2,3-diaryl-1,3-butadiene materials as potential charge carriers for electronic applications. However, no examples have been reported of using 1,3-diynes and bis(silylhydrides) as monomers for the preparation of poly(2,3-disilyl-1,3-butadienyl) polymers.

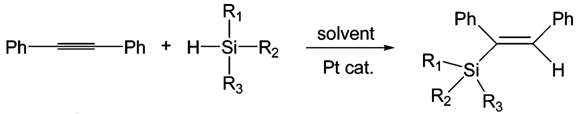


(3)

Herein are reported the initial results of the hydrosilylation reactions between 1,3-diynes and silylhydrides.

Model Reactions

As noted above, hydrosilylation of alkynes and silylhydrides is a facile process, but one that may produce several regio- or stereoisomers.[12] Wanting to be certain of the addition products, several sets of model reactions were carried out. As shown in Table 1, the reaction of diphenylacetylene and dimethylphenylsilane in the presence of Karstedt's catalyst gave the expected vinyl silane **3a** in good yield. Even sterically congested monomeric silylhydrides gave good to excellent yields of the vinylsilanes (eq 4). Triphenyl silane (entry 2) gave the *cis*-product **3e** in nearly quantitative yield, and tris(trimethylsiloxy)-silane (M_3T^H) (entry 3) gave a 68% isolated yield of **3f**, although GC analysis of the reaction mixture indicated >90% conversion.



(4)

1 **2** **3**

a R_1=Me R_2=Me R_3=Ph
e R_1=Ph R_2=Ph R_3=Ph
f R_1=OSiMe$_3$ R_2=OSiMe$_3$ R_3=OSiMe$_3$

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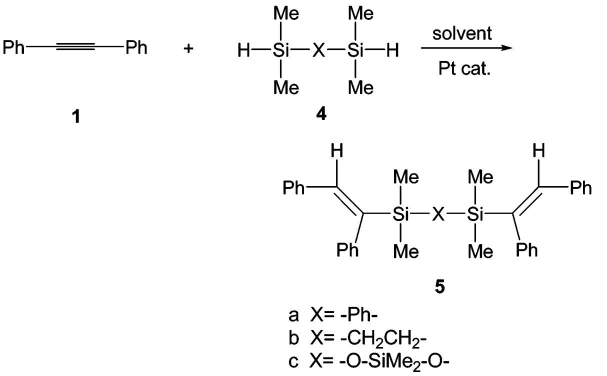
10.1021/ma062663s CCC: $37.00

Table 1. Reaction of Diphenylacetylene with Hydridosilanes

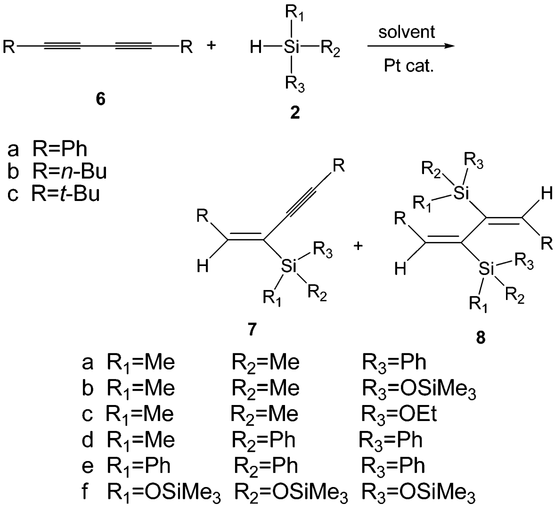
entry	R_1	R_2	R_3	solvent	*T* (°C)	*t* (h)	product	yield (%)
1	Me	Me	Ph	toluene	90	2.5	**3a**	73
2	Ph	Ph	Ph	toluene	95	21	**3e**	97
3	$OSiMe_3$	$OSiMe_3$	$OSiMe_3$	toluene	95	30	**3f**	68

To confirm that bis(silylhydrides) would react as expected with alkynes, three readily available hydrides were allowed to react with diphenylacetylene (eq 5). Table 2 showed that high isolated yields of expected products were obtained overnight at modest temperatures.



(5)

To determine if bis-hydrosilylation would occur in the expected manner with 1,3-diynes and silylhydrides, another series of model reactions were run to determine what steric or electronic limitations might be present in the reaction (eq 6). Table 3 illustrates the breadth of substrates tried.



(6)

The initial reaction of 1,4-diphenylbutadiyne with dimethylphenylsilane (entry 7) in refluxing toluene gave high yield of a monosubstituted product as shown by ^{13}C NMR analysis. Half-product **7aa** arose from a single hydrosilylation reaction, giving the *cis*, *β* adduct (Scheme 1). The same regiochemistry was observed from the mono hydrosilylation of 1,4-bis(trimethylsilyl)-1,3-butadiyne with silylhydrides.[10a,13]

Believing that formation of **7aa** may be due to some minimal steric congestion, the same reaction was repeated but at higher temperature (refluxing xylene) and for longer duration. The more forcing conditions resulted in an excellent yield of the desired bis-adduct **8aa** (entry 8).

Similar results were seen when another hindered silyl hydride (pentamethyldisiloxane) was used in the hydrosilylation reaction at lower temperature (entry 9). In this case a poor yield of the half-product was observed along with a substantial amount of starting material, even in xylene. However, keeping the solvent constant and raising the temperature to 125 °C provided for a 70% isolated yield of **8ab** after several days reaction (entry 10).

Running subsequent reactions in xylene at temperatures between 125 and 140 °C for 1−3 days was the standard protocol that was adopted for further reactions of diynes with silylhydrides. This procedure worked well for the ethoxy and diphenyl silylhydride reactions with 1,4-diphenylbutadiyne (entries 11 and 12) but fell short with the very sterically hindered triphenylsilane and tris(trimethylsiloxy)silane derivative (entries 13 and 14). In the latter two cases, only fair yields of the half-products **7ae** and **7af** were obtained. Extended reaction times did not significantly alter the reaction products or yield.

Reactions with the less crowded 5,7-dodecadiyne gave the desired bis-adducts even with the sterically demanding hydrides such as triphenylsilane and tris(trimethylsilyl)silane (entries 15−17). In contrast to reactions with diphenylbutadiyne, high yields of **8be** and **8bf** were obtained in overnight runs indicating there was a significantly lower barrier to reaction.

To be certain that the successful reactions with 5,7-dodecadiyne were related to steric and not electronic parameters, two reactions were run using 2,2,7,7-tetramethyl-3,5-octadiyne. Entries 18 and 19 show that only half-products **7ca** and **7cc** were observed with no significant formation of the desired bis-adduct, even when using the relatively unhindered dimethylphenyl silane and dimethylethoxysilane that worked well in the diphenylbutadiyne examples. These results indicated that bis(hydrosilylation) adducts could be obtained in high yields if the steric constraints were not too high.

In all reactions monitored by GC, a small amount (<5%) of another product was formed. GC/MS showed the same parent ion, but with a slightly different fragmentation pattern, suggesting another regio-isomer was also formed.

Equation 6 indicated that the hydrosilylation reactions proceeded in a cis fashion with the hydrogen adding to the more external (α) position of the triple bond. While the *cis* addition is anticipated for Pt-mediated Si−H additions,[2] we wished to confirm that the stereo- and regiochemistry illustrated was that obtained from the reactions. To this end, compound **8ad** was subjected to a detailed NMR study.

