Synthesis of a New Hyperbranched Poly(silylenevinylene) with Ethynyl Functionalization

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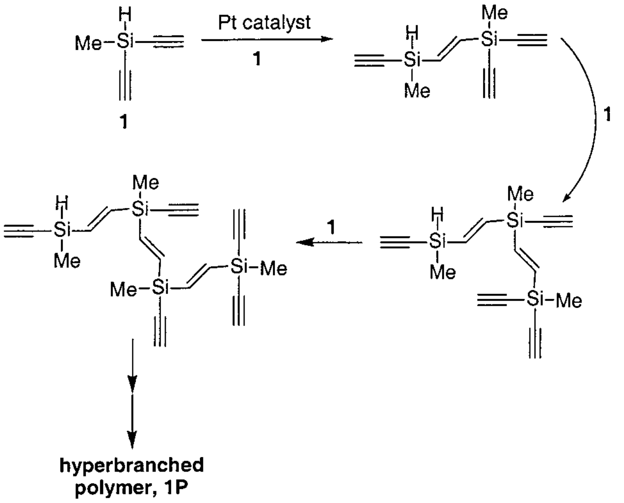
Organosilicon hyperbranched polymers are inorganic−organic hybrid polymers that are beginning to attract considerable interest for materials applications. For example, these highly processable polymers have already shown promise as preceramic polymer precursors,[1,2] degradable template molecules,[3,4] high-temperature elastomer precursors,[5] and modifiers of composite polymers.[6] A common method for the preparation of organosilicon hyperbranched polymers is the hydrosilylation polymerization of AB_n monomers in which the A and B groups represent SiH and terminal double-bond moieties. Because of the nonstoichiometric ratio of B to A groups, there always exist excess B groups in the hyperbranched polymer which impart specific properties to the polymer or can be chemically manipulated for further polymer functionalization. Thus far, organosilicon AB_n monomers in which B represents a *triple*-bond moiety have not been polymerized. Compared to simple double bonds, ethynyl B groups would be of interest for a number of reasons. For instance, ethynyl groups react with each other readily with heating or irradiation and thus provide a cross-linking mechanism in which catalysts are not required and byproducts are not formed.[7] Terminal ethynyl groups are also quite reactive with regards to other chemical transformations such as hydrosilylation and deprotonation reactions. Furthermore, the fact that ethynyl groups are well-known σ- and π-donor ligands[8] suggests the possibility of preparing new polymer-supported transition-metal complexes. As part of our ongoing investigations into the syntheses of new functional highly branched organosilicon polymers,[5,9−12] we describe here a new ethynyl-substituted hyperbranched poly(silylenevinylene), prepared via the hydrosilylation polymerization of methyldiethynylsilane.

Methyldiethynylsilane (**1**) was prepared using a slight modification of the reported synthesis of diethynyldimethylsilane.[13] Reaction of sodium acetylide with methyldichlorosilane in 1,2,4-trimethylbenzene with Kryptofix 222 as the catalyst resulted in the isolation of **1** as a clear liquid in 50% yield after distillation (it should be noted that attempted syntheses of triethynylsilane via this method were unsuccessful and resulted in violently exothermic reactions). Although **1** is colorless immediately after distillation, a slight yellow coloration develops on prolonged storage. However, ^{1}H NMR spectral measurements did not indicate that any impurities formed with the coloration.

Polymerization of **1** proved to be straightforward. The polymerization was initiated by adding several drops of Karstedt's catalyst solution to a toluene solution of **1**. After IR spectroscopy had confirmed that the polymerization was complete, the hyperbranched polymer **1P** was isolated as a clear, yellow sticky solid by precipitation into cold hexane. Polymer **1P** is air- and moisture-stable and very soluble in common organic solvents such as diethyl ether, toluene, and chloroform. An absolute molecular weight average was obtained using vapor pressure osmometry and determined to be 2720. As expected, the molecular weight of **1P** was dependent on the starting concentration of monomer; dilution of the monomer solutions resulted in lower average molecular weights. We also observed that **1P** became insoluble within 1 week when the flask containing the polymer was left exposed to ambient light conditions. We attribute this to light-induced cross-linking reactions involving the pendant ethynyl groups in the polymer. Further support for this hypothesis is gained from the fact that a sample of **1P** kept in the dark for 4 weeks remained fully soluble and experienced only a minimal increase in molecular weight (from 2720 to 3091).

Scheme 1. Hypothetical Polymerization of 1



The proposed polymerization of methyldiethynylsilane is illustrated in Scheme 1. The ^{1}H NMR spectrum of **1P** (Figure 1) provides important evidence concerning the regiospecificity of the hydrosilylation additions during polymerization. Small model compounds that represent the possible α-addition and β-addition products[14] are 1,1-bis(trimethylsilyl)ethylene and 1,2-bis(trimethylsilyl)ethylene, respectively. Because the vinylic protons in 1,1-bis(trimethylsilyl)ethylene resonate at 6.25 ppm[15] and the vinylic protons in *cis*- and *trans*-1,2-bis(trimethylsilyl)ethylene resonate at 6.59−6.76 ppm,[16] an examination of the 6−7 ppm region in Figure 1 strongly suggests that the hydrosilylation reactions proceeded to give exclusively the β-addition products. A similar conclusion was reached in the reported polymerization of dimethylethynylsilane, which yielded a linear poly(silylenevinylene).[17] The other features of the ^{1}H NMR spectrum also correspond well with the expected polymerization. The integration ratio of the vinylic, acetylenic, and SiMe resonances is equal to the expected 2:1:3 ratio in the polymer. Furthermore, the SiMe signal is divided into three peaks of varying intensity, each corresponding to one of the three possible SiMe environments within the polymer (Figure 2) and

