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Disilanylenearylene Oligomers and Polymers from Dehydropolymerization of 1,4-$RH_2SiC_6H_4SiH_2R$ (R = Methyl, Ethyl, and Hexyl)

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The dehydropolymerization of 1,4-$RH_2SiC_6H_4SiH_2R$ (R = Me, Et, hexyl) monomers with CpCp*Zr[Si(SiMe$_3$)$_3$]Me catalyst produces linear $RH_2Si-(C_6H_4SiHRSiHR)_n-C_6H_4SiH_2R$ oligomers under mild conditions (room temperature). Further heating of the polymerization mixtures (for R = Me or Et) leads to increases in molecular weight, which appear to result partially from cross-linking reactions that occur by dehydrocoupling of "backbone" SiH groups. Eventually, insoluble polymers form at higher conversion. The new materials have been characterized spectroscopically, and by thermal gravimetric analysis. The insoluble (cross-linked) $EtH_2Si-(C_6H_4SiHEtSiHEt)_n-C_6H_4SiH_2Et$ polymer gives a much higher ceramic yield (67% to 1100 °C) than do the corresponding, low molecular weight oligomers (35% to 1100 °C for $M_w = 860$).

Introduction

In 1985, Harrod and co-workers reported that titanocene and zirconocene complexes catalyze the dehydrocoupling of primary silanes to relatively long $H(SiHPh)_nH$ oligomers ($n = 10-20$).[1] This important observation led to anticipation that convenient, selective routes to high molecular weight polysilanes based on coordination polymerizations might be possible.[2] Mechanistically, it appears that this reaction can occur by a metal-mediated condensation that operates through four-center transition states.[3] Modifications to the original reaction, particularly in light of mechanistic information, have resulted in significant advances in control over the polysilane molecular weight properties. Thus, the competing formation of cyclic oligomers can be greatly suppressed by modification of the catalyst or by changes in reaction temperature and monomer concentration.[3a] Mechanistic considerations have also aided in development of "mixed-ring" (η^5-C_5H_5)(η^5-C_5Me_5)Zr (CpCp*Zr) catalysts, which currently are the most active toward chain elongation.[3] With such catalysts, the longest chains obtained have ca. 70–100 silicon atoms in the $(SiHPh)_n$ backbone (estimated from M_n values of 5000–7000).[3a,4] Generally, alkylsilane monomers are less active than phenylsilane, but methylsilane has been found to be an exceptionally active monomer which can be dehydropolymerized to $(SiHMe)_n$ polysilanes containing several hundred silicons. For the latter polysilanes, spectroscopic evidence suggests some degree of cross-linking.[5] In general, secondary silanes are much less reactive than primary silanes, such that chains based on these monomers are currently limited to ≤10 silicon atoms. Corey has shown that $PhMeSiH_2$ is dehydrocoupled with the $Cp_2ZrCl_2/{}^nBuLi$ catalyst over 4 days at 90 °C, to $H(SiMePh)_nH$ oligomers with $n = 2-8$.[6]

Further improvements in the dehydropolymerization described above will depend largely on design of more efficient catalysts. Alternatively, it seems possible that the catalysts currently known can be used to carry out dehydrocouplings to fundamentally different silicon-containing polymer structures, via monomer design. We have recently reported that $[CpCp^*ZrH_2]_2$ catalyzes the dehydropolymerization of bis- and tris(silyl)arenes containing primary silane centers (e.g., 1,4-$H_3SiC_6H_4SiH_3$) to highly cross-linked and insoluble disilanylenearylene polymers such as $[1,4\text{-}H_{1.5}SiC_6H_4SiH_{1.5}]_n$.[7] These materials, like related linear polymers obtained via Wurtz-coupling methods, appear to possess significant $\sigma-\pi$ conjugation. Such $\sigma-\pi$ conjugated materials represent a new class of electroactive polymers which are attracting much interest.[8]

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[1] Aitken, C.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11.

[2] For reviews, see: (a) Harrod, J. F.; Mu, Y.; Samuel, E. *Polyhedron* **1991**, *10*, 1239. (b) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37. (c) Corey, J. In *Advances in Silicon Chemistry*; Larson, G., Ed.; JAI Press, Inc.: Greenwich, CT, 1991; Vol. 1, p327. (d) Laine, R. M. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Kluwer Academic Publishers: Amsterdam, 1990; p 37.

[3] (a) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22. (b) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047.

[4] Harrod, J. F., personal communication.

[5] Mu, Y.; Harrod, J. F. In *Inorganic and Organometallic Oligomers and Polymers*; Harrod, J. F.; Laine, R. M., Eds.; Kluwer Academic Publishers: Amsterdam, 1991, p 23.

[6] Corey, J. Y.; Zhu, X.-H.; Bedard, T. C.; Lange, L. D. *Organometallics* **1991**, *10*, 924.

[7] Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* **1991**, *24*, 6863.

