

**Corresponding Member of  
the Academy of Sciences  
of the USSR K. A.  
ANDRIANOV and A. A.  
ZHDANOV**

1961

SovietRxiv

---

View the original and related papers at <https://sovietrxiv.org/items/ru-196101.15657>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

## Abstract

## Full Text

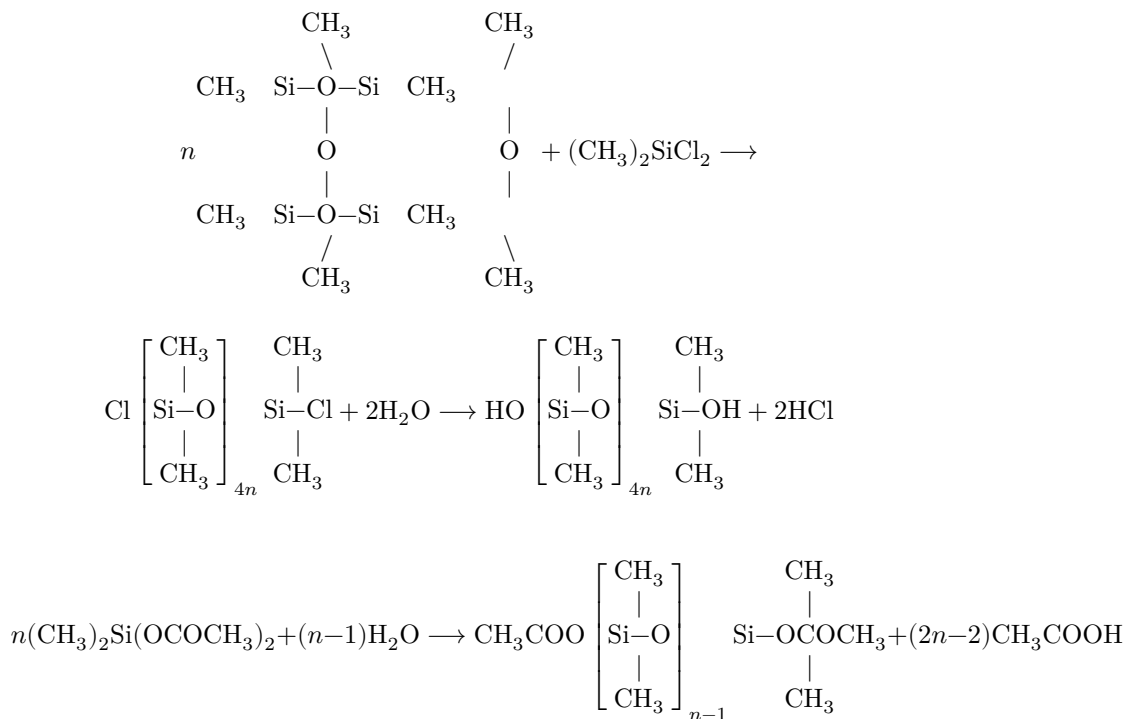
## Chemistry

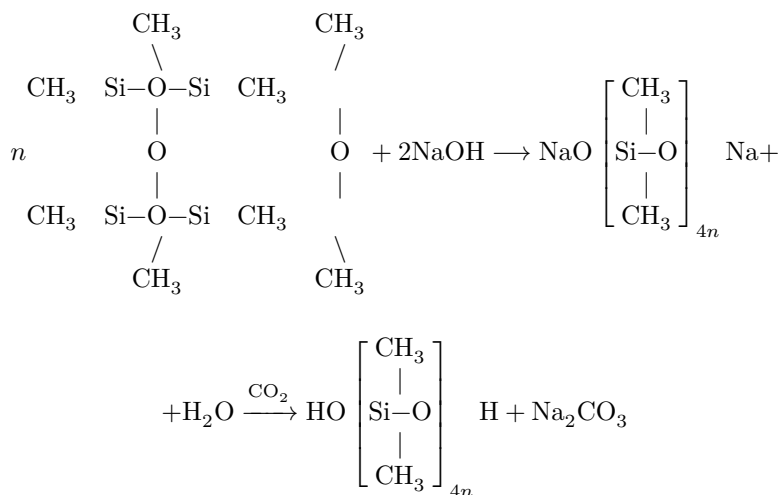
Corresponding Member of the Academy of Sciences of the USSR K. A. ANDRI-  
ANOV and A. A. ZHDANOV

