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Unexpectedly Rapid Hydrosilation Polymerization of the Diallyl Derivative of Bisphenol A and 2,6-Diallylphenol

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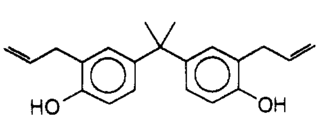
Introduction. Reports of the use of hydrosilation to obtain linear,[1,2] comb,[3] and hyperbranched polymers[4,5] are extensive, with one of the earliest reports appearing in 1956.[6] In recent years, our group has been extending the use of platinum-catalyzed hydrosilation for the production of linear, star, and hyperbranched polymers.[7–9] A key aspect of our use of the polymers obtained is reaction of terminal Si–H groups with olefinic compounds containing various functional groups such as carboxylic acids and amines. All such reactants examined possessing vinyl, allyl, or longer terminal olefin tether groups and unprotected functional groups displayed reduced or completely inhibited addition. We were therefore surprised at the extremely rapid and quantitative reaction which occurred between a wide variety of terminal S–H derivatives and 2-allylphenol. In fact, initial reactions often took place with explosive results and it was necessary to dilute or cool the reaction mixtures to control the violent exotherm which developed. In addition, reaction occurred with exclusive anti-Markovnikov addition. A published model study involving siloxysilanes and allylphenyl ethers also showed high conversion of allyl groups without isomerization of the double bond;[10] we have observed that rates of reactions of the 2-allylphenol groups are orders of magnitude faster than the allylphenyl ether analogs and just as regioselective. The fast rates and quantitative addition to this type of allyl group make polyhydrosilation an attractive route to functional silicon-containing polymers. This prompted evaluation of the reaction of disilanes with the bisallyl derivative of Bisphenol A (BPA, 1; produced by Ciba-Geigy as a component in their Matrimid 5292 composite resin system) and 2,6-diallylphenol (2).



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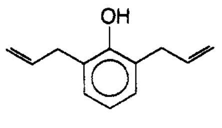

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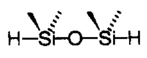

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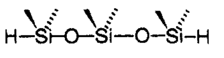

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We here describe preliminary results of the facile AA–BB polyaddition reaction and characterization of polymers from these two diallyl monomers with two disilane comonomers along with formation of allyl-terminated oligomers obtained using material imbalance.

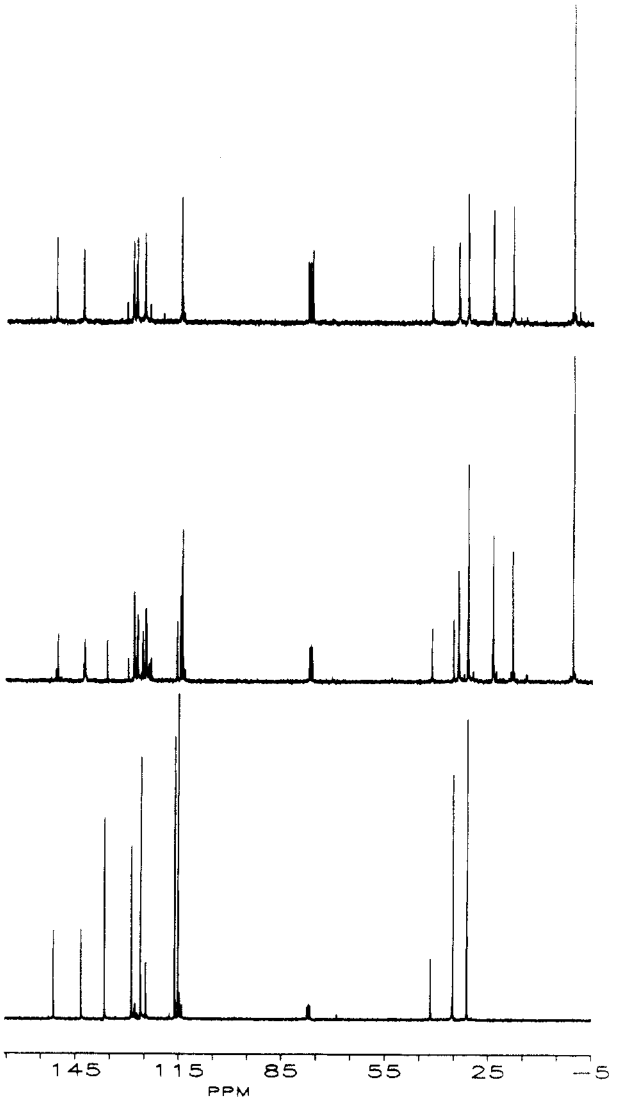
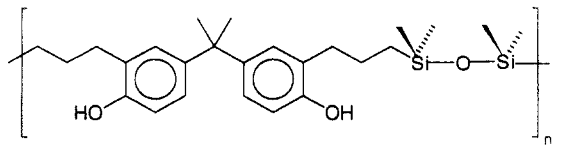


Figure 1. ^{13}C NMR spectra of the 2,2′-diallyl derivative of Bisphenol A (bottom), the oligomer of this monomer with 1,1,3,3-tetramethyldisiloxane (middle), and the polymer from these monomers (top).

Results and Discussion. The polymerizations of the *diallyl* monomers with either tetramethyldisiloxane (3) or hexamethyltrisiloxane (4) were strongly exothermic with high conversion to polymer in seconds-to-minutes at ice bath temperatures.[11] Solvent was necessary to promote miscibility of the coreactants and to allow heat transfer. Even with precautions, molecular weights could be limited by a stoichiometric imbalance caused by siloxane volatility. However, careful temperature control allowed formation of polymer for both diallyl monomers.