[8] (a) Barton, T. J.; Ijadi-Maghsoodi, S.; Pang, Y. *Macromolecules* **1991**, *24*, 1257. (b) Ohshita, J.; Kanaya, D.; Ishikawa, M.; Koike, T.; Yamanaka, T. *Macromolecules* **1991**, *24*, 2106. (c) Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1990**, *23*, 4485. (d) Iwahara, T.; Hayase, S.; West, R. *Macromolecules* **1990**, *23*, 1298. (e) Ishikawa, M.; Hasegawa, Y.; Kunai, A. *J. Organomet. Chem.* **1990**, *381*, C57. (f) Corriu, R. J. P.; Guerin, C.; Henner, B.; Kuhlmann, T.; Jean, A.; Garnier, F.; Yassar, A. *Chem. Mater.* **1990**, *2*, 351. (g) Corriu, R. J. P.; Douglas, W. E.; Yang, Z. *J. Polym. Sci., Polym. Lett.* **1990**, *28*, 431. (h) Liu, H. Q.; Harrod, J. F. *Can. J. Chem.* **1990**, *68*, 1100. (i) Ishikawa, M.; Kanaya, D.; Ohshita, J.; Yamanaka, T. *J. Organomet. Chem.* **1989**, *369*, C18. (j) Weber, W. P.; Hu, S. *Polym. Bull.* **1989**, *22*, 363. (k) Weber, W. P.; Hu, S. *Polym. Bull.* **1989**, *21*, 133. (l) Weber, W. P.; Hu, S. *Polym. Bull.* **1989**, *22*, 355. (m) Nate, K.; Ishikawa, M.; Ni, H.; Watanabe, H.; Saheki, Y. *Organometallics* **1987**, *6*, 1673. (n) Shiina, K. *J. Organomet. Chem.* **1986**, *310*, C57. (o) Nate, K.; Sugiyama, H.; Inoue, T.; Ishikawa, M. *Electro. Chem. Soc. Extended Abstr.* **1984**, *94* (2), 778. (p) Ishikawa, M.; Hongzhi, N.; Matsusaki, K. *J. Polym. Sci., Polym. Lett.* **1984**, *22*, 669.

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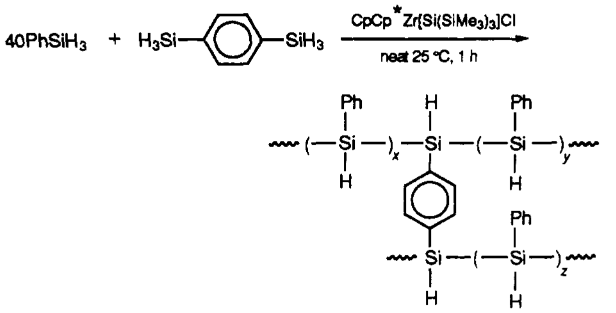
We have also shown that this dehydrocoupling reaction can be used to produce soluble, high molecular-weight polysilanes that are extensively cross-linked.[9] For example, CpCp*Zr[Si(SiMe$_3$)$_3$]Cl catalyzes the copolymerization of PhSiH$_3$ and 1,4-(H$_3$Si)$_2$C$_6$H$_4$ (in a 40:1 ratio) to a soluble polymer (M_w = 180 000) with a very broad molecular-weight distribution (M_w/M_n = 45). The high polydispersity is probably due to significant cross-linking (eq 1).[9b]

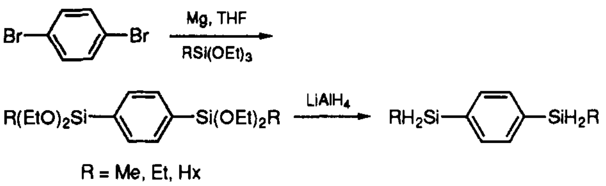


(1)

In this report, we describe investigations into the possibility of producing disilanylenearylene polymers of the type (–C$_6$H$_4$–SiHRSiHR–)$_x$ (R = Me, Et, Hx (hexyl)) via the dehydrocoupling of RH$_2$SiC$_6$H$_4$SiH$_2$R monomers. Introduction of the R group results in a secondary silicon center, which should considerably moderate the dehydrocoupling activity at silicon, thereby decreasing the chance for cross-linking reactions. For these polymerizations, the reaction required for linear chain growth corresponds to the "dimerization" of a secondary silane center, as in the dehydrocoupling of PhMeSiH$_2$ to PhMeHSiSiHMePh, which has ample precedent.[1,6,10]

Results and Discussion

Synthesis of Monomers. The bis(silyl)benzene 1,4-Me(EtO)$_2$SiC$_6$H$_4$Si(OEt)$_2$Me has been described previously,[11] but the synthesis reported here, modeled after the method developed by Shea,[12] seems superior. Coupling of the triethoxides RSi(OEt)$_3$ (R = Me, Et, Hx) with the di-Grignard BrMgC$_6$H$_4$MgBr gave in each case a good yield of 1,4-R(EtO)$_2$SiC$_6$H$_4$Si(OEt)$_2$R products. These compounds were then reduced with lithium aluminum hydride to the monomers of interest (eq 2). The monomers are readily purified by vacuum distillation.



(2)

Model Studies on the Dehydrocoupling of PhMeSiH$_2$. Since the synthesis of a (–C$_6$H$_4$–SiHRSiHR–)$_x$ polymer by dehydrocoupling of RH$_2$SiC$_6$H$_4$SiH$_2$R compounds requires a catalyst that dehydrocouples secondary silanes, we began by examining more readily analyzed "model" reactions of PhMeSiH$_2$. In our previous studies on the polymerization of H$_3$Si–arylene–SiH$_3$ monomers, we employed the mixed ring catalyst [CpCp*ZrH$_2$]$_2$.[7] We have since determined that the corresponding silyl methyl complex, CpCp*Zr[Si(SiMe$_3$)$_3$]Me (1), is nearly as active as the hydride and is more easily prepared and stored. Therefore the latter catalyst was used in the investigations reported here.