# POLYCONDENSATION AS A METHOD FOR OBTAINING POLYDIALKYLSEILOXANE AND POLYALUMODIALKYLSEILOXANE ELAS- TOMERS

At the present time, among elastomers having inorganic main chains and flank-  
ing organic radicals, only polydimethylsiloxane elastomers and their various  
modifications are known, associated with some change in the nature of the or-  
ganic radicals flanking the siloxane chain.

Methods for obtaining such elastomers are based on the reaction of catalytic  
polymerization of cyclic products of hydrolysis or of individual dialkylsiloxane  
cycles with the formation of linear polymers.





All attempts to carry out the synthesis of elastomers by means of the reaction of hydrolysis and polycondensation, or heterofunctional polycondensation, of various difunctional monomers have not led to the preparation of linear high-molecular-weight compounds—elastomers. The unsuccessful attempts to obtain elastomers by the polycondensation method are explained by the development of side reactions leading to the formation not only of linear but also of cyclic products.

In the present work a new method is considered for the synthesis of polydialkylsiloxane elastomers with linear molecular chains, based on the polycondensation of difunctional oligomers with difunctional organosilicon monomers. This process is carried out in two stages. The first stage consists in obtaining oligomers by one of the known methods shown by the reactions (see above) (1-3).

In the second stage, the oligomers obtained are subjected to polycondensation or heterofunctional polycondensation with the formation of high-molecular-weight elastomers.

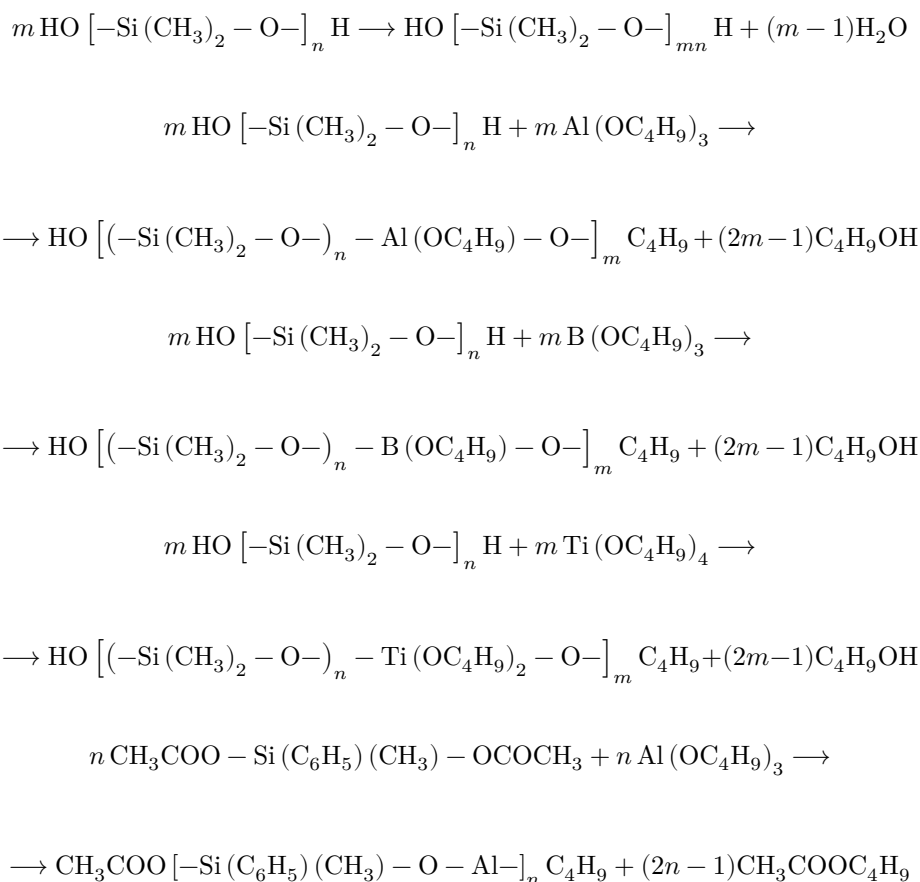
The distinctive feature of the method we describe is that, when the process is carried out in two stages, in the final stage the possibility of formation of low-molecular-weight cycles is eliminated, since the oligomers entering into the polycondensation reaction have such a degree of polymerization that, at which