The spectroscopic characterization of the monomers and polymers was carried out using IR and ^{1}H and ^{13}C NMR.[12] Figure 1 shows the ^{13}C NMR spectra of the allylic Bisphenol A monomer, a low molecular weight polymer with allyl end groups obtained through stoichiometric imbalance, and polymer 5 (intrinsic viscosity 0.21 dL/g). In contrast to the spectrum of the monomers, no alkene peaks or unreactive Si–H groups were seen in any of the polymer spectra (other than end-functionalized oligomers), consistent with complete polyaddition. Residual alkene peaks in the ^{1}H NMR spectrum of the oligomers were used to determine degrees of polymerization, which was found to



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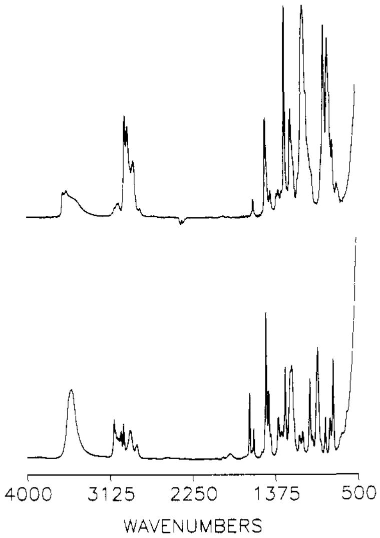
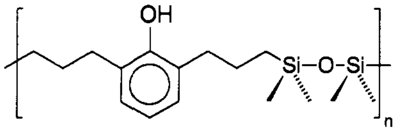


Figure 2. FTIR spectra of neat thin films of 2,6-diallylphenol (bottom trace) and its polymer with 1,1,3,3-tetramethyldisiloxane (upper trace).

be ca. 7 for the sample described here. Such reactive oligomers are usable as coreactants (and perhaps toughening agents) in the Matrimid resin system, in formation of block copolymers through reaction with other disilane materials, and as cross-linkers for polymers containing multiple Si–H groups.

The 2,6-diallylphenol monomer was also extremely reactive toward hydrosilation polymerization and gave polymer **6** in a matter of seconds when reacted with the disilane comonomer. The FTIR spectra of the diallyl monomer and polymer are given in Figure 2 and clearly confirm complete reaction by the absence of peaks in the polymer spectrum for the allyl vinyl groups (1637 cm^{-1}) and Si–H moieties (medium peak at 2127 cm^{-1}). ^{1}H and ^{13}C NMR spectra were consistent with polymer formation occurring only through anti-Markovnikov addition of the Si–H to the alkene bond with no allyl-to-propene rearrangement.



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DSC analysis of the polymers showed pronounced glass transitions. For the BPA-containing material, T_g occurred at 28–34 °C with the disiloxane comonomer, which is relatively high compared to siloxane homopolymers (T_g's of ca. −120 °C). The low molecular weight oligomer from BPA and disiloxane was a liquid at room temperature. The polymer obtained from 2,6-diallylphenol and disiloxane showed a T_g at ca. −29 °C. The TGA for the BPA–disiloxane polymer showed no weight loss below 250 °C, with the major inflection occurring at approximately 350 °C under a N_2 atmosphere; these are good values for siloxysilane polymers.

Solution properties of these polymers are somewhat unusual. They showed high solubility in chlorinated solvents, C_1–C_5 alcohols, and polar aprotic solvents but were insoluble in water and hexanes. Dilute-solution viscosity measurements in THF at 30 °C gave intrinsic viscosities of 0.21–0.23 dL/g. The BPA-containing polymer showed a broad distribution by size-exclusion chromatography (SEC, THF solvent, polystyrene standards) with M_n of ca. 2200 and M_w 27 000. This may indicate cyclization of some of the low molecular weight species early in the reaction since no end groups are detectable by NMR or IR analysis.

Deliberate or accidental monomer imbalance gave oligomers with reactive allyl terminal groups which should allow their incorporation into block copolymers. In addition, these polymers possess a reactive phenolic functionality on every repeat unit with potential for derivatization before or after polymerization. For example, we have made the pendant phenylcarbonate derivative by reaction of phenyl chloroformate with the BPA-containing silane polymer using CH_2Cl_2 solvent and triethylamine as HCl scavenger; essentially quantitative substitution occurred (based on ^{1}H and ^{13}C spectral changes) to give soluble polymer.

Conclusions. We have synthesized new oligomers and polymers containing siloxysilane segments *via* hydrosilation polyaddition of disilanes with 2,6-diallylphenol or the 2,2′-diallyl derivative of Bisphenol A. Initial characterization results confirm reasonable molecular weight, excellent organic solubility, and good thermal stability for these polymers. Pendant phenylcarbonate formation demonstrates the potential of these materials for side-chain incorporation.

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(11) Solvents and reagents were used as received. The *o,o′*-diallylphenol (**2**) was synthesized using a literature procedure. Polymerizations were carried out in stirred reactors under a N_2 atmosphere using the appropriate concentration of monomer and methylene chloride to make 50% solutions. One drop of a soluble platinum catalyst (the divinyldisiloxane complex in xylene; Hüls Chemical Co.) was used. Reactions were so exothermic that they were performed in an ice bath to prevent violent solvent loss. Catalyst was then removed with activated charcoal, the solution filtered, and solvent evaporated to give polymer.
(12) Characterization by ^{1}H and ^{13}C NMR was carried on a Bruker AC-300, and analysis by FTIR was performed on a Perkin-Elmer 1600A. Thermal analysis was performed on a Du Pont 9900 equipped with DSC 910 and TGA 952 modules using a heating rate of 10 °C/min under a N_2 atmosphere. Dilute-solution viscosity measurements were taken using a Cannon–Ubbelohde #50 semimicroviscometer with THF at 30 °C.