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Corresponding Member of the Academy of Sciences of the USSR K. A. ANDRIANOV and V. V. SEVERNYI

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Abstract

Full Text

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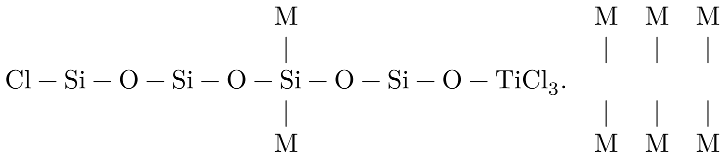
ON THE TELOMERIZATION REACTION OF ORGANOCYCLOSILOXANES

The telomerization reaction (1) is widely used for the synthesis of various organic compounds in the polymerization of unsaturated organic compounds in the presence of substances that terminate the growth of the molecular chain. As substances capable of terminating a growing polymer chain, various organic compounds are used—halogenated paraffins (2,3,4), alcohols (5), acids (6), etc. —as well as a number of organosilicon compounds containing an Si—H bond (7–9). It is of great theoretical and practical interest to carry out the telomerization reaction in order to obtain oligomers with inorganic main molecular chains bordered by organic groups. Such reactions have not been described in the literature, and the absence of organoelement monomers containing double bonds between an element and oxygen and capable of polymerization does not make it possible to use the experience of the telomerization reaction, which has been well studied in the synthesis of organic telomers.

It was previously shown by one of us that, upon the action of titanium tetrachloride on octamethylcyclotetrasiloxane, ring cleavage occurs with formation of the compound



$$\mathrm{Cl - Si - O - Si - O - \overset{\overset{M}{|}}{\underset{\underset{M}{|}}{Si}} - O - Si - O - TiCl_3.} \qquad \begin{array}{ccc} \mathrm{M} & \mathrm{M} & \mathrm{M} \\ | & | & | \\ & & \\ | & | & | \\ \mathrm{M} & \mathrm{M} & \mathrm{M} \end{array}$$

This compound was formed as a result of cleavage of the siloxane ring and addition of chlorine and the trichlorotitanium group (10).

To carry out the telomerization reaction we used rings composed of inorganic atoms, bordered by organic groups. As the cyclic compound, octamethylcyclotetrasiloxane was taken, and as the substance terminating the molecular chain, dimethyldichlorosilane. Experiments showed that dimethyldichlorosilane is not only a reagent terminating the growth of the molecular chain, but also a compound that polymerizes octamethylcyclotetrasiloxane.

In studying the reaction of octamethylcyclotetrasiloxane and dimethyldichlorosilane it was established that the ring-opening reaction proceeds at a high rate at a temperature of 200–250° in the absence of catalysts. Thus, when the reaction between octamethylcyclotetrasiloxane and dimethyldichlorosilane was carried out in a molar ratio of 2 : 1, the reaction was completely finished after only 3 hours at 250°. As a result, oligomers were obtained whose composition corresponded to compounds described by the reaction given below:

$$n(\mathrm{M_2SiO})_4 + \mathrm{M_2SiCl_2} \rightarrow \mathrm{Cl} - (-\mathrm{M_2SiO}-)_{4n} - \mathrm{M_2SiCl}.$$

Repeated experiments reproduced the results well in accordance with this reaction. As a result of the experiments carried out, about 75% of reaction products distilling up to a temperature of 260° at 3 mm were obtained, and only about 25% boiled higher. On rectification, the following were isolated: α,ω-dichlorodecamethylpentasiloxane ($n = 1$) in a yield of 16.7%, α,ω-dichlorooctadecamethylnonasiloxane ($n = 2$) in a yield of 20.0%, and α,ω-dichlorohexacosamethyltridecasiloxane ($n = 3$) in a yield of 7.7%. The physical properties of the isolated products are given in Table 1.

The formation of oligomers containing 5, 9, and 13 silicon atoms in the molecule indicates the successive addition of octamethylcyclotetrasiloxane molecules to dimethyldichlorosilane.

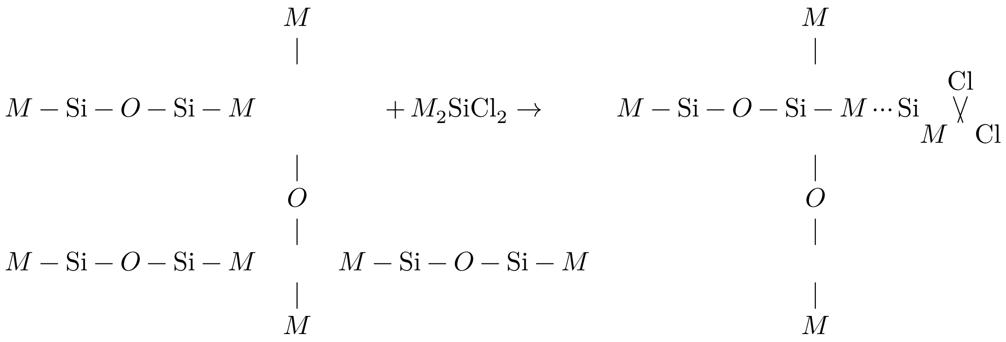
Table 1

Physical properties of telomers

Compound	b.p., °C/mm	n_D^{20}	d_4^{20}	MR, calc.	MR, found
1. $\mathrm{Cl[(CH_3)_2SiO]_4(CH_3)_2SiCl}$	220–221°*	1.4032	1.0048*	102.68	103.22
2. $\mathrm{Cl[(CH_3)_2SiO]_8(CH_3)_2SiCl}$	176–178°/3	1.4065	0.9945	179.06	178.56
3. $\mathrm{Cl[(CH_3)_2SiO]_{12}(CH_3)_2SiCl}$	246–248°/3	1.4060	0.9885	253.85	253.13

