Chemistry

Corresponding Member of the Academy of Sciences of the USSR K. A. Andrianov, N. A. Kurasheva,

1961

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR K. A. Andrianov, N. A. Kurasheva,
I. K. Kuznetsova, and E. I. Gerhardt

On the Synthesis of Polymers of Regular Structure in the Polydimethylsiloxane Series

Polymers with inorganic main molecular chains of the polydimethylsiloxane series, containing, along with dimethylsiloxane units, also phenylmethylsiloxane (^{1}), methylvinylsiloxane (^{2}), and other units, have been obtained by the joint hydrolysis of various monomers followed by their polymerization. In the polymers obtained in this way, the distribution of different groups in the molecular chain relative to the dimethylsiloxane units is irregular.

In the present work the polycondensation reaction of the methyl diethoxysilylmethyl ester of dimethylphosphinic acid with various α, ω-dihydroxydimethylsiloxanes was studied. By using α, ω-dihydroxydimethylsiloxanes with different numbers of dimethylsiloxane units between the hydroxyl groups, it is possible to regulate the distance between the dimethylphosphinic groups and to ensure the regularity of their distribution in the molecular chain. To carry out the synthesis of polymers with a definite position of methylphosphinic groups in the chain, α, ω-dihydroxydimethylsiloxanes were synthesized by a reaction known for diphenylsilanediol (^{3})

$$\mathrm{Cl{-}Si(CH_3)_2{-}\left[O{-}Si(CH_3)_2\right]_{n-1}Cl + 2NaHCO_3 \rightarrow 2NaCl + 2CO_2 + HO{-}Si(CH_3)_2{-}\left[O{-}Si(CH_3)_2\right]_{n-1}OH}.$$

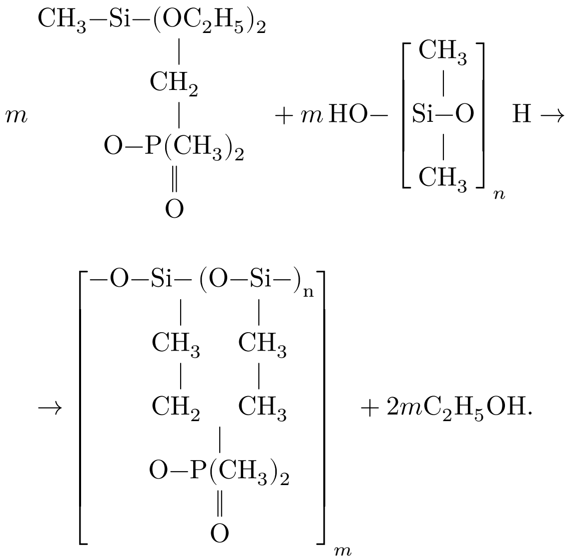
By this reaction α, ω-dihydroxydimethylsiloxanes with degree of polymerization $n = 9, 13, 53$ were obtained. Their properties are given in Table 1.

Table 1

Substance	Yield, %	Mol. wt., found	Mol. wt., calculated	OH, %, found	OH, %, calculated	C, %, found	C, %, calculated	H, %, found	H, %, calculated	Si, %, found	Si, %, calculated
$HO\left[\begin{array}{c}CH_3\\ \vert\\ Si{-}O\\ \vert\\ CH_3\end{array}\right]_{9} H$	70.9	684	678.866	4.97	4.44 4.58	31.5	32.17 32.32	8.29	8.03 7.84	36.82	36.92
$HO\left[\begin{array}{c}CH_3\\ \vert\\ Si{-}O\\ \vert\\ CH_3\end{array}\right]_{13} H$	88.9	980	1016 1032	3.47	3.52 3.99	31.9	32.07 32.13	8.16	8.09 8.16	37.16	37.63 37.70
$HO\left[\begin{array}{c}CH_3\\ \vert\\ Si{-}O\\ \vert\\ CH_3\end{array}\right]_{53} H$	66.5	3930*	4263**	–	0.84 9.90	–	–	–	–	–	–

* Molecular weight calculated from the hydroxyl groups.
** Molecular weight determined by the viscometric method.

α,ω-Dihydroxydimethylsiloxanes, on heating with the methyl-diethoxysilylmethyl ester of dimethylphosphinic acid without a catalyst, react with liberation of ethyl alcohol according to the reaction:



$$m\begin{array}{c}CH_3{-}Si{-}(OC_2H_5)_2\\ |\\ CH_2\\ |\\ O{-}P(CH_3)_2\\ \|\\ O\end{array} + m\,HO{-}\left[\begin{array}{c}CH_3\\ |\\ Si{-}O\\ |\\ CH_3\end{array}\right]_n H \rightarrow$$

$$\rightarrow\left[\begin{array}{cc}{-}O{-}Si{-} & (O{-}Si{-})_n\\ | & |\\ CH_3 & CH_3\\ | & |\\ CH_2 & CH_3\\ | & \\ O{-}P(CH_3)_2 & \\ \| & \\ O & \end{array}\right]_m + 2mC_2H_5OH.$$

The reaction was carried out at a temperature of 170°. The end of the reaction was determined from the liberation of ethyl alcohol, the amount of which, in the case of condensation of α,ω-dihydroxydimethylsiloxane with degree of polymerization $n = 9$, was 76.5% of theory; in the case of condensation of α,ω-dihydroxydimethylsiloxane with degree of polymerization $n = 13$, 73% of theory. The end of the reaction in the condensation of α,ω-dihydroxydimethylsiloxane with degree of polymerization $n = 53$ was determined by attainment of a constant viscosity. Determination of the molecular weights of the polymers by the viscometric method showed that they correspond to: 2190, 7250, 31620.