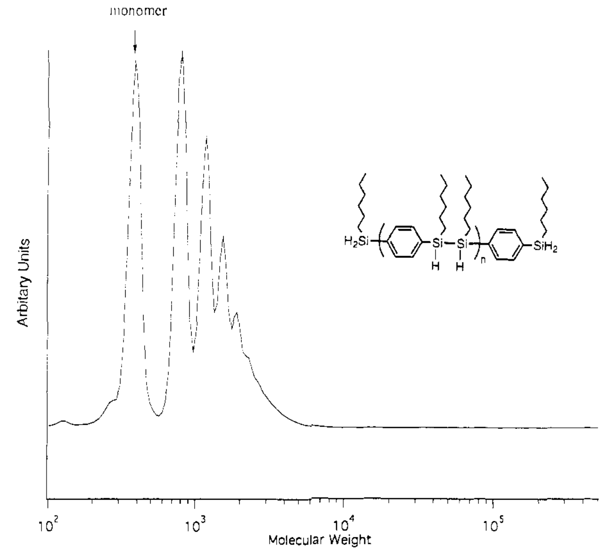
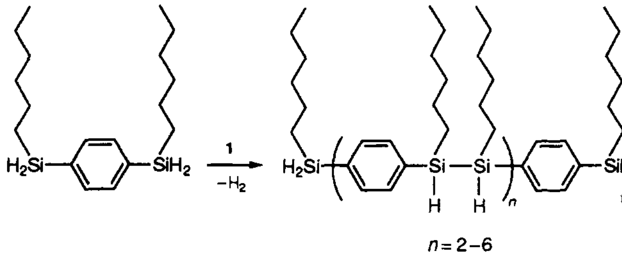


Figure 1. GPC trace for the HxH$_2$Si–(C$_6$H$_4$SiHHxSiHHx)$_n$–C$_6$H$_4$SiH$_2$Hx oligomer.

Reaction of neat PhMeSiH$_2$ with the catalyst (2 mol %) at room temperature produced after 2 days a mixture of starting monomer (31%), the disilane (60%), trisilane (6%), and some tetrasilane (ca. 3%), by gel permeation chromatography (GPC). Further reaction of this mixture over 4 days at 70 °C under a static vacuum resulted in nearly complete conversion of the starting material to a mixture of disilane (82%), trisilane (8%), and tetrasilane (ca. 10%). Only a trace of monomer remained. These results showed that 1 was potentially a good catalyst for the polymerization reactions of interest.

Polymerization Reactions. Initial attempts to obtain disilanylenearylene polymers of the type (–C$_6$H$_4$–SiHR-SiHR–)$_x$ focused on the bis(hexylsilyl) monomer shown in eq 3. Addition of the catalyst to neat monomer resulted in a brown mixture, which was stirred at room temperature for 24 h. The course of the reaction was monitored by GPC and NMR spectroscopy. As shown by the GPC trace of Figure 1, only ca. 75% of the monomer was converted, to a mixture of oligomers containing 2–6 monomer units.



(3)

It has proven difficult to achieve higher conversion in this reaction, since raising the reaction temperature to 75 °C, and extending the reaction time to 60 h, produced essentially an identical GPC trace. The ^{1}H NMR spectrum of this mixture of oligomers revealed two broad peaks which

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[9] (a) Walzer, J. F.; Woo, H.-G.; Tilley, T. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *32*, 441. (b) Walzer, J. F.; Tilley, T. D., to be published.

[10] Nakano, T.; Nakamura, H.; Nagai, Y. *Chem. Lett.* **1989**, 83.

[11] Breed, L. W.; Haggerty, W. J.; Baiocchi, F. *J. Org. Chem.* **1960**, *25*, 1633.

[12] Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700.