There are 9 possible products arising from the bis-addition reaction as shown above in Scheme 2. Three, all *cis* additions with both external (α) and internal (*β*) triple bond addition giving *E,E*-isomers, three all *trans* additions (*Z,Z*-isomers) and three mixed stereochemical products were all considered. A single resonance at 6.9 ppm in the ^1H NMR spectrum that integrated to 2 protons, indicated the product had a symmetrical structure. Further support was seen with the total number of distinct carbons in the ^{13}C NMR spectrum. The NMR data narrowed the potential products to A, C, G and I. If the mechanism of addition of Si−H across a triple bond proceeds with *cis* orientation, G and I would be eliminated. The structure

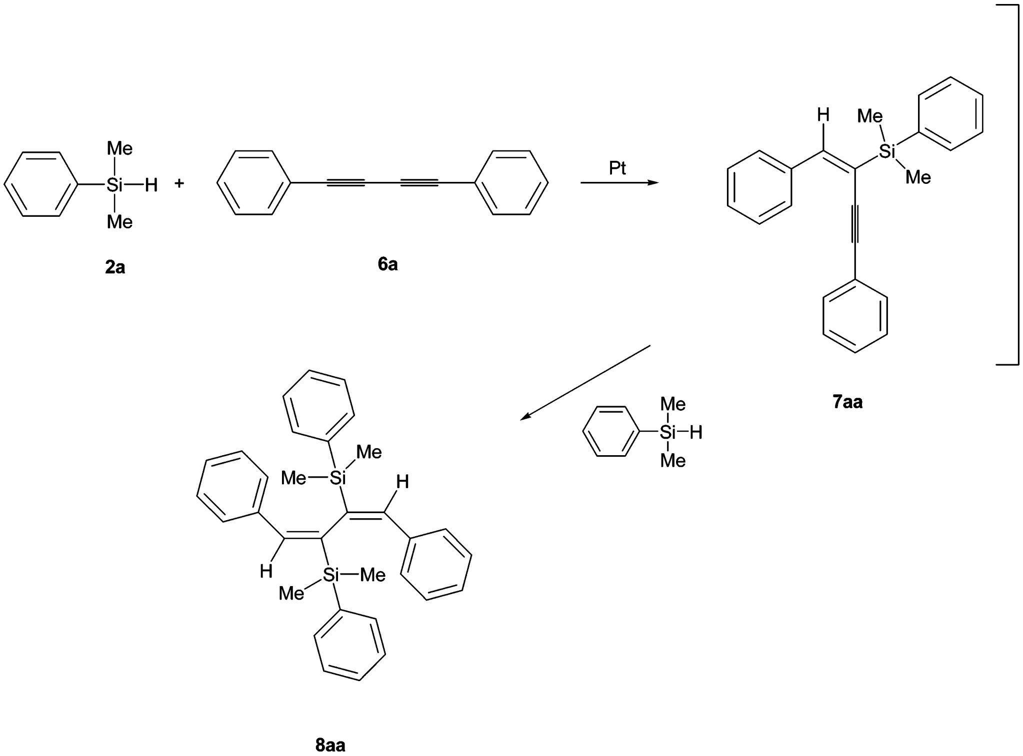
Table 2. Reaction of Alkynes with Dihydridosilanes

entry	R	R_1	R_2	X	solvent	*T* (°C)	*t* (h)	product	yield (%)
4	Ph	Me	Me	−Ph−	toluene	85	18	**5a**	99
5	Ph	Me	Me	$-CH_2CH_2-$	toluene	90	22	**5b**	77
6	Ph	Me	Me	$-O-SiMe_2-O-$	toluene	95	18	**5c**	91

Table 3. Reaction of Diynes with Hydridosilanes

entry	R	R_1	R_2	R_3	solvent	*T* (°C)	*t* (h)	product	yield (%)
7	Ph	Me	Me	Ph	toluene	85	2.5	**7aa**	88
8	Ph	Me	Me	Ph	xylene	125	9	**8aa**	92
9	Ph	Me	Me	$OSiMe_3$	xylene	80	24	**7ab**	36
10	Ph	Me	Me	$OSiMe_3$	xylene	125	68	**8ab**	70
11	Ph	Me	Me	OEt	xylene	140	70	**8ac**	92
12	Ph	Me	Ph	Ph	xylene	140	72	**8ad**	82
13	Ph	Ph	Ph	Ph	xylene	145	24	**7ae**	61
14	Ph	$OSiMe_3$	$OSiMe_3$	$OSiMe_3$	xylene	130	40	**7af**	52
15	*n*-Bu	Me	Me	Ph	xylene	140	20	**8ba**	78
16	*n*-Bu	Ph	Ph	Ph	xylene	140	18	**8be**	93
17	*n*-Bu	$OSiMe_3$	$OSiMe_3$	$OSiMe_3$	xylene	140	70	**8bf**	77
18	*t*-Bu	Me	Me	Ph	xylene	140	22	**7ca**	99
19	*t*-Bu	Me	Me	OEt	xylene	140	22	**7cc**	75

Scheme 1. Stepwise Formation of Bis-Adduct 8aa

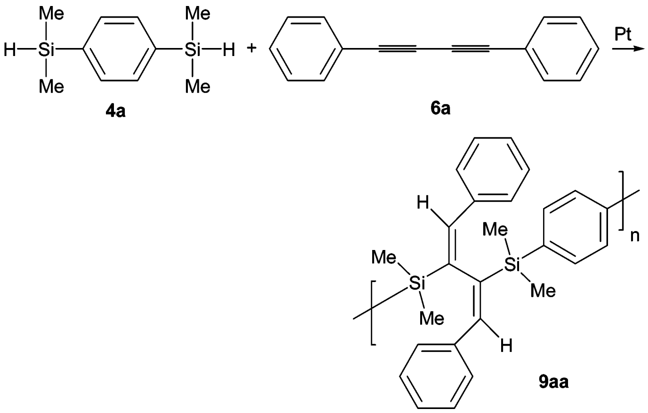


of this material was unequivocally determined using ^{1}H and ^{13}C NMR spectroscopy, and the 2D NMR correlation techniques g2QCOSY for proton−proton correlations, gHMQC for one-bond proton−carbon correlations, gHMBC for longer range proton−carbon correlations, and 2D-INADEQUATE for carbon skeleton determination through C−C coupling.[14]

A brief examination of two other catalyst systems did not show any significant change in yield or product distribution in the reaction of **6a** and **2a**. GC analysis of reaction mixtures catalyzed by Wilkinson's or Karstedt's catalyst showed >90% formation of product **8aa** with 2−5% of another isomeric product. The reaction using chloroplatinic acid also gave **8aa** as the predominate product along with ~5% of another isomer and two other unidentified minor products seen by GC (<3%). Karstedt's catalyst was carried forward into the polymerization reactions.

Polymerization Reactions

The initial polymerization reaction was run using bis-hydride **4a** and diyne **6a** as shown below. Figure 1 shows the increase in molecular weight vs time. There was no change after 12 h. The size exclusion chromatogram (SEC) of the polymer precipitated into methanol showed two distinct components. The first was the expected distribution of linear polymer and the second was a series of low molecular weight species that suggested cyclic oligomers.



Most of the cyclics and low molecular weight linears could be removed by precipitation into a 3:1 MeOH:acetone mixture. Figure 2 shows the chromatogram of the polymer mixture initially precipitated into MeOH and the isolated linear polymer and the soluble cyclic fraction.

