Linear and Star-branched Siloxy-silane Polymers: One Pot A-B Polymerization and End-capping

A-B monomers were synthesized containing one alkene and one Si-H group per molecule. 3-Propenyl(dimethyldisiloxaneyl)silane and 8-octenyl(dimethyldisiloxaneyl)silane were obtained in good yield by interfacial reaction of the alkene with a silicon hydride. Polymerization involved hydrosilation with chloroplatinic acid or the more reactive divinyltetramethyl-disiloxanesilane platinum complex (Ashby's catalyst). Homopolymerization with an end-capping group gave linear polymer which can react with a core containing Si-H groups to give star polymers by a convergent approach. The core of tetrakis(dimethyldisiloxaneyl)silane with monomer polymerized to give stars with terminal Si-H groups which with olefins such as allyl phenyl would end-cap the star. Polymerization with 2-armed (tetramethyldisiloxane) gave linear polymers with terminal Si-H groups capable of end-capping with a variety of alkenes. Polymer characterization by 1H, 13C and 29Si NMR confirmed repeat unit structure and allowed estimation of number-average molecular weights of 2,400 to 6,500 by 1H integration. Size-exclusion chromatography molecular weights (with respect to styrene standards) were comparable to or somewhat smaller, and both values were less than those predicted based on the ratio of star-core to monomer.
Linear and Star-branched Siloxy-silane Polymers: One-pot A-B Polymerization and End-capping

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Results and Discussion

Silane and siloxane polymers form an important family of commercial materials. They possess a unique combination of thermal stability, biocompatibility, and segmental mobility which gives them low temperature flexibility and properties useful in demanding application where their high cost is justified. Recent reports of silicone dendrimers3,4 make available new classes of hyperbranched polymers which are to be described later in the text. We have developed an alternative approach to siloxy-silane hyperbranched polymers in which a 1.2 monomer possessing one alkene moiety and Si-H groups. Addition of a platinum hydrosilation catalyst leads to star formation of polymer (ca, 10,000-20,000 molecular weight) with a high content of terminal Si-H groups that can be reacted (end-capped) with a variety of alkenes such as allyl phenyl ether and the allyl ether-ethylenedimethylether of oligoethylene.5

Application of the general approach is possible using A-B and B2 monomers incorporating various alkene groups and substituted Si-H groups.6 The A-B monomer has been synthesized by the condensation of alkynylchlorosilane and dimethylchlorosilane. (Scheme 1). Polymerization monomer and a B2 functional group with Ashby's catalyst7 gave star polymer by divergent synthesis. This allows the formation of the star polymers where the growing arms have a terminal Si-H functionality. The post polymerization approach to star formation has also been investigated. Polymerization of monomer with an end-capping group gave linear polymers which can be attached to the node to give convergent stars.

Perimetal Synthesis
A round-bottom flask with stirring bar was sealed with a rubber septum d purged with nitrogen. 1-ocyneyldimethylchlorosilane (18.55 g, 0.091 m) d dimethylchlorosilane (11.94 g, 0.13 m) were introduced into the flask via a septum needle using nitrogen pressure to keep the system under inert atmosphere. Diethyl ether was used as solvent and 50 ml of a 0.06 M H2PO4/KH2PO4 buffer solution was added to initiate the condensation of chlorosilanes. The desired A-B monomer was obtained in 92% yield, 84% (by gc) with 16% impurity due to isomerized alkene groups.

Allyl Synthesis
A round-bottom flask with 20 ml of xylene was purged with nitrogen. monomer (3.43 g, 0.014 m) and allyl phenyl ether (0.41 g, 0.0031 m) were added into the flask and three drops of a 1x10^-3 solution of Ashby's catalyst was added to initiate polymerization. After complete disappearance of Si-H groups by NMR, the star synthesis was purified by synthesizing the core in the presence of the catalyst solution. The concentration of the solvent in the catalyst solution. The concentration of the solvent was constant, so reaction can be monitored by relative peak intensity. The top trace is of the end-capped polymer with catalyst removed. The residual peaks at 5.3 ppm show a small amount of residual linear polymer with less reactive internal double bonds. The SEC trace gave a molecular weight slightly higher than from NMR integration.

Figure 3 presents 1H spectra that focus on the methyl hydrogens attached to silicon. At 0.27 and 0.22 ppm are doublets of methyl hydrogens coupled to Si-H moieties of the core and monomer, respectively. Disappearance of the core peaks (labeled a) shows that substitution occurs at all four arms, plus there is a shift for the methyl hydrogens to 0.135 ppm (peak c) upon incorporation into the polymer. Since the backbone methyl hydrogens of both silicones are now identical, there is a decrease in the monomer methyl hydrogen at 0.11 ppm (labeled b) and concomitant increase in the 0.096 ppm peak (labeled c). Residual peaks at 0.11 ppm and 0.22 ppm are from end-group methyis.

SEC analysis of polymer 5 gave a retention time corresponding to polystyrene of molecular weight 5,400 while 1H NMR integration of end-capping groups versus repeat units gave a number average value of 3,250. The star nature of this polymer is expected to give a more compact structure in solution that should lead to a lower molecular weight estimate by SEC than for a corresponding linear polymer. Molecular weight distributions for the linear polymers and star polymers made with this method were broad (ca 2 or greater) probably due to the (presumed) step-growth nature of the polymerization coupled with an expected nonhomogeneous distribution of catalyst particle sizes (which would effect rapid migration of the catalyst particles) and the broadening due to the internal double bonds acting as premature terminating groups due to their reduced reactivity.

The star nature of these materials might be questioned based on a difference in reactivity of the core Si-H groups versus the monomer Si-H. We have carried out extensive model compound reactions which confirm the rapid reaction of the core units and high-yield formation of tetrasubstituted derivatives from hydrosilation of the core species with various alkenes. We have also observed side-reactions with water, for example, involving hydrolysis of Si-H groups and formation of Si-O-Si units which would effectively crosslink the star polymers. These reactions can be controlled by careful drying and maintenance of an inert atmosphere during polymerization, and their occurrence easily monitored spectoscopically.

We conclude that both propenyl and octenyl monomers polymerize well although each suffers from a drawback: cyclization of the propenyl.
nomer and the presence of internal and less reactive alkenes in the aryl compound. Elimination of the latter should make 2b a general monomer for a wide variety of linear, star and even comb-branched polymers that combine unique physical properties (hydrophobicity, very low Tg's, and chemical and thermal stability) with potential for end-group functionalization leading to novel applications as single-molecule reactors, artificial blood and precursors to ideal siloxy-silane networks.

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References

Figure 1. 1H NMR spectra in CDCl3 of 8b, full scale (bottom trace) and expanded inset (top trace).

Figure 2. 1H NMR spectra in CDCl3 of monomer 2b and node (bottom trace), polymerization at 18 min, 60 min, 26 hours and 2 days after addition of allyl phenyl ether cleaved of Ashby's catalyst (from second-to-bottom up).

Figure 3. 1H NMR spectra in CDCl3 of monomer 2b and node (bottom trace), polymerization at 1 min, 60 min, 26 hours and 2 days after addition of allyl phenyl ether cleaved of Ashby's catalyst (from second-to-bottom up).