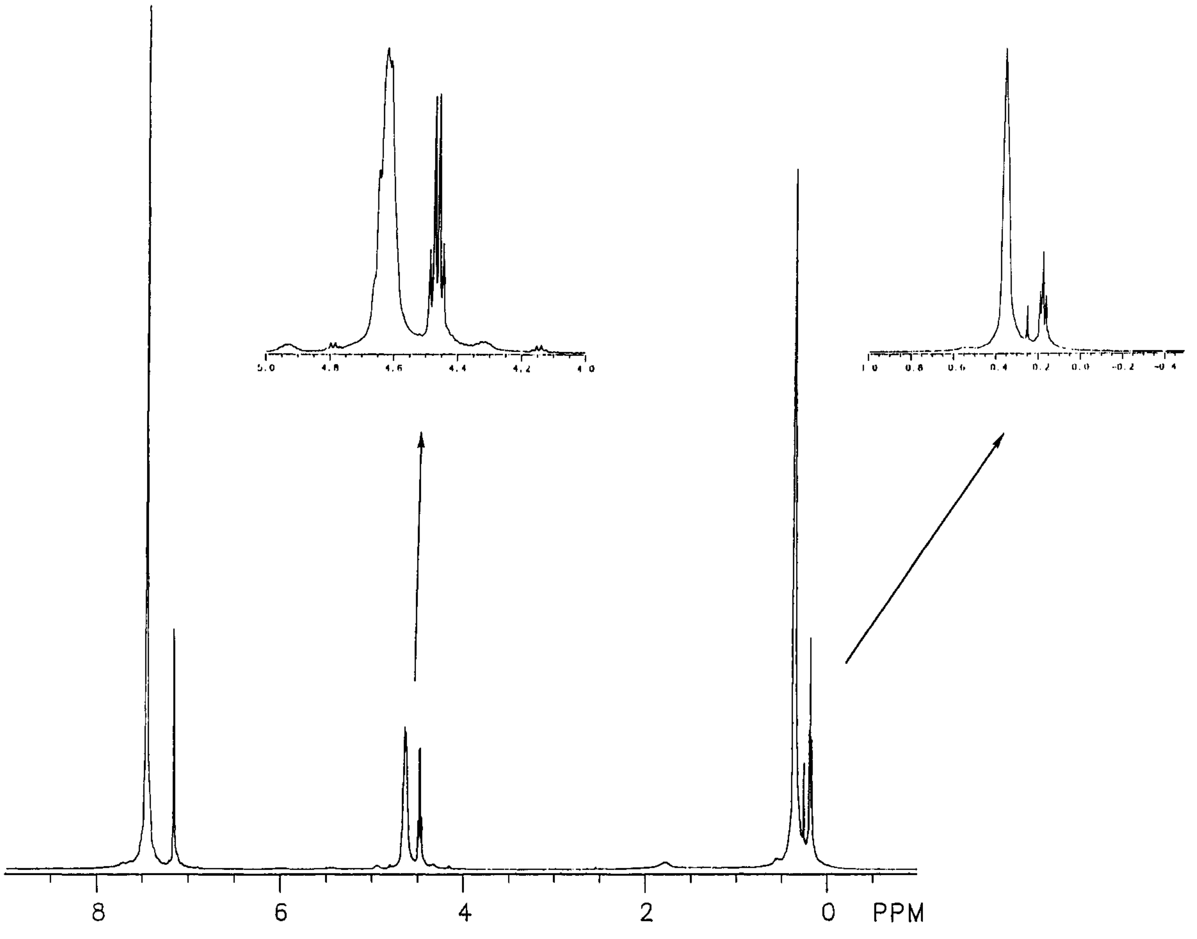


Figure 2. ^1H NMR spectrum for $MeH_2Si–(C_6H_4SiHMeSiHMe)_n–C_6H_4SiH_2Me$ with M_n = 780 (GPC, polystyrene standards).

correspond to Si–H groups. A triplet resonance at δ 4.50 is assigned to the terminal $SiH_2(Hx)$ end groups, by comparison to the spectrum for the monomer. A multiplet centered at δ 4.70 is assigned to the "backbone" (Hx)SiH groups. The ratio of SiH_2 to SiH resonances in this spectrum is 2.3, implying an average degree of oligomerization of ca. 2, which is consistent with the GPC trace of Figure 1.

Since hexyl groups in the above reaction appear to sterically inhibit extensive dehydropolymerization, we examined the analogous methyl-substituted monomer. Reaction of neat $MeH_2SiC_6H_4SiH_2Me$ with 1 (2 mol %) under dinitrogen (1 atm) for 24 h gives a mixture of oligomers (with 2 to ca. 10 monomer units; the first 6 are resolved by GPC), with an M_n value of 600. If this reaction is allowed to proceed for an additional 24 h under dynamic vacuum, the number average molecular weight value (M_n) calculated from the GPC trace is increased to 780 (M_w = 1430). For $MeH_2Si–(C_6H_4SiHMeSiHMe)_n–C_6H_4SiH_2Me$ oligomers obtained under mild conditions such as these, M_w/M_n values fall within the range 1.5–2.0. These materials are colorless solids, which can be purified by column chromatography (florosil).

The ^1H NMR spectrum of the $MeH_2Si–(C_6H_4–SiHMeSiHMe)_n–C_6H_4SiH_2Me$ oligomer with M_n = 780 (Figure 2) exhibits a relatively sharp peak in the aromatic region, and two multiplets centered at δ 4.63 and 4.47, which correspond to backbone and end Si–H groups, respectively. The more distinctive quartet at higher field (δ 4.47) was assigned to the end-group based on comparisons to spectra for the monomer. Likewise, the high-field SiMe triplet at δ 0.18 is assigned to the end group.

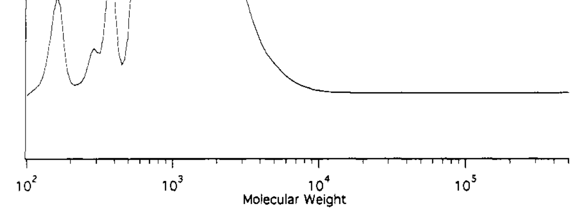


Figure 3. GPC trace for $MeH_2Si–(C_6H_4SiHMeSiHMe)_n–C_6H_4–SiH_2Me$ with M_n = 780 (GPC, polystyrene standards).

Integration of the SiH signals relative to each other, or integration of SiMe resonances, allows an end-group analysis of the molecular weight. For this sample, the average degree of polymerization calculated from the integrations is about 3 (molecular weight = 500). Therefore, the average molecular weight values determined by GPC measurements (polystyrene standards) appear to be overestimated by a factor of ca. 1.6. However, the GPC trace of Figure 3 clearly shows that significant quantities of higher oligomers are present in the sample.

The DEPT ^{29}Si NMR spectra[13] for the $MeH_2Si–(C_6H_4–SiHMeSiHMe)_n–C_6H_4SiH_2Me$ oligomers are similar and