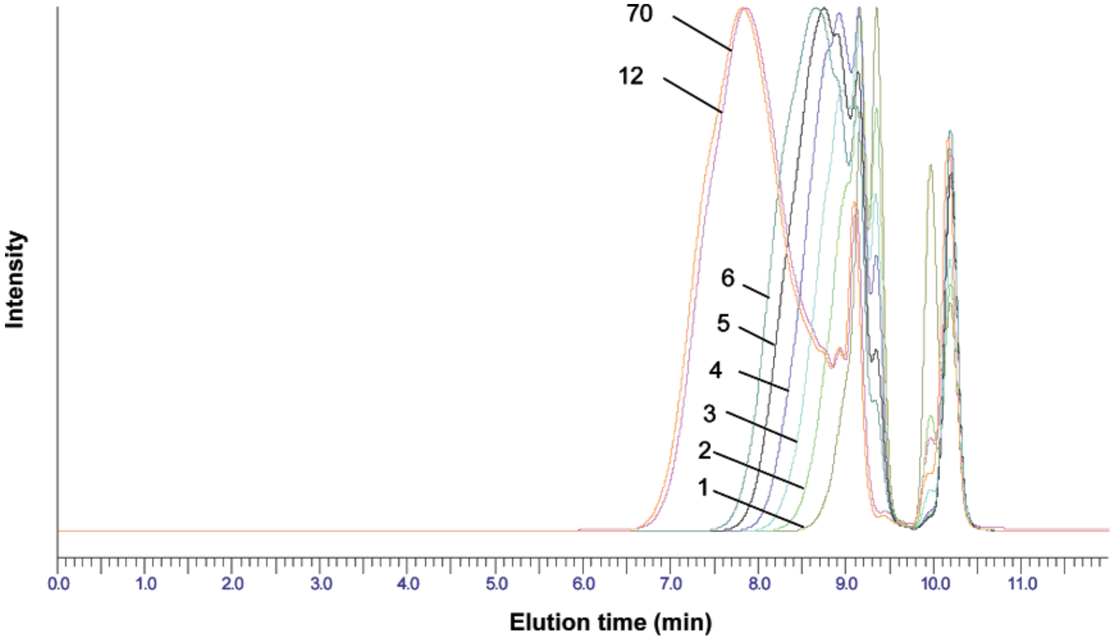
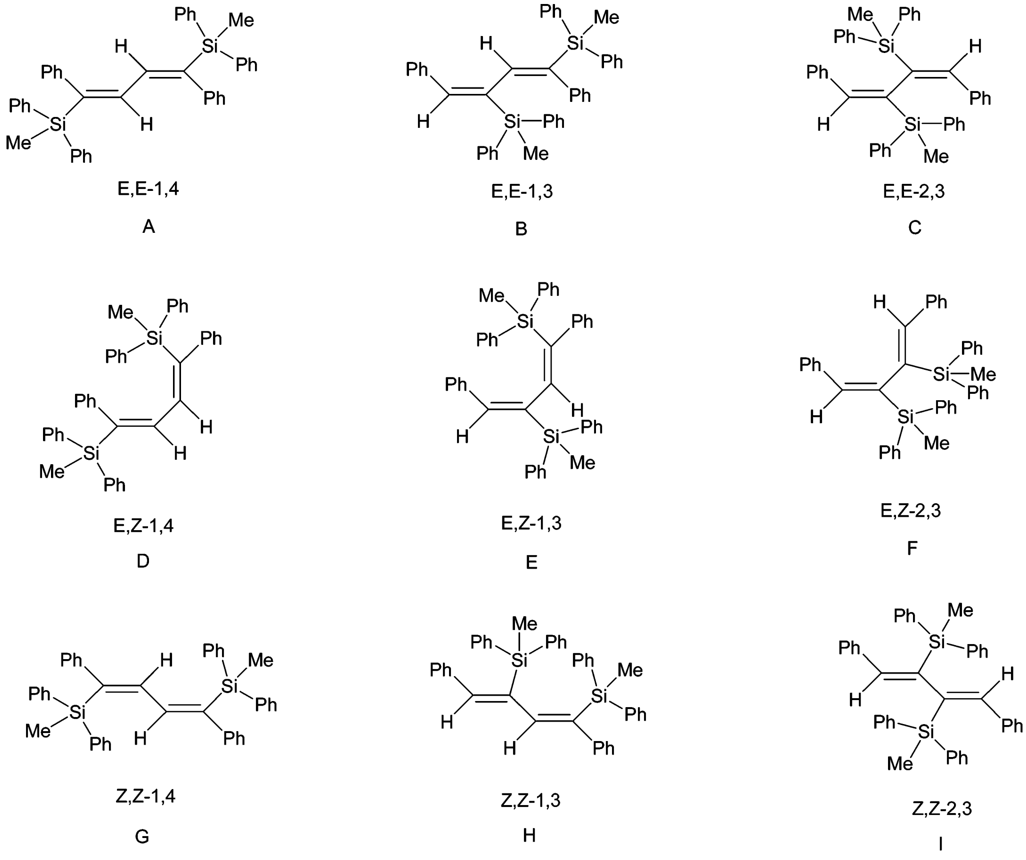


Figure 1. SEC of polymer **9aa** growth vs time (hours).

Scheme 2. Possible Additions Products from Bis-Hydrosilylation of Diyne 6a



Support for the formation of cyclics was supplied by Ag ion assisted MALDI. Figure 3 shows the series of peaks that correspond to the cyclic dimer, trimer, tetramer, etc plus Ag (peak clusters around 900, 1296, and 1692, etc.). Also seen were small amounts of linear material that appeared to be terminated with an eneyne at one end and H at the other (clusters at 1104, 1500, and 1896) that may have arisen from partial reduction of the triple bond.

The reaction of bis-hydride **4a** with diyne **6a** was further investigated by examining the effect catalyst level had on the rate of polymerization (Figure 4). As expected, the greater the amount of catalyst, the faster the reaction proceeded to its ultimate molecular weight. Peak molecular weights were used as a measure of reaction rates rather than M_w or M_n values because the size exclusion chromatograms included solvent and cyclic peaks that skewed the polymer analyses. When no further increase in peak molecular weight was observed, the reactions were deemed complete, and the polymers were isolated and M_w, M_n, and polydispersity (PDI) values reported (Table 4).

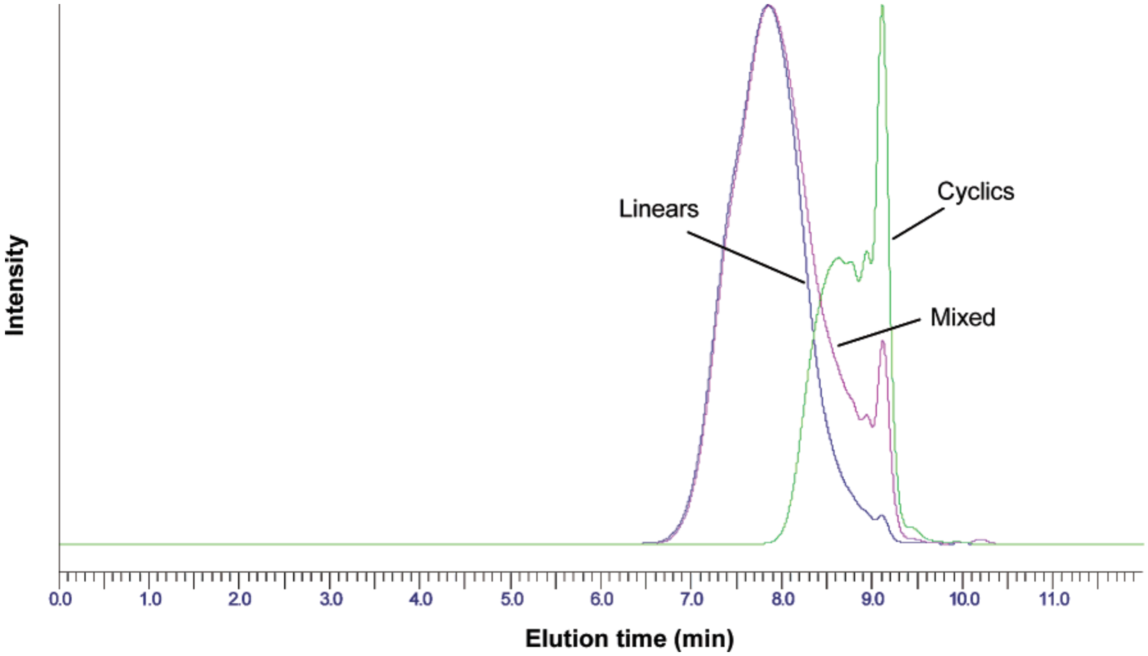


Figure 2. SEC of polymer **9aa** components.

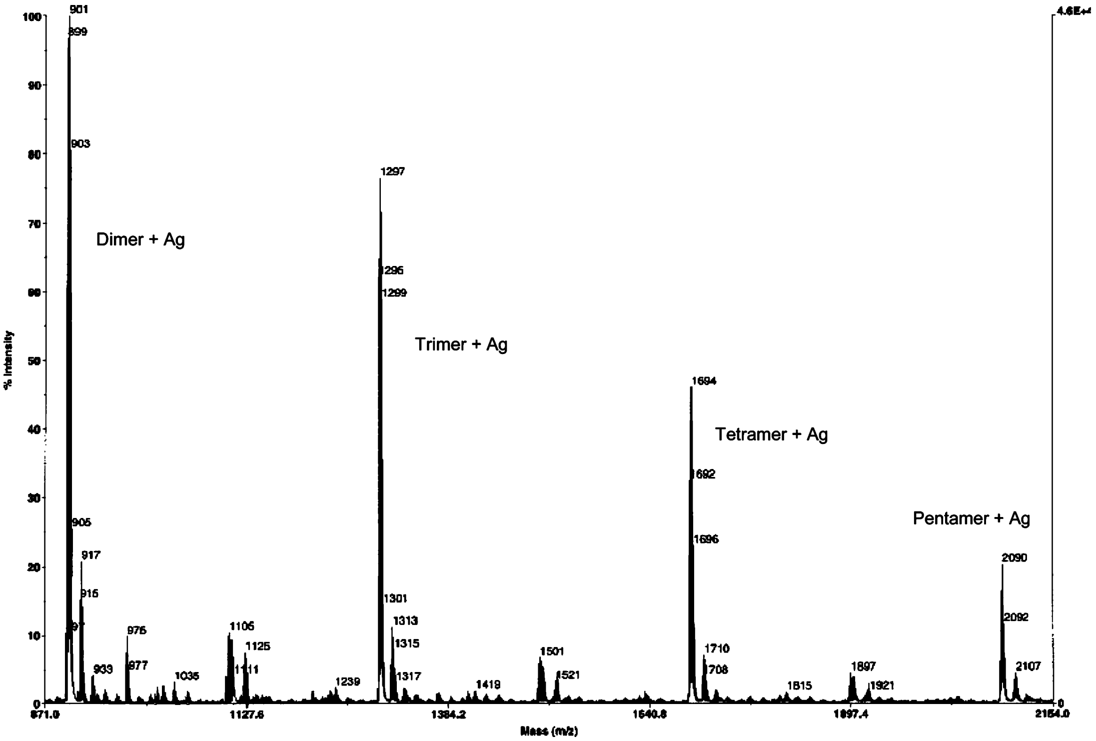


Figure 3. MALDI spectrum for **9aa** cyclic component.

