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Preliminary communication

PREPARATION OF LONG-CHAIN POLY(METHYLPHENYLSILANE)

R.E. TRUJILLO
Sandia Laboratories, Albuquerque, New Mexico 87185 (U.S.A.)*
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Summary

A long chain poly(methylphenylsilane) has been synthesized and characterized. It is shown to be of high molecular weight and to have appreciable solubility in common solvents.

Permethylpolysilanes and perphenylpolysilanes have been extensively studied [1—3] since their preparation by Burkhard [4] and Kipping and Sands [5], respectively. Most of these studies have focused on the lower molecular weight polysilanes which are soluble and, therefore, amenable to analysis and characterization. For example, the largest soluble permethylpolysilane was prepared by Boberski and Allred [6,7] and was characterized as being permethyltetracosasilane, $Me(SiMe_2)_{24}Me$. The largest soluble perphenylpolysilane [8,9] was determined to be three to four times larger than permethyltetracosasilane, i.e., $n \sim 80$ versus $n = 24$.

This difference in polymer size suggested that still larger soluble silane polymers could be prepared by appropriate monomer selection. Wessen and Williams [10] and West and David [11] have recently prepared random copolymeric polysilanes which are of high molecular weight and soluble in common solvents. The preparation of such soluble polymeric polysilanes is a major first step in the development of polysilanes as high glass transition structural materials. This report describes the synthesis and characterization of a high molecular weight, soluble, polymethylphenylsilane.

A 500 ml three-necked, round-bottomed flask was fitted with reflux condenser, thermometer, and a 125 ml pressure equalizing addition funnel. This apparatus was thoroughly dried and purged with nitrogen. All subsequent reaction operations were carried out in nitrogen. A dispersion of 0.07 g atom of 5 μ sodium particles in 20 ml of dodecane was added to the reaction flask

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and the stirred mixture was heated to gentle reflux. (Caution: do not use a Teflon-coated stirring bar as a violent reaction between molten sodium and Teflon could result.) Methylphenyldichlorosilane (0.035 mol) was added dropwise to the vigorously stirred mixture during 5 to 15 min. The rate of monomer addition influences the molecular weight distribution of the resulting polymer. After 2 h, the hot reaction mixture was cooled to room temperature and filtered through a dry sintered-glass funnel. The solid residue was washed sequentially with two 20 ml portions of each of hexane, methanol, water, methanol, and hexane. The solid residue is made up of the polysilane, sodium chloride, and unreacted sodium. The washing procedure removes the sodium chloride and sodium and permits the isolation of solid poly(methylphenylsilane).

This procedure yields poly(methylphenylsilane) in 65% yield with an elemental analysis for C_7H_8Si of found (calcd.): C, 68.4 (70.0); H, 6.67 (6.67); Si, 22.8 (23.4)%. The ratio of methyl protons (δ 0.17 broad) to phenyl protons (δ 7.38 broad) was 0.604/1 (calcd. 0.60/1) as determined from the integrated NMR spectrum in deuterated chloroform. The infrared spectrum showed Si-methyl at 1250 cm^{-1} (m), Si-phenyl at 1433 and 1100s cm^{-1} (s), carbon-hydrogen (aliphatic) at 2941w and 2890w cm^{-1}, and carbon-hydrogen (aromatic) at 3049m cm^{-1}. The molecular weight, determined by membrane osmometry in toluene at 35°C, was 21,400 for sample A in which monomer was added to the reaction mixture during six minutes, and 55,000 for sample B in which monomer addition occurred during fifteen minutes. These number average molecular weights correspond to n = 178 and n = 458 monomer units per respective polymer preparation. The respective solubilities of samples A and (B) in common solvents are: toluene 0.29 M (0.16 M), carbon tetrachloride 0.28 M (0.15 M), chloroform 0.5 M (0.3 M). These preparations were insoluble in acetone, methanol, hexane, and acetonitrile. Thermo-gravimetric analysis showed that the polysilane was stable in air or argon to 300°C after which rapid weight loss occurred.

Further studies of the physical and chemical properties of these long-chain poly(methylphenylsilanes) are in progress.

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