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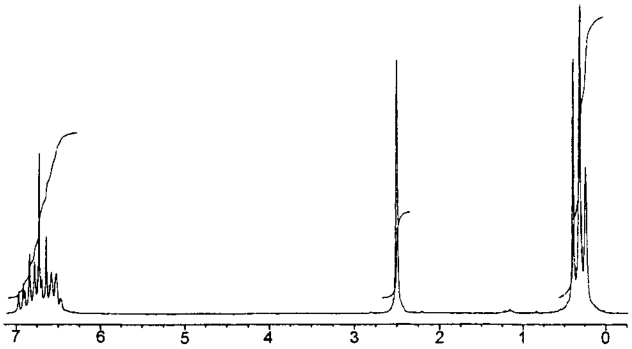

Figure 1. ^{1}H NMR spectrum of **1P** in $CDCl_3$.

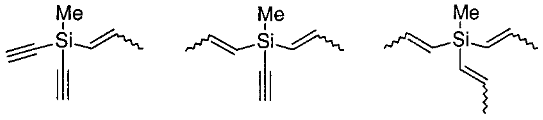

Figure 2. Three possible Si atom environments in the polymer.

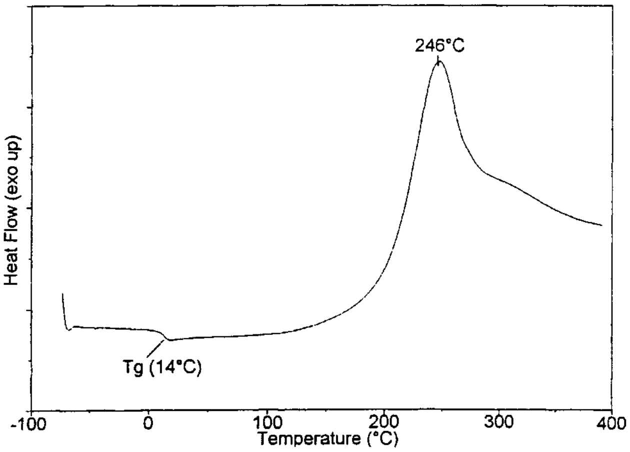

Figure 3. DSC characterization of **1P** (10 °C/min in nitrogen).

confirming the branched nature of the polymer. Additional evidence for the three separate Si environments was provided by the quantitative[5,18] ^{29}Si NMR spectrum of **1P**,[19] in which three distinct regions of peaks were observed. From the spectral integration, a degree of branching[20−22] value of 0.56 was calculated, close to the theoretically expected value of 0.50.[22] As an additional note, we did not observe any spectral evidence that suggested that additional hydrosilylation of the double bonds in the polymer had occurred.

Thermal characterizations of **1P** were performed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC thermogram (Figure 3) indicated that **1P** possessed a glass transition temperature of 14 °C and that a strong exotherm occurred with a maximum at 246 °C. This exotherm is a general characteristic of ethynyl-terminated resins and is evidence of the thermally induced ethynyl cross-linking reaction. The excellent thermal stability of the cross-linked polymer was demonstrated by TGA experiments in which heating **1P** to 1300 °C at a rate of 10 °C/min in nitrogen or air resulted in weight losses of 13 and 38%, respectively (Figure 4). The apparent thermal stability in air can at least partially be attributed to the oxidation of Si in the cross-linked polymer to form SiO_2, which begins to occur at approximately 200 °C (see Figure 4).

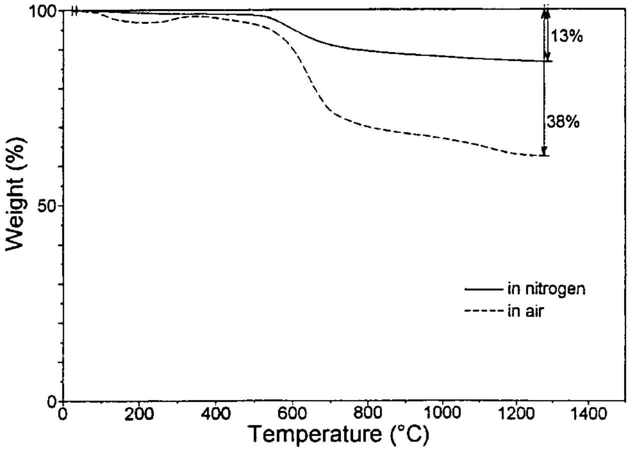

Figure 4. TGA characterization of **1P** (10 °C/min in either nitrogen or air).

In summary, a new organosilicon hyperbranched polymer possessing pendant ethynyl groups has been prepared via the hydrosilylation polymerization of methyldiethynylsilane. The tacky, highly soluble air- and moisture-stable polymer undergoes light- and heat-induced cross-linking reactions through the ethynyl groups. The highly branched nature of the polymer was confirmed by multinuclear NMR spectroscopy, and the excellent thermal stability of the cross-linked polymer was demonstrated by TGA studies in both air and nitrogen. The inherent reactive nature of terminally unsubstituted ethynyl groups suggests that many chemical functionalizations can be performed on the polymer. These studies are ongoing and will be described in a forthcoming publication.

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Supporting Information Available: Synthetic and characterization details for monomer **1** and polymer **1P** and UV and ^{29}Si NMR spectra for **1P**. This material is available free of charge via the Internet at http://pubs.acs.org.

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