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Preliminary communication

POLYMERIZATION OF PRIMARY SILANES TO LINEAR POLYSILANES CATALYZED BY TITANOCENE DERIVATIVES*

CLAIRE AITKEN, JOHN F. HARROD
Chemistry Department, McGill University, Montreal (Canada)
and EDMOND SAMUEL
Ecole Nationale Superieure de Chimie de Paris, Paris (France)

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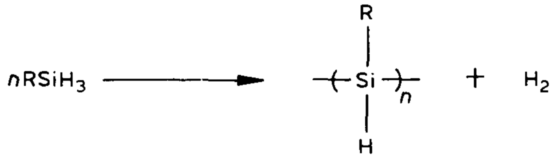
Summary

The dehydrogenative coupling of primary silanes to linear polysilanes is catalyzed by Cp_2TiR_2 ($R = CH_3$ or $C_6H_5CH_2$). The degree of polymerization of the polymers thus far obtained is ca. 10. Some physical and chemical characteristics of the polymers are described.

Macromolecules with backbones composed entirely of carbon atoms are most commonly synthesized through the catalyzed addition polymerization of ethylene, or acetylene derivatives. The virtual absence of analogous derivatives in the chemistry of silicon has precluded the use of a similar strategy for the production of macromolecular polysilanes [1].

In the course of studying the reactions of organotitanium compounds with silanes, we have adventitiously discovered a new catalytic reaction which generates linear polysilanes from primary organosilanes with the concurrent evolution of dihydrogen, according to eq. 1 [2]. The production of polysilanes, accompanying the redistribution of phenylsilane catalyzed by Wilkinson's catalyst, has been previously reported [3]. The present system is



$$n\mathrm{RSiH_3} \longrightarrow -\!\left(\overset{\mathrm{R}}{\underset{\mathrm{H}}{\mathrm{Si}}}\right)_{n}\!- + \mathrm{H_2} \qquad (1)$$

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*This paper is dedicated to Professor J. Halpern on the occasion of his 60th birthday.

orders of magnitude more active than the rhodium catalyst and much more selective in that no redistribution occurs.

High catalytic activity has been observed for the compounds Cp_2TiR_2 (I), where Cp = η^5-cyclopentadienyl or alkylcyclopentadienyl, and R = methyl or benzyl, but not phenyl. Reaction of I with RR'R''SiH (e.g. R and R' = aryl, alkyl or H, R'' = H; R and R' = alkyl or aryl, R'' = alkoxyl or siloxyl) at room temperature under an inert atmosphere and in inert solvents leads to reaction 2 [2].

$$\underset{(I)}{4Cp_2TiR'_2} + \underset{(II)}{8R_3SiH} \rightarrow \underset{(III)}{2[(Cp_2TiH)_2H]} + 6R_3SiR' + \underset{(IV)}{R_6Si_2} + 2R'H \qquad (2)$$

This reaction does not occur for trialkyl- and triarylsilanes (triethylsilane can be used as an inert solvent for the reaction of other silanes). Halosilanes give a different reaction, which leads to the formation of dichlorotitanocene, rather than the hydride, III. Trialkoxysilanes react mainly by reaction 2, but the hydride III so produced is always contaminated by alkoxytitanium(III) species.