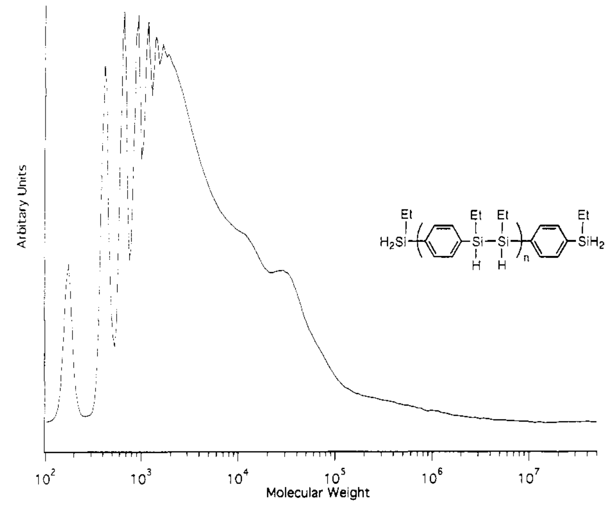


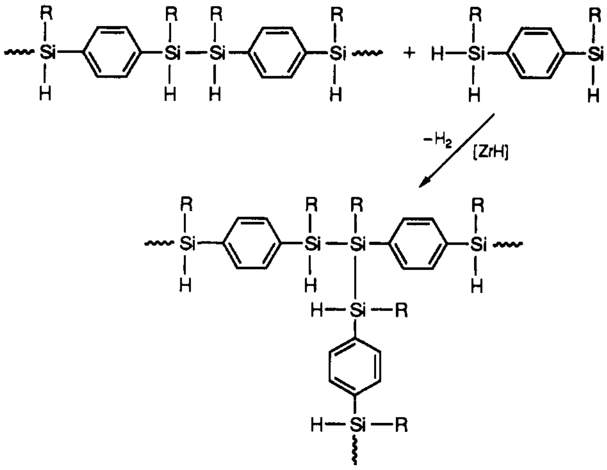
Figure 4. GPC trace for the soluble portion of the (–C$_6$H$_6$-SiHEtSiHEt)$_n$ polymer obtained after heating the reaction mixture. M_w = 117 000 (M_w/M_n = 6.3; GPC, polystyrene standards).

contain three resonances. A sharp peak at δ −35.7 is assigned as an SiH$_2$Me end group, based on polarization transfer experiments. Multiplets centered at δ −36.0 and −36.5 apparently arise from possible diastereomeric –SiHMe–SiHMe– structures that form.[14]

Further increases in molecular weight are accomplished with elevated temperatures. Thus, reaction of MeH$_2$SiC$_6$H$_4$SiH$_2$Me with the catalyst at 70 °C over 60 h provided material with M_n = 1560 and M_w = 7150. For this sample, the molecular weight determined from an end-group analysis is 1100. Addition of small amounts of toluene solvent (2 mL) and further heating (80 °C, 60 h) results in production of an insoluble poly(disilanylenearylene), along with a soluble fraction (ca. 10%) with molecular weight values of M_n = 1700 and M_w = 13 000. The high polydispersity of the latter material is attributed to cross-linking. Thus, under more forcing conditions, higher molecular weights are obtained, but this appears to be accompanied by cross-linking reactions which give rise to higher polydispersities, and eventually, insoluble material. Extended reaction (4 days) at 90 °C produced an insoluble polymer that displayed three broad signals in the CRAMPS solid-state ^{1}H NMR spectrum at δ 0.4, 4.4, and 6.6. Integration of these signals indicated that the polymer was ca. 10% cross-linked via reaction at the Si–H backbone positions.

Similar results were observed in attempts to dehydropolymerize EtH$_2$SiC$_6$H$_4$SiH$_2$Et, under conditions analogous to those described above. After 24 h at room temperature, only short oligomers were obtained (M_w/M_n = 1100/580). Upon exposure of the dehydrocoupling reaction to vacuum for 48 h, an M_n value of 1750 was reached (M_w = 4700). In a separate reaction over 5 days at 70 °C and under static vacuum, an insoluble polymer was obtained as the major product, along with small amounts of soluble material with M_w = 117 000 (M_w/M_n = 6.3). The higher molecular weights observed for the ethyl derivatives are attributed to the lower crystallinity (and higher solubility) of the oligomers and polymers formed, which allows higher molecular weight species to dissolve. Also, a more fluid reaction medium may allow for more extensive reaction. Consistent with this, the material obtained from the room temperature polymerization was a viscous liquid rather than a solid, as observed under similar conditions for the methyl-substituted monomer.

At present, the nature of the cross-linking process is not known, but there are two possibilities that seem most likely. One process would simply involve reaction of an Si–H group in the backbone of an oligomer via dehydrocoupling (eq 4). It is also possible that branching could occur by a redistribution process, which could act (for example) to convert SiH$_2$R end groups to more reactive SiH$_3$ functionalities (eq 5). Early-metal metallocene catalysts (for example, Cp$_2$TiMe$_2$[10]) are known to catalyze the redistribution of silanes under forcing conditions. The two possible structures that would result are difficult to differentiate analytically. Cross-linking sites produced by dehydrocoupling reactions (silicon centers with no Si–H bonds) were not evident from ^{29}Si NMR polarization transfer experiments.



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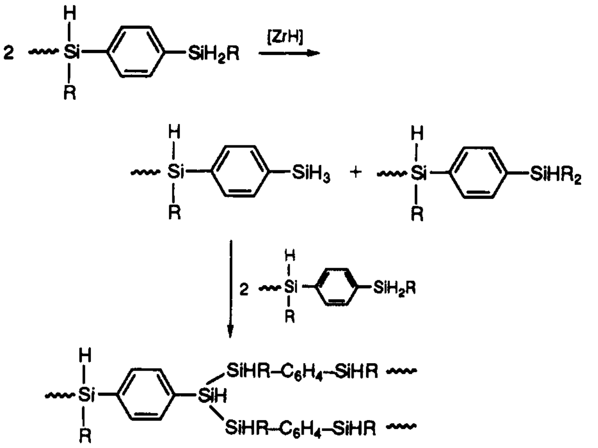

(5)

If redistribution is important as a cross-linking reaction, it seems likely that low molecular weight redistribution products (e.g., MeSiH$_3$ and Me$_2$SiH$_2$) might also be produced.[15] To investigate the latter possibility, we heated the (C$_6$H$_4$SiHEtSiHEt)$_x$ material with M_n = 1750 to 70 °C (with catalyst) for 48 h under vacuum, and trapped the volatile elimination products at −196 °C. The only trapped

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(13) Blinka, T. A.; Helmer, B. J.; West, R. *Adv. Organomet. Chem.* **1984**, *23*, 193.