secondary cyclization is no longer possible. By means of this method we obtained polydimethylsiloxane elastomers with a molecular weight of about 200,000, which upon vulcanization form rubbers with properties analogous to those of standard polydimethylsiloxane rubbers.

As our investigations have shown, by the described polycondensation method it is also possible to obtain high-molecular-weight compounds whose molecu-

lar chains contain not only silicon and oxygen atoms, but also atoms of metals. Thus, we established that  $\alpha,\omega$ -dihydroxypolydimethylsiloxanes with various degrees of polycondensation enter into reaction with aluminum butylate, tetrabutoxytitanium, or tributoxyboron, with the formation of linear polymers containing atoms of the corresponding element in the inorganic polymer chain.

Depending on the nature of the terminal functional groups in linear polydimethylsiloxane oligomers, the polycondensation process may proceed with the formation of various low-molecular-weight products. The polymer-forming reactions studied by us may be represented by the equations (see beside):

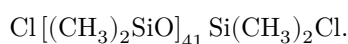


The polymers obtained by the reactions described are elastic soluble substances with molecular weights of 100,000-200,000 and are distinguished by high reactivity due to the preservation of the functional group at the metal atom. The rubbers obtained upon vulcanization of these elastomers are close in their properties to rubbers based on polydimethylsiloxanes, and in some properties surpass them.

## Experimental Part

1.  $\alpha,\omega$ -**Dichloropolydimethylsiloxanes** were obtained by the procedure described previously <sup>4</sup>. Into an autoclave were charged 326 g (1.1 mol) of octamethylcyclotetrasiloxane and 11.37 g (0.088 mol) of dimethyldichlorosilane. The reaction time was 3.5 hours at 200°. The liquid reaction products were filtered, and the volatile substances were distilled off to 200° at 4 mm Hg in the still. A total of 237 g of  $\alpha,\omega$ -dichloropolydimethylsiloxane with molecular weight 3170 (by terminal groups) was obtained.

Found, %: C 31.64; 31.43; H 8.04; 8.12; Si 36.98; 37.41; Cl 2.19; 2.22



Calculated, %: C 31.83; H 8.01; Si 37.22; Cl 2.24

By the described procedure, with variation of the ratios between octamethylcyclotetrasiloxane and dimethyldichlorosilane, oligomers were obtained

with different lengths of the siloxane chain, which were subsequently subjected to hydrolysis to convert them into  $\alpha,\omega$ -dihydroxypolydimethylsiloxanes.

2.  $\alpha,\omega$ -**Dihydroxypolydimethylsiloxanes** were obtained by the procedure described in the literature <sup>(5)</sup>. Into a flask equipped with a stirrer, dropping funnel, thermometer, and reflux condenser were charged 24.68 g (0.29 mole) of sodium bicarbonate, 125 ml of acetone, 125 ml of benzene, and 1 ml of water; into the solution heated to 50°, a solution of 237 g of the above-prepared  $\alpha,\omega$ -dichloropolydimethylsiloxane in 250 ml of benzene was added dropwise with stirring. After addition of the chloride was complete, the mixture was stirred for 2 hours at 45-50°, the precipitate was filtered off, and the solvent and volatiles were distilled from the filtrate under vacuum to a flask temperature of 200° at 4 mm Hg. This gave 212 g of  $\alpha,\omega$ -dihydroxypolydimethylsiloxane with molecular weight 8200 (from end groups, determined by Terent'ev's method).

