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# Chemistry

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## Abstract

## Full Text

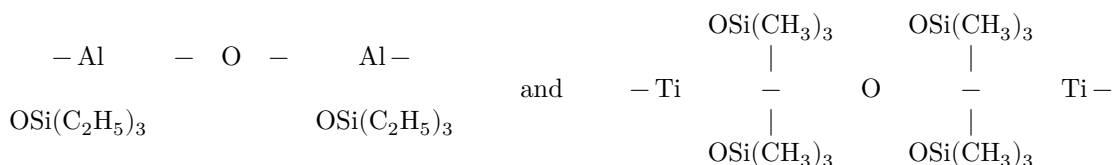
### Chemistry

Corresponding Member of the Academy of Sciences of the USSR K. A. Andrianov, A. A. Zhdanov, N. A. Kurasheva, and V. G. Dulova

## Synthesis of Polyorganosiloxanoalumoxanes and Polyorganosiloxanotitanoxanes

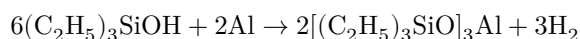
The development of the idea of edging mineral chains of molecules, built from atoms of silicon, oxygen, and metals, with organic groups has led to the synthesis of a large group of new polymers. Along with the organosilicon polymers widely described in the literature, methods are known for obtaining polyorganosiloxanes<sup>(1)</sup>, polyorganoborosiloxanes<sup>(2)</sup>, polyorganotitanosiloxanes<sup>(3)</sup>, polyorganostannosiloxanes<sup>(2)</sup>, and some other polymers. The introduction of trialkylsiloxane radicals  $R_3SiO-$  as edging groups has led to the synthesis of polymers whose molecular chains consist of aluminum and oxygen (analogously to the chains of the spatial polymer corundum), and of polymers with molecular chains of titanium and oxygen atoms (analogously to the chains of molecules of inorganic polytitanates).

In the present communication we describe general processes for the synthesis of polymers with molecular chains of the following structure:



Polymers with a molecular structure of this kind have not previously been described, although the search for routes for the synthesis of such polymers and the study of their properties are of definite interest.

As starting substances for obtaining the indicated polymers we used nonaethylalumoxytrisiloxane (a crystalline product with m.p. 159°) and dodecamethyltitanoxytetrasiloxane (a liquid with b.p. 110°/10 mm). These monomers were synthesized by us according to the following reaction schemes:



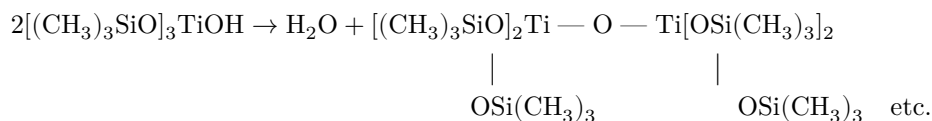
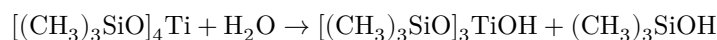


Number of moles of water per 1 mole of nonaethylalumoxytrisiloxane	Time to gelatinization of the solution, min
2.32	12960
2.80	320
3.27	100
3.73	6

From these data it is evident that, with an increase in the amount of water taken for the reaction, the time for the onset of structuring of the polymer formed is sharply shortened, since the probability of branching of the polymer molecule, as is seen from the reaction scheme given, depends on the amount of water taken for the reaction.

Dodecamethyltitanoxytetrasiloxane, heated at 50° for 3 hr with 0.5 mole of water in acetone, does not form a dimer. On distillation of the reaction product, the monomer can be isolated almost quantitatively. The introduction of acid catalysts, when the water content is more than 1 mole per 1 mole of dodecamethyltitanoxytetrasiloxane, leads to the formation of a polymer.

Hexamethyldisiloxane and trimethylsilanol were isolated as by-products of the reaction. In the initial stage of hydrolysis, polymers soluble in organic solvents are formed, but on further heating with an excess of water an insoluble polymer can be obtained. The formation in the reaction of polymeric products, hexamethyldisiloxane, and trimethylsilanol shows that dodecamethyltitanoxytetrasiloxane is hydrolyzed and converted into a polymer according to the following scheme:



The polymers obtained are soluble in benzene, toluene, chlorobenzene, and mixtures of the indicated solvents with alcohols. When a polymer solution is applied to the surface of metals, after evaporation of the solvents hard films are formed. Using the described method of framing the inorganic chains of molecules with trialkylsiloxane groups, we are currently developing methods for the synthesis of polymers whose main chain contains oxygen atoms and other elements of Groups III and IV of the periodic system.

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3. K. A. Andrianov, A. A. Zhdanov, L. M. Volkova, Proceedings of the 9th Conference on General Problems of the Chemistry and Physics of High-Molecular Compounds, Publishing House of the Academy of Sciences of the USSR, 1956, p. 45.

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

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