(14) Durham, J. E.; Corey, J. Y.; Welsh, W. J. *Macromolecules* **1991**, *24*, 4823.

(15) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

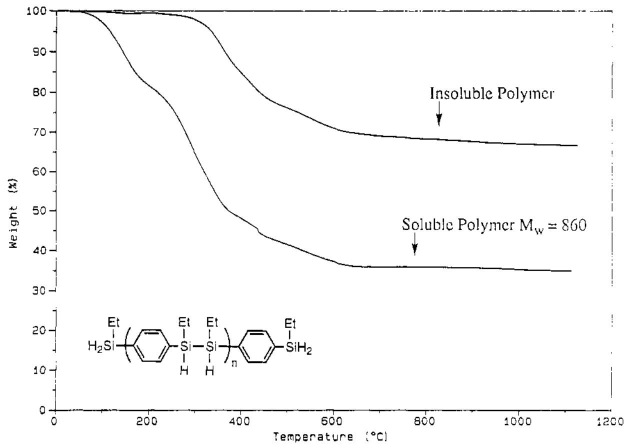

Figure 5. Thermal gravimetric analysis traces for $EtH_2Si-(C_6H_4SiHEtSiHEt)_n-C_6H_4SiH_2Et$ materials under argon.

compounds observed (by ^1H NMR spectroscopy) were small quantities of unreacted $EtH_2SiC_6H_4SiH_2Et$ monomer and $HSi(SiMe_3)_3$, from decomposition of the catalyst. Thus, no small-molecule products that might have been formed by redistribution were detected. Further evidence against redistribution reactions of this kind is provided by the $PhMeSiH_2$ dehydrocoupling experiments mentioned above. The volatiles from this reaction contained no traces of redistribution products ($MeSiH_3$, SiH_4, Ph_2MeSiH, etc.) by ^1H NMR spectroscopy. Furthermore, note that reactions in this system which produce the observed $PhMeHSi(SiMePh)_nSiHMePh$ (n = 1, 2) products correspond to the cross-linking process of eq 4, since they involve dehydrocoupling of tertiary silicon centers. Therefore it appears that the major cross-linking process occurs simply by dehydrocoupling of backbone positions, probably with the less crowded $-SiH_2R$ groups.

For $MeH_2Si-(C_6H_4SiHMeSiHMe)_n-C_6H_4SiH_2Me$ (M_w/M_n = 4440/1330) and $EtH_2Si-(C_6H_4SiHEtSiHEt)_n-C_6H_4SiH_2Et$ (M_w/M_n = 5010/1670), UV absorptions are observed at ca. 250 (254 and 249 nm, respectively). Thus, the electronic properties of these materials appear to be similar to those for disilanylenearylene polymers reported earlier, including $[H_{1.5}SiC_6H_4SiH_{1.5}]_n$ (260 nm),[7] $[SiEtMeSiEtMeC_6H_4]_n$ (262 nm),[8m] and $[SiPhMeSiPhMeC_6H_4]_n$ (254 nm).[8m]

The thermal stability of the $EtH_2Si-(C_6H_4SiHEtSiHEt)_n-C_6H_4SiH_2Et$ materials was investigated by thermal gravimetric analysis (TGA, Figure 5). As expected the insoluble, cross-linked polymer exhibits a much higher "ceramic yield" (67% to 1100 °C) than do the corresponding, low molecular-weight oligomers (35% to 1100 °C for M_w = 860).

Conclusions

The dehydrocoupling of $RH_2SiC_6H_4SiH_2R$ compounds (R = alkyl), as catalyzed by $CpCp^*Zr[Si(SiMe_3)_3]Me$, produces oligomers which appear to have linear $RH_2Si-(C_6H_4SiHRSiHR)_n-C_6H_4SiH_2R$ structures. Higher molecular weights can be achieved in these reactions, under somewhat more forcing conditions which produce extensive cross-linking. To obtain high molecular-weight, linear disilanylene(arylene) polymers by this method, a more selective catalyst which rapidly couples secondary (but not tertiary) silicon centers is apparently required. However, potential applications for dehydropolymerizations of the type described here are suggested by the very different properties for the disilanylenearylenes produced, and the control that is readily exerted over these properties. Thus, under relatively mild conditions, processible (soluble, liquid) oligomers are obtained. Application of gentle heating then converts these oligomers, via cross-linking reactions, to insoluble (and presumably more inert) solid networks that exhibit much higher ceramic yields. Potential applications may take advantage of such two-stage polymerizations to ceramic precursors.