The polymers isolated from the 30 and 100 ppm Pt catalyzed reactions were essentially identical with one another the exception of the residual color.[15] The polymer made with the higher Pt level was decidedly more yellow in color that the 30 ppm reaction.[16] Further reactions were run at 30 ppm catalyst levels.

To determine if the concentration of the reaction had an impact on the polymerization, several experiments were run varying the solids content from 10 to 30%. Table 5 shows that there was a correlation between the lowest solids level and the greater amount of cyclic oligomer formed in the reaction. The percent solids effect is consistent with an intramolecular cyclization reaction that is favored by more dilute conditions.

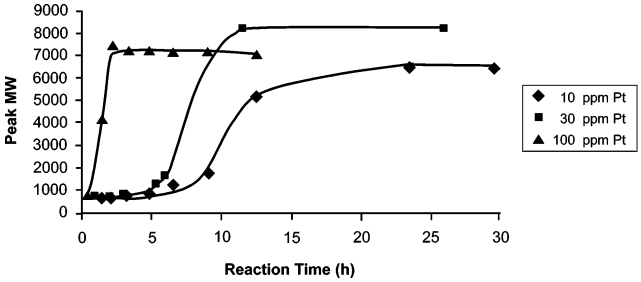


Figure 4. Molecular weight increase vs catalyst level.

This data is also represented in Figure 5 that shows a trend toward a more pronounced shoulder on the high molecular

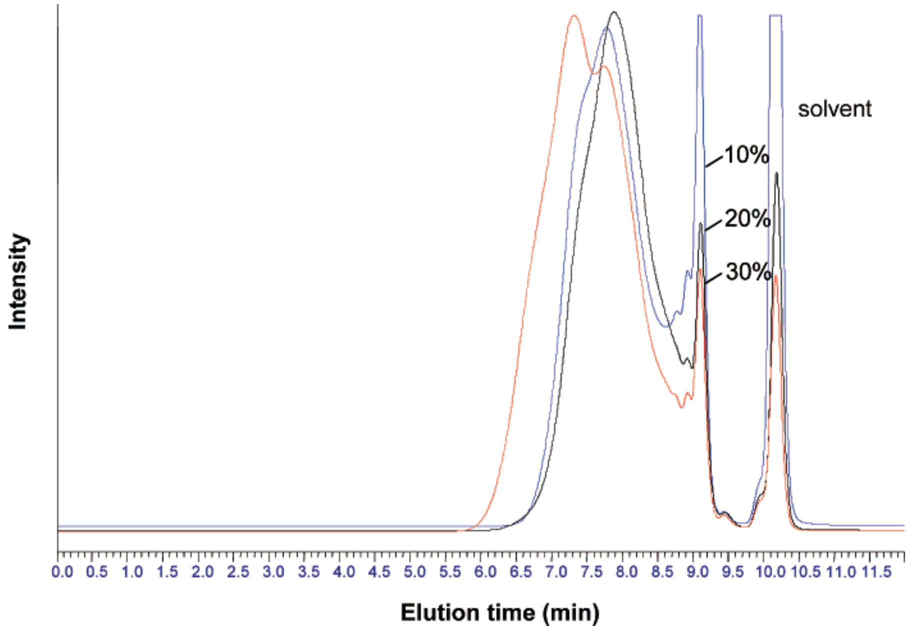


Figure 5. Effect of polymerization concentration on cyclic formation.

Table 4. Isolated Molecular Weight Data for Catalyst Loading Experiments

entry	cat (ppm)	M_w	M_n	PDI
20	10	7212	3245	2.22
21	30	9540	4130	2.31
22	100	9568	4813	2.00

Table 5. Effect of Concentration on Polymerization

entry	% solids	M_w	M_n	PDI
23	10	11 168	5528	2.02
24	20	9540	4130	2.31
25	30	23 509	9018	2.61

weight side of the chromatogram. It is not clear at this time if an alternate polymerization mechanism is operating at the higher concentration.

Next, the effect of stoichiometry was examined. With this type of polymerization, the highest molecular weights should be achieved with an exact stoichiometric balance of silyl hydride and alkyne. Figure 6 shows that the highest molecular weight was obtained when a slight deficiency of diyne (or slight excess of silyl hydride) was used.[17] ^{29}Si NMR analysis of the polymers made at 0% and 1.4% excess hydride showed that, in addition to the expected Si resonance at −7.6 ppm, the lower molecular weight material possessed higher levels of Si−O−Si linkages (−1.3 ppm) and Si−OH terminal groups (9.5 ppm). This is consistent with the theory that some of the silyl hydride had hydrolyzed during the reaction and needed to be offset with additional hydride to attain higher molecular weight.

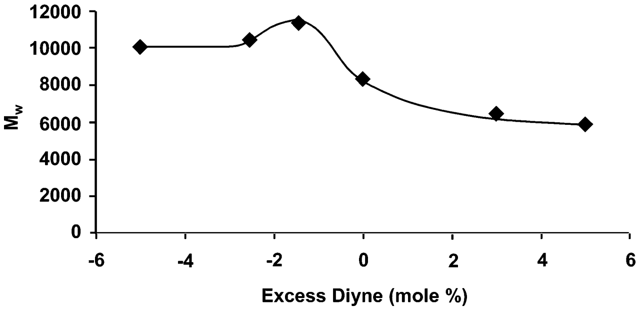
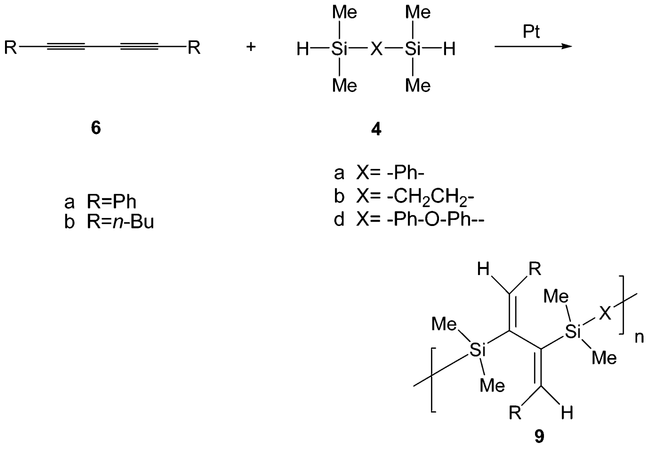


Figure 6. Effect of stoichiometry on molecular weight.



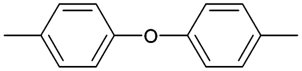
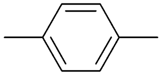
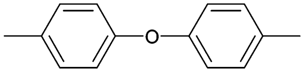
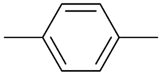
With the partially optimized polymerization conditions described above, several more novel polymers were made beyond that obtained from **4a** and **6a** (Table 6, entry 23). The reaction between the aliphatic bishydride **4b** with diphenyldiacetylene **6a** was not successful in generating any polymeric material (entry 26). Rather, only low molecular weight oligomers or cyclics were obtained.

However, when the diphenylether derivative **4d** was used with the same diyne, moderately high molecular weight polymer was formed (entry 29). The T_g of **29** was 90 °C. If the diyne was changed to the butyl derivative **6b**, then reactions with both aromatic bishydrides proceeded well to give polymer (entries 27 and 28). These polymers were not solids however and had T_gs below room temperature.