Found, %: C 31.97; 32.21; H 8.09; 8.13; Si 37.61; 37.93;  
OH 0.43; 0.41

HO[(CH<sub>3</sub>)<sub>2</sub>SiO]<sub>110</sub>H. Calculated, %: C 32.32; H 8.16; Si 37.80;  
OH 0.42

3.  $\alpha,\omega$ -**Dihydroxypolydimethylsiloxanes from dimethyldiacetoxysilane**. 91.5 g (0.52 mole) of dimethyldiacetoxysilane was hydrolyzed with 9 g (0.5 mole) of water at 50° for 2.5 hours. Acetic acid was distilled off from the hydrolysis products to a temperature (in the vapors) of 123° at 13 mm, and 28.6 g of an oligomer having molecular weight 1660 (from end groups) was obtained.

Found, %: C 32.86; 32.98; H 8.16; 8.12;  
Si 35.43; 35.79; OCOCH<sub>3</sub> 7.13;  
6.98

CH<sub>3</sub>COO[(CH<sub>3</sub>)<sub>2</sub>SiO]<sub>20</sub>Si(CH<sub>3</sub>)<sub>2</sub>OCOCH<sub>3</sub>. Calculated, %: C 33.29; H 8.02;  
Si 35.55; OCOCH<sub>3</sub> 7.12

The product obtained was dissolved in 50 ml of ether, washed twice with 30 ml portions of water containing 1% NH<sub>4</sub>OH, and then with distilled water. After drying the organic layer and distilling off the solvent in vacuum to 72° (in the vapors) at 13 mm, 23.8 g of a viscous  $\alpha,\omega$ -dihydroxypolydimethylsiloxane was obtained, with molecular weight 2100 (from end groups).

Found, %: C 31.84; 31.65; H 8.03; 8.12; Si 37.26; 37.73;  
OH 1.68; 1.56

HO[(CH<sub>3</sub>)<sub>2</sub>SiO]<sub>28</sub>H. Calculated, %: C 32.11; H 8.18; Si 37.55;  
OH 1.62

4. **Polycondensation of  $\alpha,\omega$ -dihydroxypolydimethylsiloxane.** 75 g of  $\alpha,\omega$ -dihydroxypolydimethylsiloxane with molecular weight 23000 (viscometric) <sup>(5)</sup> was condensed at 200° in an atmosphere of pure nitrogen at a residual pressure of 2–3 mm Hg. After 12 hours, a high-molecular-weight polymer with molecular weight 200000 (viscometric) was obtained, readily soluble in benzene and toluene.
5. **Polycondensation of  $\alpha,\omega$ -dihydroxypolydimethylsiloxane with aluminum butylate.** 23.8 g of  $\alpha,\omega$ -dihydroxypolydimethylsiloxane with molecular weight 2100 was mixed with a 20% solution of 2.78 g of aluminum butylate in benzene (molecular ratio 1 : 1), the solvent was distilled off under vacuum, and the mixture was condensed in an atmosphere of pure nitrogen at 150° for 3 hours and then for 30 min at 200° under a pressure of 15 mm Hg. An elastic rubber-like product was obtained, soluble in benzene and toluene. The polymer has molecular weight 30000 (viscometric).

Found, %: C 32.77; 32.61; H 8.16; 8.23; Si 36.45;  
36.61; Al 1.31; 1.43

[(CH<sub>3</sub>)<sub>2</sub>SiO]<sub>28</sub>[Al(OC<sub>4</sub>H<sub>9</sub>)O]. Calculated, %: C 32.86; H 8.14; Si 35.87;  
Al 1.23

The polymer readily structures on storage in air, with formation of a product partially soluble in toluene.