Experimental Section

Manipulations were performed under an atmosphere of argon or nitrogen using standard Schlenk techniques and/or a Vacuum Atmospheres drybox. Dry, oxygen-free solvents were used throughout. Elemental analyses were performed by Desert Analytics. NMR spectra were recorded on a GE QE-300 or a Varian UN-500 spectrometer. The solid-state combined rotation and multiple-pulse spectroscopy (CRAMPS) ^1H NMR spectrum was obtained on a modified Nicolet spectrometer operating at 149.32 MHz, by C. F. Ridenour at the Regional NMR Center, Colorado State University. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer. The molecular weights of polysilanes were measured with a Waters 501 gel permeation chromatograph with polystyrene standards and tetrahydrofuran as solvent. Thermal analyses were performed on a du Pont Model 2000 thermal analysis system. 1,4-Dibromobenzene (Aldrich) was used as received, $MeSi(OEt)_3$ and $EtSi(OEt)_3$ (Hüls) were distilled prior to use, and $LiAlH_4$ (Aldrich) was recrystallized from diethyl ether. The complex $CpCp^*Zr[Si(SiMe_3)_3]Me$ was prepared as described previously.[16]

1,4-$Me(EtO)_2SiC_6H_4Si(OEt)_2Me$. A mixture of Mg chips (28.0 g, 1.15 mol), $MeSi(OEt)_3$ (360 g, 2.0 mol), and 750 mL of tetrahydrofuran were placed in a 2-L three-neck flask equipped with a magnetic stir bar, a condenser, and an addition funnel. A small crystal of iodine was added to activate the magnesium. A solution of 1,4-dibromobenzene (100.0 g, 0.424 mol) in tetrahydrofuran (250 mL) was added slowly. After addition of ca. 25 mL of this solution, the addition was interrupted until a mildly exothermic reaction began (within 30–60 min). Continued addition of the bromide was held at a rate that maintained a gentle reflux. After the addition, the reaction mixture was stirred for an additional 3 h. The solution was decanted from unreacted Mg, and evaporation of the solvent under vacuum left a residue which was extracted with hexane (ca. 500 mL). The hexane was removed by evacuation, and two fractional distillations (0.1 mmHg, 98–100 °C; lit. 164 °C/5.5 mmHg[11]) gave the product as a clear, colorless oil (46.5 g, 32%). Anal. Calcd for $C_{16}H_{30}O_4Si_2$: C, 56.1; H, 8.83. Found: C, 56.4; H, 8.89. IR (neat, CsI, cm^{-1}): 3045 m, 2960 s, 2920 s, 2870 s, 2755 w, 2725 w, 1480 w, 1440 m, 1386 s, 1365 m sh, 1290 m, 1255 s, 1160 s, 1038 s, 1090 vs, 950 s, 820 s sh, 783 s, 760 s, 735 m, 670 m, 500 s. ^1H NMR (300 MHz, benzene-d_6, 22 °C): δ 0.34 (s, 6 H, Me), 1.14 (t, J = 6.9 Hz, 12 H, OCH_2CH_3), 3.72 (q, J = 6.9 Hz, OCH_2CH_3), 7.83 (s, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 22 °C): δ −3.90 (Me), 18.57 (OCH_2CH_3), 58.59 (OCH_2CH_3), 133.82, 137.44 (C_6H_4).

1,4-$Et(EtO)_2SiC_6H_4Si(OEt)_2Et$. The above procedure was employed using $EtSi(OEt)_3$ in place of $MeSi(OEt)_3$. Two distillations (0.27 mmHg, 159–162 °C) gave a colorless liquid (50.0 g, 32%). ^1H NMR (300 MHz, benzene-d_6, 22 °C): δ 0.85 (m, 6 H, $SiCH_2CH_3$), 1.05 (m, 4 H, $SiCH_2CH_3$), 1.15 (t, 12 H, J = 7.1 Hz, 12 H, OCH_2CH_3), 3.72 (q, 8 H, J = 7.1 Hz, OCH_2CH_3), 7.88 (s, 4 H, C_6H_4).

1,4-$Hx(MeO)_2SiC_6H_4Si(OMe)_2Hx$. The above procedure was followed, using $HxSi(OMe)_3$ as reagent. A short-path distillation (0.18 mmHg, 145–147 °C) gave the product as a colorless liquid (11.9 g, 48%). ^1H NMR (300 MHz, benzene-d_6, 22 °C): δ 0.83–1.54 (m, 26 H, SiHx), 3.45 (s, 12 H, OCH_3), 7.88 (s, 4 H, C_6H_4).

1,4-$MeH_2SiC_6H_4SiH_2Me$. To lithium aluminum hydride (25.0 g, 0.66 mol) in diethyl ether (200 mL) was added 1,4-bis-

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[16] Elsner, F. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Organomet. Chem.* 1988, *358*, 169.

(diethoxymethylsilyl)benzene (150.0 g, 0.438 mol), and the mixture was stirred at room temperature for 20 h. Fractional distillation of the reaction mixture, followed by purification of the product by distillation at 88–90 °C/25 mmHg yielded 4.81 g (66%) of the product. Anal. Calcd for $C_8H_{14}Si_2$: C, 57.8; H, 8.48. Found: C, 58.5; H, 8.74. IR (neat, CsI, cm^{-1}): 3040 m, 2995 m, 2955 m, 2900 w, 2130 s, 1425 w, 1375 s, 1326 w, 1250 s, 1130 s, 1115 m sh, 1075 m, 1020 w, 940 s, 880 vs, 810 m, 730 s, 688 s, 500 m, 476 s. ^{1}H NMR (300 MHz, benzene-d_6, 22 °C): δ 0.19 (t, J = 4.2 Hz, 6 H, Me), 4.46 (q, J = 4.2 Hz, 4 H, SiH_2), 7.44 (s, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 22 °C): δ −7.78 (Me), 129.76, 134.65 (C_6H_4). ^{29}Si NMR (59.6 MHz, benzene-d_6, 22 °C): δ −38.40 (t, J_{SiH} = 208).