Summary

The first examples of polymers made from the bis-hydrosilylation reaction of 1,3-diynes and bis-silylhydrides have been reported. These polymers exhibited modest molecular weights and possessed a *cis,cis*-2,3-disubstituted-1,3-butadiene structure as determined NMR analysis of model compounds. Cyclic

Table 6. Polymers from Bis(silyl hydrides) and Diynes

Entry	R	X	M_w	M_n	PDI	Polymer	State	T_g (°C)
26	Ph	-CH_2CH_2-	-	-	-	**9ab**	-	-
27	n-Bu		17,610	7190	2.45	**9bd**	Liquid	-
28	n-Bu		19,770	8020	2.47	**9ba**	Liquid	-
29	Ph		16,190	6490	2.50	**9ad**	Solid	90.0
30	Ph		9540	4130	2.31	**9aa**	Solid	90.6

dimers and higher order oligomers were also likely formed as suggested by SEC and MALDI analysis. Model reactions also showed that very sterically hindered diynes or hydrides gave only the 1,3-eneyne mono-addition products. Investigation into the electronic properties of these molecules is underway.

Experimental Section

Chemicals. Karstedt's catalyst (GE Silicones intermediate 89257), 1,4-diphenylbutadiyne, diphenylacetylene, 5,7-dodecadiyne, 2,2,7,7-tetramethyl-3,5-octadiyne, 1,4-bis(dimethylsilyl)benzene, triphenylsilane (all Aldrich), M_3T^H (tris(trimethylsiloxy)silane), pentamethyldisiloxane, diphenylmethylsilane, bis(dimethylsilyl)-ethane, bis[(*p*-dimethylsilyl)phenyl] ether (all Gelest), phenyldimethylsilane, 1,1,3,3,5,5-hexamethyltrisiloxane (all Silar), dimethylethoxysilane (Huls), and xylene and toluene (both Baker) were used as received. For polymerization reactions, 1,4-diphenylbutadiyne was recrystallized from hexanes and 1,4-bis(dimethylsilyl)benzene was fractionally distilled.

Analytical Data. ^1H, ^{13}C and ^{29}Si NMR were obtained on a Bruker 400 MHz spectrophotometer. FTIR were recorded on a ThermoNicolet Avatar 370 FT-IR. SEC chromatograms were obtained on a Perkin-Elmer Series 200 SEC system with a UV/vis detector at 255 nm. Polymers were eluted with a 96:4 $CHCl_3$/IPA mixture on a heated (40 °C) Polymer Labs 5 μm, Mixed C 300 × 7.5 mm column at 0.9 mL/min. Gas Chromatographic analyses were performed on an HP6890 Series GC using a DB-5 column (30 m × 0.25 mm; 0.25 μm) with a temperature profile of 40 °C start (4 min hold), ramp at 20 °C/min to 100 °C (hold 2 min), and then ramp at 20 °C/min to 250 °C (hold 13 min). GC−MS experiments were performed using a Hewlett-Packard 5890 Series II gas chromatograph with H_2 carrier gas a flow 11 mL/min. The injection port used was held at 300 °C. The column used was an Agilent 30 m × .538 mm ID × 1.5um thick film. The stationary phase was DB-5MS. Temperature programs were run at rate of 10 °C /min from 100-350 °C, holding at 350 °C until all analytes were eluted. The separator temperature between the column outlet and mass spectrometer was held constant at 290 °C. Mass spectrometry was performed on a JEOL JMS HX 110 double focusing high-resolution mass spectrometer.

***cis*-Dimethylphenyl-1,2-diphenylethenylsilane, 3a.** Dimethylphenylsilane, **2a** (1.45 g, 10.0 mmol), and diphenylacetylene, **1** (1.80 g, 10.0 mmol), were dissolved in toluene (7.5 g), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated to 85−90 °C for 2.5 h. The mixture was concentrated in vacuo and distilled (150−156 °C/2 mmHg) to give 2.3 g (73%) of product.[18] ^1H NMR ($CDCl_3$), δ: 0.42 (s, 6H); 6.89 (s, 1H); 6.98 (m, 4H); 7.13 (m, 3H); 7.24 (m, 1H); 7.28 (m, 2H); 7.42 (m, 4H); 7.61 (m, 2H). ^{13}C NMR ($CDCl_3$), δ: −3.0, 125.8, 127.3, 127.6, 127.7, 128.0, 128.4, 128.6, 129.2, 129.6, 134.4, 137.3, 137.8, 139.3, 142.0, 145.1. FTIR (KBr): 3067, 3021, 2957, 1600, 1571, 1493, 1446, 1427, 1248, 1113, 1071, 1029, 953, 901, 832, 776, 756, 734, 700, 653 cm^{-1}.

***cis*-Triphenyl-1,2-diphenylethenylsilane, 3e.** Triphenylsilane, **2e** (520 mg, 2.0 mmol), and diphenylacetylene, **1** (356 mg, 2.0 mmol), were dissolved in toluene (5 mL), treated with Karstedt's catalyst (5 μL of 0.235 wt % Pt in IPA solution), and heated to 95 °C for 21 h. The mixture was concentrated in vacuo and triturated with hexanes to give a white powdery solid as product (842 mg, 97%). Lit. mp 122−123 °C.[19] ^1H NMR ($CDCl_3$), δ: 7.05 (m, 2H); 7.11 (m, 2H); 7.18 (s, 1H); 7.20 (m, 3H); 7.26 (m, 3H); 7.44 (ps t, J = 7.3 Hz, 6H); 7.52 (ps t, J = 7.3 Hz, 3H); 7.61 (d, J = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$), δ: 126.1, 127.6, 127.9, 128.1, 128.5, 128.6, 139.7, 129.9, 133.9, 136.7, 137.2, 141.2, 142.0, 143.5. FTIR (KBr): 3066, 3049, 3023, 1598, 1487, 1427, 1106, 953, 756, 699 cm^{-1}.

***cis*-Tris(trimethylsiloxy)-1,2-diphenylethenylsilane, 3f.** Tris(trimethylsiloxy)silane, **2f** (1.2 g, 4.0 mmol), and diphenylacetylene, **1** (0.80 g, 4.4 mmol), were dissolved in toluene (5 mL), treated with Karstedt's catalyst (10 μL of 0.235 wt % Pt in IPA solution), and heated to 80 °C. After 20 h, the reaction was still not complete. Additional catalyst was added (50 μL) and the temperature raised to 95 °C. After 12 h, no Si−H was seen by IR. The mixture was cooled, concentrated in vacuo, and flash distilled to give 1.3 g (68%) of an oil which crystallized on standing. ^1H NMR ($CDCl_3$), δ: 0.1 (s, 27H); 7.10 (m, 2H); 7.19 (m, 4H); 7.26 (m, 1H); 7.33 (m, 1H); 7.41 (m, 2H); 7.61 (m, 1H). ^{13}C NMR ($CDCl_3$), δ: 1.7, 125.9, 127.2, 127.9, 128.4, 129.7, 137.4, 139.7, 141.1, 141.3. FTIR (KBr): 3024, 2959, 1603, 1493, 1446, 1252, 1066, 843, 755, 698, 602 cm^{-1}.

1,4-Bis(dimethyl-*cis*-1,2-diphenylethenylsilyl)benzene, 5a. 1,4-bis(dimethylsilyl)benzene, **4a** (388 mg, 2.0 mmol), and diphenylacetylene, **1** (733 mg, 4.1 mmol), were dissolved in toluene (5 g), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated at 85 °C for 18 h. The reaction mixture was concentrated in vacuo and a crystalline solid was obtained in quantitative yield (1.1 g, 99%). ^1H NMR ($CDCl_3$), δ: 0.42 (s, 12H); 6.91 (s, 2H); 6.99 (m, 4H); 7.03 (m, 4H); 7.15 (m, 6H); 7.26 (m, 2H); 7.32 (m, 4H); 7.62 (s, 4H). ^{13}C NMR ($CDCl_3$), δ: −3.1, 125.8, 127.3, 127.7, 128.0, 128.6, 129.6, 133.6, 137.3, 138.6, 139.3, 142.4, 145.1. FTIR (KBr): 3045, 2964, 1602, 1492, 1444, 1248, 1134, 951, 836, 812, 793, 772, 757, 701, 691 cm^{-1}.