When reaction 2 is run in the presence of a large excess of $RSiH_3$, or even in silane as solvent, an evolution of dihydrogen occurs for periods extending long after reaction 2 is complete. For the case of R = phenyl, the evolution of H_2 is very vigorous, even for concentrations of I of ca. 1 mol% based on silane [4]. Vigorous stirring and purging the solution with argon, to facilitate the evolution of H_2, speed up the reaction considerably. After a few hours the solution becomes noticeably more viscous due to the accumulation of polysilane. After the virtual cessation of hydrogen evolution, the polysilane may be recovered by passage of the reaction solution through a Florisil column, followed by vacuum evaporation. Polyphenylsilane obtained by this procedure is a brittle white glass, polyhexylsilane is a viscous oil. Both polymers exhibit a ν(SiH) below 2100 cm^{-1} (2090 and 2085 cm^{-1} respectively in the pure state) typical of a trisubstituted Si—H compound [5], and an intense absorption band in the near UV ($\lambda_{max} \sim 270$ nm, $\epsilon \sim 40{,}000$) typical of the Si—Si bond [6]. Both polymers undergo spontaneous oxidation to the corresponding polysiloxane on exposure to air, the polyhexylsilane having a half-life of several hours in the pure state, while that of the polyphenylsilane is about one month. These oxidation reactions are accompanied by a shift of the ν(SiH) to higher frequency (ca. 70 cm^{-1}) and the disappearance of the absorption band in the UV. The ^1H NMR spectra of the polymers show a broad, complex massif in the SiH region (δ 4—5 ppm) whose integral is 1/5 with respect to the phenyl protons of the polyphenylsilane and 1/13 with respect to the hexyl protons of the polyhexylsilane. Use of a DEPT pulse sequence [7] in the measurement of the decoupled, natural abundance ^{29}Si spectra of the polymers indicated that nearly all of the silicon atoms attached to H were present as SiH. Although some SiH_2 was detected, SiH_3 was below the level of detectability. Taken together, the above results leave little doubt that we are dealing with polymers of the type shown in eq. 1. Although we can be reasonably sure that the polymers are negligibly branched, we do not know yet whether they are linear, or annular.

The average molecular weights of several samples of both the polyphenyl- and polyhexylsilanes were measured by vapor pressure osmometry and were found to be in the range of 900 to 1400. A systematic study of the effects of various reaction parameters and of silane purity on molecular weight is in progress.

Under comparable reaction conditions, the secondary silanes react very much more slowly than primary. For example, a reaction of phenylmethylsilane (40% in toluene; 1 mol% I as catalyst; room temperature) after two weeks yielded unreacted silane (50%) and an oligomer of average degree of polymerization of four. No catalytic formation of Si—Si bonds has been observed in the case of tertiary silicon hydrides.

The Si—H groups of the polysilanes described above can easily be alkylated using catalytic hydrosilation [8]. Under the reaction conditions used by us there is no evident rearrangement, or degradation of the polymer chain. Thus, the rather stringent limits on the number of polysilanes that can be directly obtained by polymerization may be considerably enlarged by easy functionalization of the polymers.

The scope of the polymerization reaction, the chemical properties of the polymers and the extension of these catalysts to the polymerization of SiH_4 are the subjects of further study in these laboratories.

Acknowledgements. Financial support for this work from the Natural Sciences and Engineering Research Council of Canada, the Fonds F.C.A.C. de Quebec and the Dow Corning Corporation is gratefully acknowledged.

References and notes

1 Although there have been some notable successes in the synthesis of compounds with Si=Si bonds, their isolation as stable compounds is predicated on the suppression of their tendency to polymerize. See e.g. M.J. Fink, D.J. DeYoung and R. West, J. Am. Chem. Soc., 105 (1983) 1070.
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4 In a typical reaction, $PhSiH_3$ (2 ml, 20 mmol) in toluene (3 ml) was degassed and saturated with argon. After addition of dimethyltitanocene (40 mg, 0.2 mmol) the mixture was vigorously stirred under a stream of argon for 24 h and then pumped dry under vacuum. After re-dissolution in toluene/hexane (1/2 v/v) the catalyst was allowed to oxidize by exposure to the air for a few seconds and the product solution was passed rapidly through a Florisil® column. The colorless effluent was evaporated to dryness to give a brittle white solid (1.5 g) with a molecular weight (vapor pressure osmometry) of 1200.
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7 Distortionless Enhancement by Polarization Transfer. SeeD.M. Doddrell, D.T. Pegg and M.R. Bendall, J. Magn. Resonance, 48 (1982) 323.
8 In a typical hydrosilation procedure, polyphenylsilane (1.0 g) was dissolved in a mixture of benzene (5 ml) and 1-hexene (5 ml). Following addition of cyclooctadienedimethylplatinum (5 mg) the mixture was stirred at room temperature under argon for 24 h. During this time, the ν(Si—H) band disappeared. Evaporation of the solution under vacuum yielded a stiff gum whose ^{1}H NMR spectrum showed no evidence of Si—H, but had resonances due to phenyl and hexyl groups in equivalent amounts.