1,4-$EtH_2SiC_6H_4SiH_2Et$. The procedure for 1,4-$MeH_2SiC_6H_4SiH_2Me$ was used to obtain the product by distillation at 40–43 °C/0.01 mmHg in 71% yield (18.6 g). Anal. Calcd for $C_{10}H_{18}Si_2$: C, 61.8; H, 9.33. Found: C, 61.8; H, 9.33. ^{1}H NMR (300 MHz, benzene-d_6, 22 °C): δ 0.74 (m, 6 H, $SiCH_2CH_3$), 0.96 (m 4 H, $SiCH_2CH_3$), 4.42 (t, J = 3.8 Hz, 4 H, SiH_2), 7.47 (s, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 22 °C): δ 2.41, 8.93 (Et), 134.17, 135.03 (C_6H_4).

1,4-$HxH_2SiC_6H_4SiH_2Hx$. Lithium aluminum hydride (1.16 g, 0.0306 mol) and 100 mL of diethyl ether were placed in a 250-mL flask containing a magnetic stir bar. A diethyl ether (25 mL) solution of 1,4-$Hx(MeO)_2SiC_6H_4Si(OMe)_2Hx$ (11.87 g, 0.0278 mol) was added, and the resulting mixture was stirred for 40 h. The volatiles were evacuated, the product was extracted into pentane, and the pentane extract was evaporated to give the crude product, which was distilled with a Kugelrohr apparatus (0.02 mmHg/120–127 °C) to afford 5.0 g (58%). Anal. Calcd for $C_{18}H_{34}Si_2$: C, 70.5; H, 11.2. Found: C, 69.8; H, 11.0. ^{1}H NMR (300 MHz, benzene-d_6, 22 °C): δ 0.78–0.88 (m, Hx), 1.13–1.31 (m, Hx), 1.34–1.43 (m, Hx), 4.48 (t, J = 3.8 Hz, 4 H, SiH_2), 7.53 (s, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 22 °C): δ 10.27, 14.28, 22.93, 25.42, 31.81, 32.89 (Hx), 134.47, 135.20 (C_6H_4). ^{29}Si NMR (59.6 MHz, benzene-d_6, 22 °C): δ −30.65 (t, J_{SiH} = 192).

Dehydrocoupling of $PhMeSiH_2$. To 0.30 g (2.45 mmol) of $PhMeSiH_2$ in a 20-mL Schlenk flask was added CpCp*Zr[Si($SiMe_3$)$_3$]Me (0.0272 g, 0.049 mmol), and the resulting mixture was stirred at room temperature for 2 days. Analysis of the reaction mixture by GPC revealed the presence of $PhMeSiH_2$ (31%), PhMeHSiSiHMePh (60%), PhMeHSiSiMePhSiHMePh (6%), and PhMeHSi(SiMePh)$_2$SiHMePh (ca. 3%). The reaction mixture was then heated under static vacuum at 70 °C for 4 days, resulting in conversion to PhMeHSiSiHMePh (82%), PhMeHSiSiMePhSiHMePh (8%), and PhMeHSi(SiMePh)$_2$SiHMePh (ca. 10%). Transfer of the volatiles from this reaction mixture at −196 °C yielded only trace amounts of unreacted $PhMeSiH_2$ and some HSi($SiMe_3$)$_3$ as a decomposition product of the catalyst.

Polymerization of 1,4-$RH_2SiC_6H_4SiH_2R$. In a typical procedure, ca. 0.5 g of monomer was added to the CpCp*Zr[Si($SiMe_3$)$_3$]Me catalyst (ca. 30 mg) in an inert atmosphere glovebox. For reactions exposed to vacuum, the reaction flask was transferred to a Schlenk line. For isolation of the product, toluene (ca. 40 mL) was added to the reaction flask, and the resulting mixtured was stirred while being exposed to air for 3 h to destroy the catalyst. The solution was then passed through a Florosil column with toluene used as the elutant. The colorless effluent was evaporated to dryness to produce the disilanylenearylene as a white solid in ≥80% yield.

For MeH_2Si–(C_6H_4SiHMeSiHMe)$_n$–$C_6H_4SiH_2Me$ (24 h at room temperature under 1 atm N_2 and then 24 h at room temperature under dynamic vacuum; M_w/M_n = 1180/700): ^{1}H NMR (300 MHz, benzene-d_6, 22 °C): δ 0.18 (m, SiMe), 0.35 (m, SiMe), 4.46 (q, SiH), 4.63 (m, SiH), 7.44 (s, C_6H_4).

For EtH_2Si–(C_6H_4SiHEtSiHEt)$_n$–$C_6H_4SiH_2Et$ (24 h at room temperature under 1 atm of N_2 and then 48 h at room temperature under dynamic vacuum; M_w/M_n = 6860/1810): ^{1}H NMR (300 MHz, benzene-d_6, 22 °C): δ 0.75 (m, SiEt), 0.97 (m, SiEt), 4.41 (m, SiH), 4.56 (m, SiH), 7.50 (m, C_6H_4).

For HxH_2Si–(C_6H_4SiHHxSiHHx)$_n$–$C_6H_4SiH_2Hx$ (24 h at room temperature under 1 atm N_2, then 24 h at room temperature under dynamic vacuum; M_w/M_n = 1260/780): ^{1}H NMR (300 MHz, benzene-d_6, 22 °C): δ 0.86 (m, SiHx), 1.05 (m, SiHx), 1.21 (m, SiHx), 1.40 (m, SiHx), 4.50 (m, SiH), 4.70 (m, SiH), 7.55–7.64 (m, C_6H_4).

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