1,2-Bis(dimethyl-*cis*-1,2-diphenylethenylsilyl)ethane, 5b. 1,4-bis(dimethylsilyl)ethane, **4b** (146 mg, 1.0 mmol), and diphenylacetylene, **1** (356 mg, 2.0 mmol), were dissolved in toluene (2.5 g), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated at 90 °C for 22 h. The reaction mixture was concentrated in vacuo and distilled at >200 °C/1 mmHg to give product as a colorless oil (387 mg, 77%). ^1H NMR ($CDCl_3$), δ: 0.18 (s, 12H); 0.62 (s, 4H); 6.85 (s, 2H); 7.04 (m, 8H); 7.16 (m, 6H); 7.26 (m, 2H); 7.34 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: −3.8, 6.8, 125.6, 127.1, 127.4, 128.0, 128.7, 129.6, 138.0, 142.8, 146.1. FTIR (KBr): 3054, 3021, 2954, 2906, 1599, 1571, 1492, 1446, 1406, 1247, 1131, 1071, 1053, 1030, 953, 920, 829, 777, 755, 700 cm^{-1}.

1,5-Bis(*cis*-1,2-diphenylethenyl)-1,1,3,3,5,5-hexamethyltrisiloxane, 5c. 1,1,3,3,5,5-hexamethyltrisiloxane, **4c** (416 mg, 2.0 mmol), and diphenylacetylene, **1** (720 mg, 4.04 mmol), were dissolved in toluene (5 g), treated with Karstedt's catalyst (10 μL of 0.235 wt % Pt in IPA solution), and heated at 95 °C for 20 h. The reaction mixture was concentrated in vacuo to give 1.03 g (92%) of product. ^{1}H NMR ($CDCl_3$), δ: 0.24 (s, 3H); 0.26 (s, 3H); 0.36 (s, 3H); 0.39 (s, 9H); 7.13 (s, 2H); 7.14 (m, 4H); 7.22 (m, 10H); 7.34 (m, 2H); 7.43 (ps t, J = 8.0 Hz, 4H). ^{13}C NMR ($CDCl_3$), δ: 0.3, 1.4, 125.9, 127.3, 127.9, 128.1, 128.8, 129.8, 137.3, 138.1, 142.0, 146.1. FTIR (KBr): 3055, 3022, 2959, 2900, 1601, 1572, 1492, 1446, 1258, 1043, 959, 831, 794, 756, 700 cm^{-1}.

***E*-2-Dimethylphenylsilyl-1-phenyl-2-phenylethynylethene, 7aa.** Dimethylphenylsilane, **2a** (1.11 g, 8.2 mmol), and 1,4-diphenylbutadiyne, **6a** (0.75 g, 3.7 mmol), were dissolved in toluene (5 g), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated at 85 °C for 2.5 h. The reaction mixture was concentrated in vacuo and the residue distilled (>200 °C/2 mm Hg) to give 1.02 g of product (88%) as a bright yellow oil that crystallized on standing. ^{1}H NMR ($CDCl_3$), δ: 0.61 (s, 6H); 6.89 (s, 1H); 7.4 (m, 4H); 7.72 (m, 2H); 8.03 (m, 2H). ^{13}C NMR ($CDCl_3$), δ: −3.0, 90.5, 101.5, 121.8, 124.3, 127.9, 128.1, 128.3, 128.4, 128.7, 129.0, 129.5, 131.4, 134.3, 137.1, 137.7, 145.7. ^{29}Si NMR ($CDCl_3$): −5.2 ppm. FTIR (KBr): 3071, 2960, 1556, 1487, 1442, 1427, 1246, 1113, 1018, 923, 851, 836, 813, 762, 775, 703 cm^{-1}.

***E*,*E*-1,4-Diphenyl-2,3-bis(dimethylphenylsilyl)-*trans*-1,3-butadiene, 8aa.** Dimethylphenylsilane, **2a** (300 mg, 2.20 mmol), and 1,4-diphenylbutadiyne, **6a** (202 mg, 1.00 mmol), were dissolved in xylene (5 mL), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated at 125 °C for 9 h. The reaction mixture was concentrated in vacuo to give 436 mg of product (92%) as a bright yellow oil. ^{1}H NMR ($CDCl_3$), δ: 0.19 (s, 3H); 0.21 (s, 3H); 6.90 (s, 2H); 7.3 (m, 4H); 7.4 (m, 8H); 7.48 (m, 4); 7.62 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: −2.2, −1.3, 127.4, 127.6, 128.3, 128.90, 128.92, 134.3, 138.2, 138.5, 139.6, 146.1. ^{29}Si NMR ($CDCl_3$): −7.8 ppm. FTIR (KBr): 3067, 3050, 3022, 2957, 2899, 1597, 1491, 1443, 1427, 1248, 1110, 1026, 901, 833, 817, 773, 750, 734 cm^{-1}.

***E*-2-Pentamethyldisiloxy-1-phenyl-2-phenylethynylethene, 7ab.** Pentamethyldisiloxane, **2b** (287 mg, 2.0 mmol), and 1,4-diphenylbutadiyne, **6a** (202 mg, 1.00 mmol), were dissolved in xylene (3 g), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated at 80 °C for 24 h. The reaction mixture was concentrated in vacuo and the residue chromatographed on silica gel column (hexanes as eluant) to give 125 mg of product (36%). ^{1}H NMR ($CDCl_3$), δ: 0.22 (s, 9H); 0.42 (s, 6H); 7.04 (s, 1H); 7.4 (m, 6H), 7.54 (d, J = 7.0 Hz, 2H); 8.07 (d, J = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$), δ: −0.1, 2.0, 90.2, 100.9, 123.2, 124.4, 128.0, 128.3, 128.4, 128.7, 129.0, 131.3, 137.7, 144.6. FTIR (KBr): 3061, 2958, 1597, 1560, 1489, 1443, 1254, 1063, 909, 842, 785, 754, 734, 690 cm^{-1}.

***E*,*E*-1,4-Diphenyl-2,3-bis(pentamethyldisiloxy)-*trans*-1,3-butadiene, 8ab.** Pentamethyldisiloxane, **2b** (350 mg, 2.4 mmol) and 1,4-diphenylbutadiyne, **6a** (202 mg, 1.00 mmol) were dissolved in xylene (5.5 mL), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated at 125 °C for 68 h. The reaction mixture was concentrated in vacuo and then chromatographed on silica gel (hexanes) to give 342 mg of product (70%) as a colorless oil. ^{1}H NMR ($CDCl_3$), δ: 0.02 (s, 6H); 0.06 (s, 18H); 0.08 (s, 6H); 6.83 (s, 2H); 7.21 (m, 2H); 7.28 (m, 4H); 7.60 (d, J = 7.5 Hz, 4H). ^{13}C NMR ($CDCl_3$), δ: 1.4, 1.7, 2.0, 127.2, 128.3, 128.9, 136.1, 139.6, 147.3. FTIR (KBr): 3059, 3022, 2956, 2899, 1598, 1558, 1492, 1444, 1408, 1252, 1061, 839, 752, 692 cm^{-1}.

***E*,*E*-1,4-Diphenyl-2,3-bis(dimethylethoxysilyl)-*trans*-1,3-butadiene, 8ac.** Dimethylethoxysilane, **2c** (520 mg, 5.1 mmol) and 1,4-diphenylbutadiyne, **6a** (404 mg, 2.00 mmol) were dissolved in xylene (5 mL), treated with Karstedt's catalyst (30 μL of 0.235 wt % Pt in IPA solution), and heated at 140 °C for 70 h. The reaction mixture was concentrated in vacuo and then chromatographed on silica gel (first with hexanes and then with 6:1 hexanes:EtOAc) to give 757 mg of product (92%) as a light orange oil. ^{1}H NMR ($CDCl_3$), δ: 0.05 (s, 6H); 0.08 (s, 6H); 1.19 (t, J = 7.0 Hz, 6H); 3.66 (m, 4H); 6.95 (s, 2H); 7.28 (m, 6H); 7.61 (d, J = 6.3 Hz, 4H). ^{13}C NMR ($CDCl_3$), δ: −1.4, −1.1, 18.4, 58.4, 127.4, 128.2, 128.9, 137.1, 139.4, 145.6. FTIR (KBr): 3057, 3022, 2970, 2897, 1491, 1443, 1389, 1252, 1163, 1105, 1079, 1027, 947, 830, 782, 693 cm^{-1}.