All the polymers tested had a very low glass-transition temperature in the range −110° to −130°. At the same time, a slight shift of the glass-transition temperature toward higher temperatures was observed as the distance between the dimethylphosphinic groups in the polymer chain decreased. Thus, for a polymer with 9 dimethylsiloxane units between dimethylphosphinic groups, the glass-transition temperature is 110°, while with 13 units it is 120°. The low glass-transition temperatures of polymers containing polar dimethylphosphinic groups in the chain can be explained by the fact that, owing to their large size compared with methyl groups, they decrease the packing density of the molecular chains.

Experimental part. 1. Synthesis of dihydroxydimethylsiloxanes. A three-necked flask equipped with a stirrer, reflux condenser, and dropping funnel was charged with 15.5 g (0.185 mole) of $NaHCO_3$, 200 ml of acetone, and 200 ml of benzene, and, with stirring, the mixture was heated on a water bath. At 75°, 42.1 g (0.059 mole) of α,ω-dichlorooctadecamethylnonasiloxane in 50 ml of benzene was added dropwise. After all the chloride had been introduced into the reaction, the mixture was stirred for eight hours. The end of the reaction was determined by the absence of chlorine in solution.

The precipitate was filtered off on a Büchner funnel, and the solvent was removed from the filtrate to constant weight. The product obtained was filtered again. A total of 28.36 g of α,ω-dihydroxydimethylsiloxane with degree of polymerization $n = 9$ was isolated, which was 70.9% of theory.

Found, %: C 32.17; 32.32; H 8.03, 7.84; Si 36.92; OH 4.58, 4.44
$C_{18}H_{19}Si_9O_{10}$. Calculated, %: C 31.5; H 8.19; Si 36.82; OH 4.97

Mol. wt.: found 678.7; 669.2; calculated 684.

2. Similarly, from 54 g (0.053 mole) of α,ω-dichlorohexamethyltridecasiloxane in 200 ml of benzene and 200 ml of acetone and 13.4 g (0.159 mole) of $NaHCO_3$, 46.4 g of the corresponding α,ω-dihydroxydimethylsiloxane was obtained. Yield 88.9% of theoretical.

Found, %: C 32.07; 32.13; H 8.09; 8.16; Si 37.63; 37.70; OH 3.52; 3.99
$C_{26}H_{80}Si_{13}O_{14}$. Calculated, %: C 31.9; H 8.16; Si 37.1; OH 3.47

3. Similarly, from 80 g (0.026 mole) of α,ω-dichlorodimethylsiloxane, 3 g (0.036 mole) of $NaHCO_3$ in 150 ml of acetone and 200 ml of benzene, 70.5 g of the corresponding α,ω-dihydroxydimethylsiloxane was obtained. Yield 66.5% of theory. OH content 0.90%; 0.84%. Molecular weight, determined viscosimetrically, 4266; from hydroxyl groups, 3930.

Condensation reaction of methyldiethoxysilylmethyl ester of dimethylphosphinic acid with α,ω-dihydroxydimethylsiloxanes having degrees of polymerization $n = 9; 13; 53$.

1). A Claisen flask equipped with a stirrer, thermometer, and straight condenser was charged with 10 g (0.147 mole) of α,ω-dihydroxydimethylsiloxane with $n = 9$ and 3.5 g (0.147 mole) of methyldiethoxysilylmethyl ester of dimethylphosphinic acid. The mixture was stirred and heated at 150° for 6 hours; during the reaction, ethyl alcohol distilled off at 60°–0.47 g, with $n_D^{20} = 1.3626$. Yield of ethyl alcohol 76.5% of theory. The product was then vacuum-treated to constant weight. A total of 12.72 g was obtained.

$C_{20}H_{59}Si_{10}H_{11}P$.	Found, %:	C 32.5; H 8.09; Si 32.67; P 3.55;
	Calculated, %:	C 33.2; H 8.00; Si 33.5; P 3.66

Molecular weight, determined viscosimetrically, 2194; glass-transition temperature −110°.

2). Similarly, from 5 g (0.005 mole) of α,ω-dihydroxydimethylsiloxane with $n = 13$ and 1.23 g (0.0051 mole) of methyldiethoxysilylmethyl ester of dimethylphosphinic acid, 5.51 g of a substance was obtained, with molecular weight 7250 and glass-transition temperature −120°. During the reaction, 0.16 g of ethyl alcohol was evolved, 73% of theory.

3). Similarly, from 30 g (0.0076 mole) of α,ω-dihydroxydimethylsiloxane with $n = 53$ and 1.85 g (0.0077 mole) of methyldiethoxysilylmethyl ester of dimethylphosphinic acid, 29.44 g of a substance with molecular weight 31620 was obtained. During the reaction the relative viscosity of a 1% solution was measured; when the viscosity ceased to change, the reaction was stopped.

$C_{110}H_{329}Si_{54}O_{56}P_1$.	Found, %:	C 32.59; 32.42; H 8.12; 8.09; Ash 80.25; 80.09
	Calculated, %:	C 32.2; H 8.04; Ash 81.1

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
17 V 1961

CITED LITERATURE

1. K. A. Andrianov, S. E. Yakushkina, *Vysokomolek. soed.*, **1**, issue 4 (1959).
2. K. A. Andrianov, L. M. Khanashvili, N. F. Kononenko, *Vysokomolek. soed.*, **2**, issue 5, 719 (1960).
3. Foshio Takiguchu, *Bull. Chem. Soc. Japan*, **32**, No. 6, 665 (1959).

Note: Figure translations are in progress. See original paper for figures.