6. **Polycondensation of  $\alpha,\omega$ -dihydroxypolydimethylsiloxane with tributoxyboron** was carried out by the procedure described in the preceding experiment. For the reaction, 20 g of  $\alpha,\omega$ -dihydroxypolydimethylsiloxane with molecular weight 2600 and 1.77 g of tributoxyboron were taken (molar ratio of oligomer to tributoxyboron

1 : 1). An elastic rubber-like product was obtained, soluble in benzene and toluene and having a molecular weight of 34,000 (viscometrically).

The polymer obtained has the property of elastic deformation under sudden loads and the property of plastic deformation under slow application of force.

Found, %: C 32.48; 32.16; H 8.21; 8.19; Si 37.06; 37.12

$[(CH_3)_2SiO]_{35}[B(OC_4H_9)O]$ . Calculated, %: C 32.97; H 8.19; Si 36.47

**7. Polycondensation of  $\alpha,\omega$ -dihydroxypolydimethylsiloxane with tetrabutoxytitanium** was carried out by the procedure described above. For the reaction, 20 g of  $\alpha,\omega$ -dihydroxypolydimethylsiloxane with molecular weight 2600 and 2.62 g of tetrabutoxytitanium were taken. A tough elastic polymer with molecular weight 27,000 was obtained, readily soluble in benzene and toluene.

Found, %: C 32.65; 32.91; H 8.03; 8.11; Si 34.47; 34.26; Ti 1.53; 2.17

$[(CH_3)_2SiO]_{35}[Ti(OC_4H_9)_2O]$ . Calculated, %: C 33.39; H 8.19; Si 35.04; Ti 1.71

**8. Polycondensation of phenylmethyldiacetoxysilane with aluminum butylate.** 47.6 g (0.2 mole) of phenylmethyldiacetoxysilane and 49.3 g (0.2 mole) of aluminum butylate were heated with stirring at 180°, distilling off the butyl acetate that separated. After 6 h, 41 g of butyl acetate had been collected in the receiver (found  $OCOCH_3$  48.17; 48.42; calculated  $OCOCH_3$  50.8). A transparent light-yellow polymer, soluble in benzene, toluene, and acetone, was obtained in the residue. The relative viscosity of a 10% solution of the polymer in toluene is 2.3.

Found, %: C 51.42; 51.14; H 6.93; 7.02; Si 10.65; 10.38; Al 9.73; 10.45

$\{(C_6H_5)(CH_3)SiOAl(OC_4H_9)O\}_n$ . Calculated, %: C 52.36; H 6.79; Si 11.13; Al 10.69

**Table 1**

Aging time, days	Tensile strength, kg/cm <sup>2</sup>	Tensile strength, kg/cm <sup>2</sup>	Relative elongation, %	Relative elongation, %	Permanent deformation, %	Permanent deformation, %
	without Al	with Al	without Al	with Al	without Al	with Al
Initial	22.1	21.9	131	140	1–2	1–2
1	25.8	35.5	95	95	1–2	1–2
7	51.4	48.9	25	75	0	0

Polydimethylsiloxane obtained in experiment 4 and polyalumodimethylsiloxane obtained in experiment 5 were used to prepare rubber mixtures of the following composition (in parts by weight): polymer 100, white carbon black U-333 40, benzoyl peroxide 3, zinc oxide 5. After milling, the mixtures were vulcanized

for 15 min in a press at 143° and a pressure of 35 kg/cm<sup>2</sup> and then for 12 h in a thermostat at 200°. The properties of the rubbers obtained as a function of aging time at 250° are given in Table 1.

Institute of Organoelement Compounds  
Academy of Sciences of the USSR

Received  
6 II 1961

## REFERENCES

1. K. A. Andrianov, V. V. Severnyi, DAN, **134**, 1347 (1960).
2. J. F. Hyde, J. Am. Chem. Soc., **75**, 2166 (1953).
3. T. Takiguchi, Bull. Chem. Soc. Japan, **32**, 556 (1959).
4. K. A. Andrianov, V. V. Severnyi, B. G. Zavin, Izv. AN SSSR, OKhN, in press.
5. A. Ya. Korolev, K. A. Andrianov, A. S. Utesheva, T. E. Vvedenskaya, DAN, **89**, 65 (1953).

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

*Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.*