***E*,*E*-1,4-Diphenyl-2,3-bis(diphenylmethylsilyl)-*trans*-1,3-butadiene, 8ad.** Diphenylmethylsilane, **2d** (1.63 g, 8.21 mmol) and 1,4-diphenylbutadiyne, **6a** (808 mg, 4.00 mmol) were dissolved in xylene (8 g), treated with Karstedt's catalyst (30 μL of 0.235 wt % Pt in IPA solution), and heated at 140 °C for 72 h. The reaction mixture was concentrated in vacuo and then triturated with hexanes to give 1.62 g mg of product as a light yellow solid. mp 127−128 °C. The hexane solution was slowly concentrated to get an additional 342 mg of product. Yield was 82%. ^{1}H NMR ($CDCl_3$), δ: 0.15 (s, 6H); 7.03 (s, 2H); 7.25 (m, 8H); 7.35 (m, 18H); 7.68 (d, J = 7.2 Hz, 4H). ^{13}C NMR ($CDCl_3$), δ: -4.3, 127.52, 127.57, 127.69, 128.4, 128.93, 128.94, 129.1, 135.0, 135.3, 135.4, 137.2, 139.5, 141.2, 143.6. FTIR (KBr): 3067, 3023, 2926, 1492, 1443, 1427, 1251, 1110, 1023, 791, 735, 724, 696 cm^{-1}.

***E*-2-Triphenylsilyl-1-phenyl-2-phenylethynylethene, 7ae.** Triphenylsilane, **2e** (530 mg, 2.02 mmol) and 1,4-diphenylbutadiyne, **6a** (202 mg, 1.00 mmol) were dissolved in xylene (5 mL), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated at 125 °C for 20 h then at 145 °C for an additional 24 h. The reaction mixture was concentrated in vacuo and the residue chromatographed on silica gel column (hexanes as eluant) to give 221 mg recovered starting hydride (41%) and 281 mg of product (61%). ^{1}H NMR ($CDCl_3$), δ: 7.04 (s, 1H); 7.3 (m, 5H); 7.5 (m, 12H); 7.80 (dd, J = 8.0, 1.5 Hz, 6H); 8.06 (d, J = 6.7 Hz, 2H). ^{13}C NMR ($CDCl_3$), δ: 91.4, 102.1, 118.2, 124.1, 127.9, 128.28, 128.29, 129.2, 129.9, 131.3, 133.4, 136.5, 137.6, 149.7. FTIR (KBr): 3067, 1487, 1427, 1261, 1109, 802, 755, 699 cm^{-1}.

***E*-2-Tris(trimethylsiloxy)silyl-1-phenyl-2-phenylethynylethene, 7af.** Tris(trimethylsiloxy)silane, **2f** (599 mg, 2.05 mmol), and 1,4-diphenylbutadiyne, **6a** (202 mg, 1.00 mmol), were dissolved in xylene (5 mL), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated at 130 °C for 40 h. The reaction mixture was concentrated in vacuo and the residue chromatographed on silica gel column (hexanes as eluant) to give 60 mg recovered starting diyne (30%) and 260 mg of product (52%). ^{1}H NMR ($CDCl_3$), δ: 0.21 (s, 27H); 7.16 (s, 1H); 7.42 (m, 6H); 7.54 (m, 2H); 8.07 (d, J = 7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$), δ: 1.8, 90.4, 99.2, 118.0, 124.5, 127.9, 128.3, 128.4, 128.8, 129.2, 131.3, 137.7, 146.8. FTIR (KBr): 3061, 3024, 2958, 2899, 1560, 1490, 1446, 1252, 1064, 1064, 843, 754, 690 cm^{-1}.

***E*,*E*-6,7-Bis(dimethylphenylsilyl)-*trans*-5,7-dodecadiene, 8ba.** Dimethylphenylsilane, **2a** (555 mg, 4.06 mmol), and 5,7-dodecadiyne, **6b** (325 mg, 2.0 mmol), were dissolved in xylene (5 g), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated at 140 °C for 20 h. The reaction mixture was concentrated in vacuo and the residue chromatographed on silica gel (hexanes as eluant) to give product as a light yellow oil (677 mg, 78%). ^{1}H NMR ($CDCl_3$), δ: 0.34 (s, 6H); 0.35 (s, 6H); 096 (t, J = 7.0 Hz, 6H); 1.34 (m, 8H); 1.98 (M, 4H); 5.87 (t, J = 6.7 Hz, 2H); 7.41 (m, 6H); 7.59 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: −3.1, −1.5, 14.1, 22.8, 31.0, 31.6, 127.6, 128.7, 134.3, 139.3, 141.4, 141.5. FTIR (KBr): 3069, 3050, 2956, 2927, 2871, 1581, 1465, 1427, 1247, 1110, 829, 772, 732, 700, 652 cm^{-1}.

***E*,*E*-6,7-Bis(triphenylsilyl)-*trans*-5,7-dodecadiene, 8be.** Triphenylsilane, **2e** (1.04 g, 4.0 mmol), and 5,7-dodecadiyne, **6b** (324 mg, 2.0 mmol), were dissolved in xylene (7 g), treated with Karstedt's catalyst (30 μL of 0.235 wt % Pt in IPA solution), and heated at 140 °C for 18 h. The reaction mixture was concentrated in vacuo and the residue chromatographed on silica gel (hexanes as eluant) to give 51 mg (6%) of mono-hydrosilylated product **7be** and 1.268 g of the desired product as a white solid (93%). **7be.** ^{1}H NMR ($CDCl_3$), δ: 0.85 (t, J = 7.1 Hz, 3H); 0.94 (t, J = 7.1 Hz, 3H); 1.30 (m, 4H); 1.41 (m, 4H); 2.34 (m, 2H); 2.51 (m, 2H); 6.19 (t, J = 7.0 Hz, 1H); 7.42 (m, 9H); 7.65 (dd, J = 8.1, 1.5 Hz, 6H).

^{13}C NMR (CDCl$_3$), δ: 13.6, 13.9, 19.6, 21.7, 22.5, 80.2, 99.6, 119.4, 127.7, 129.5, 134.0, 136.4, 156.6. FTIR (KBr): 3068, 3049, 2957, 2930, 2871, 1588, 1464, 1428, 1378, 1188, 1110, 908, 739, 699 cm^{-1}. **8be.** ^{1}H NMR (CDCl$_3$), δ: 0.78 (t, J = 7.1 Hz, 6H); 1.2 (m, 8H); 1.83 (m, 2H); 2.17 (m, 2H); 6.08 (t, J = 6.9 Hz, 2H); 7.27 (m, 24H); 7.38 (m, 6H). ^{13}C NMR (CDCl$_3$), δ: 13.9, 22.7, 31.4, 32.1, 127.4, 129.0, 135.1, 136.7, 137.6, 147.0. FTIR (KBr): 3068, 3047, 2956, 2924, 2855, 1580, 1484, 1427, 1107, 738, 699 cm^{-1}. mp 138−140 °C.

***E,E*-6,7-Di(tris(trimethylsiloxy)silyl)-*trans*-5,7-dodecadiene, 8bf.** Tris(trimethylsilxoy)silane, **2f** (1.2 g, 4.0 mmol), and 5,7-dodecadiyne, **6b** (324 mg, 2.0 mmol), were dissolved in xylene (5 mL), treated with Karstedt's catalyst (30 μL of 0.235 wt % Pt in IPA solution), and heated at 140 °C for 71 h. The reaction mixture was concentrated in vacuo and the residue chromatographed on silica gel (hexanes as eluant) to give 1.165 g of the desired product as a colorless liquid (77%). ^{1}H NMR (CDCl$_3$), δ: 0.15 (s, 54H); 0.93 (t, J = 6.8 Hz, 6H); 1.36 (m, 8H); 1.97 (m, 2H); 2.06 (m, 2H); 5.88 (m, 2H). ^{13}C NMR (CDCl$_3$), δ: 2.1, 14.1, 22.7, 30.6, 31.5, 137.9, 142.1. FTIR (KBr): 2958, 2874, 2860, 1589, 1456, 1250, 1059, 841, 755, 686 cm^{-1}.

***Z*-2,2,7,7-Tetramethyl-4-dimethylphenylsilyl-3-octene-5-yne, 7ca.** Dimethylphenylsilane, **2a** (555 mg, 4.06 mmol), and 2,2,7,7-tetramethyl-3,5-octadiyne, **6c** (325 mg, 2.0 mmol), were dissolved in xylene (5 g), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated at 140 °C for 22 h. The reaction mixture was concentrated in vacuo and the residue chromatographed on silica gel column (hexanes as eluant) to give 593 mg of product as a colorless oil (99%). ^{1}H NMR (CDCl$_3$), δ: 0.45 (s, 6H); 1.25 (s, 9H); 1.26 (s, 9H); 5.99 (s, 1H); 7.4 (m, 3H); 7.6 (m, 2H). ^{13}C NMR (CDCl$_3$), δ: −3.1, 28.5, 29.7, 30.9, 35.7, 78.6, 109.6, 120.2, 127.5, 128.9, 134.2, 138.3, 159.2. FTIR (KBr): 3069, 3051, 2964, 2901, 2866, 1585, 1476, 1460, 1428, 1249, 1204, 1113, 1082, 893, 832, 812, 776, 732, 699 cm^{-1}.

***Z*-2,2,7,7-Tetramethyl-4-dimethylethoxysilyl-3-octene-5-yne, 7cc.** Dimethylethoxysilane, **2c** (450 mg, 4.3 mmol), and 2,2,7,7-tetramethyl-3,5-octadiyne, **6c** (325 mg, 2.0 mmol), were dissolved in xylene (2.5 g), treated with Karstedt's catalyst (10 μL of 0.235 wt % Pt in IPA solution), and heated at 140 °C for 18 h. The reaction mixture was concentrated in vacuo and the residue chromatographed on silica gel column (first with hexanes then with 10:1 hexanes:EtOAc) to give 399 mg of product (75%). ^{1}H NMR (CDCl$_3$), δ: 0.23 (s, 6H); 1.21 (t, J = 7.1 Hz, 3H); 1.22 (s, 9H); 1.29 (s, 9H); 3.72 (q, J = 7.1 Hz, 2H); 6.06 (s, 1H). ^{13}C NMR (CDCl$_3$), δ: −2.6, 18.4, 28.4, 29.6, 30.8, 35.5, 58.7, 78.2, 109.0, 120.2, 159.2. FTIR (KBr): 2967, 2902, 2867, 1582, 1476, 1460, 1391, 1361, 1251, 1204, 1165, 1108, 1082, 948, 897, 820, 786, 735, 648 cm^{-1}.

Polymer 9aa. 1,4-Bis(dimethylsilyl)benzene, **4a** (194 mg, 1.0 mmol), and 1,4-diphenylbutadiyne, **6a** (202 mg, 1.0 mmol), were dissolved in xylene (6 mL), treated with Karstedt's catalyst (20 μL of 0.235 wt % Pt in IPA solution), and heated at 130−135 °C for 18 h. The reaction mixture was precipitated into MeOH (75 mL) to give an off-white powder which was isolated by filtration and vacuum drying to give 365 mg of product (92%). ^{1}H NMR (CDCl$_3$), δ: 0.12 (s, 6H); 0.18 (s, 6H); 6.85 (s, 2H); 7.2 (m, 6H); 7.4 (m, 4H); 7.5 (m, 4). ^{13}C NMR (CDCl$_3$), δ: −2.0, −1.6, 127.4, 128.3, 129.0, 133.3, 138.3, 139.2, 139.5, 145.9. FTIR (film on NaCl): 3052, 3021, 2956, 1491, 1443, 1379, 1248, 1131, 1026, 908, 833, 920, 770, 751, 733, 694 cm^{-1}. SEC (PS equiv MW): $M_w = 8195$, $M_n = 4389$, PDI = 1.87. To remove most of the cyclics present in the polymer, the material was dissolved in CHCl$_3$ (1 mL), precipitated into a 3:1 MeOH/acetone mixture (50 mL), isolated by filtration, and vacuum-dried to give $M_w = 9540$, $M_n = 4130$, PDI = 2.31. $T_g = 90.6$ °C. ^{29}Si NMR (CDCl$_3$): −7.8 ppm.

Polymer 9ab. 1,2-Bis(dimethylsilyl)ethane, **4b** (294 mg, 2.0 mmol), and 1,4-diphenylbutadiyne, **6a** (404.6 mg, 2.0 mmol), were dissolved in xylene (2 g), treated with Karstedt's catalyst (10 μL of 0.235 wt % Pt in IPA solution), and heated at 130−135 °C for 22 h. The reaction mixture was precipitated into MeOH (75 mL) and MeOH/H$_2$O to give an oil which was vacuum-dried to give oligomeric material (610 mg, 87%). No polymer was seen by SEC. SEC (PS equiv MW): $M_w = 890$, $M_n = 690$, PDI = 1.28.

Polymer 9bd. 4,4′-Bis(dimethylsilyl)diphenyl ether, **4d** (573 mg, 2.0 mmol), and 5,7-dodecadiyne, **6b** (325 mg, 2.0 mmol), were dissolved in xylene (4 g), treated with Karstedt's catalyst (10 μL of 0.235 wt % Pt in IPA solution), and heated at 130−135 °C for 21 h. The reaction mixture was precipitated into MeOH (75 mL) to give an orange goo, which was redissolved in CHCl$_3$ (2 mL) and reprecipitated into MeOH (100 mL) to give a gooey polymer, which was vacuum-dried to give 831 mg (83%) of product. ^{1}H NMR (CDCl$_3$), δ: 0.33 (s, 6H); 0.34 (s, 6H); 0.95 (m, 6H); 1.24 (m, 8H); 1.97 (m, 4H); 5.87 (t, J = 6.6 Hz, 2H); 7.06 (d, J = 8.5 Hz, 4H); 7.54 (d, J = 8.5 Hz, 4H). ^{13}C NMR (CDCl$_3$), δ: −2.7, −1.4, 14.2, 22.8, 31.0, 31.6, 118.2, 133.5, 135.9, 141.3, 141.7, 157.8. SEC (PS equiv MW): $M_w = 17{,}840$, $M_n = 5220$, PDI = 3.42. Reprecipitated polymer gave: $M_w = 17{,}620$, $M_n = 7190$, PDI = 2.45.

Polymer 9ba. 1,4-Bis(dimethylsilyl)benzene, **4a** (388.8 mg, 2.0 mmol), and 5,7-dodecadiyne, **6b** (324.5 mg, 2.0 mmol), were dissolved in xylene (2 g), treated with Karstedt's catalyst (10 μL of 0.235 wt % Pt in IPA solution), and heated at 130−135 °C for 22 h. The reaction mixture was precipitated into MeOH (75 mL) to give a tacky polymer that was washed with 2 × 30 mL of MeOH and then vacuum-dried at 60 °C to give 628 mg (88%) of product. ^{1}H NMR (CDCl$_3$), δ: 0.31 (s, 6H); 0.32 (s, 6H); 0.92 (m, 6H); 1.31 (m, 8H); 1.95 (m, 4H); 5.83 (t, J = 6.5 Hz, 2H); 7.54 (s, 4H). ^{13}C NMR (CDCl$_3$), δ: −2.8, −1.6, 14.1, 22.8, 31.0, 31.6, 133.3, 139.7, 141.4, 141.6. SEC (PS equiv MW): $M_w = 19{,}960$, $M_n = 6190$, PDI = 3.22. Reprecipitated polymer gave: $M_w = 19{,}770$, $M_n = 8020$, PDI = 2.47.

Polymer 9ad. 4,4′-Bis(dimethylsilyl)diphenylether, **4d** (573 mg, 2.0 mmol), and 1,4-diphenylbutadiyne, **6a** (404.5 mg, 2.0 mmol), were dissolved in xylene (4 g), treated with Karstedt's catalyst (10 μL of 0.235 wt % Pt in IPA solution), and heated at 130−135 °C for 21 h. The reaction mixture was precipitated into MeOH (75 mL) to give an yellow pseudo-solid which was washed with MeOH (4 × 50 mL) dried, redissolved in CHCl$_3$ (2 mL) and reprecipitated into MeOH (70 mL) to give a solid polymer which was vacuum-dried at 60 °C (792 mg, 81%). ^{1}H NMR (CDCl$_3$), δ: 0.23 (s, 6H); 0.25 (s, 6H); 6.92 (s, 2H); 7.03 (d, J = 8.3 Hz, 4H); 7.30 (m, 6H); 7.45 (d, J = 8.5 Hz, 4H); 7.63 (d, J = 7.3 Hz, 4H). ^{13}C NMR (CDCl$_3$), δ: −1.8, −1.3, 118.2, 127.5, 128.4, 128.9, 132.7, 135.9, 138.2, 139.6, 146.2, 157.9. SEC (PS equiv MW): $M_w = 16{,}140$, $M_n = 4950$, PDI = 3.26. Reprecipitated polymer gave: $M_w = 16{,}190$, $M_n = 6490$, PDI = 2.50.

Acknowledgment. The work of the GRC NMR team of L. Williams, P. Donahue, S. Saddoughi, and T. Early is greatly appreciated as are the MALDI results from H. Grade.

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MA062663S