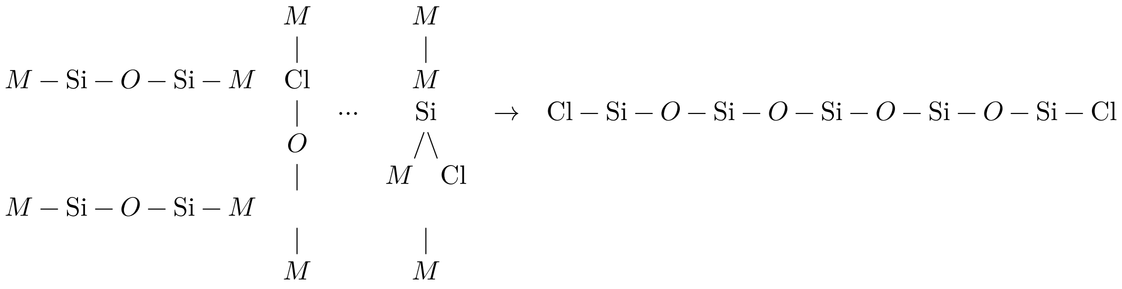
* Literature data (11): b.p. 138°/20 and d_4^{20} 1.005.

Apparently, the reaction begins with coordination of one of the oxygen atoms of octamethylcyclotetrasiloxane with the silicon atom of dimethyldichlorosilane



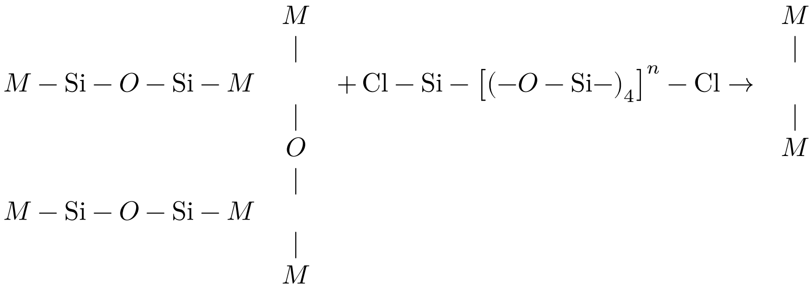
$$\begin{matrix} M-\mathrm{Si}-O-\mathrm{Si}-M & \overset{M}{|} & & & M-\mathrm{Si}-O-\mathrm{Si}-M\cdots\mathrm{Si}\overset{\mathrm{Cl}}{\underset{M\quad\mathrm{Cl}}{\lor}} \\ & \underset{|}{\overset{|}{O}} & +M_2\mathrm{SiCl}_2 \rightarrow & & \underset{|}{\overset{|}{O}} \\ M-\mathrm{Si}-O-\mathrm{Si}-M & \underset{M}{|} & M-\mathrm{Si}-O-\mathrm{Si}-M & & \underset{M}{|} \end{matrix}$$

As a result of the weakening of the Si–O bond in octamethylcyclotetrasiloxane, the strained ring is cleaved with addition of chlorine to the silicon atom and of dimethylchlorosilane to oxygen

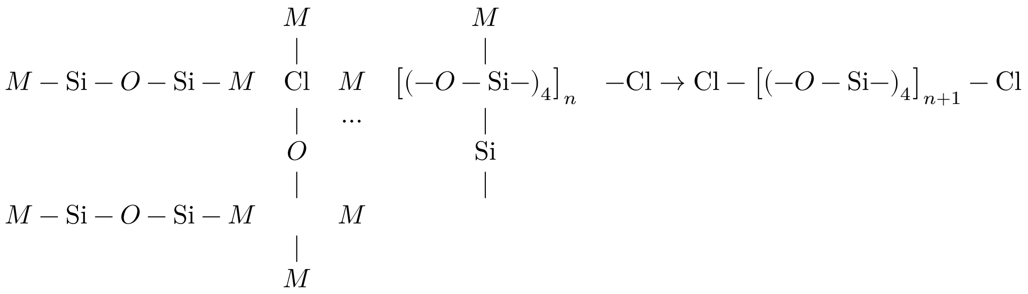


$$\begin{matrix} M-\mathrm{Si}-O-\mathrm{Si}-M & \overset{M}{\underset{\mathrm{Cl}}{|}} & & \overset{M}{\underset{M}{|}} & \\ & \overset{|}{\underset{|}{O}} & \cdots & \underset{M\quad\mathrm{Cl}}{\overset{\mathrm{Si}}{/\backslash}} & \rightarrow \mathrm{Cl}-\mathrm{Si}-O-\mathrm{Si}-O-\mathrm{Si}-O-\mathrm{Si}-O-\mathrm{Si}-\mathrm{Cl} \\ M-\mathrm{Si}-O-\mathrm{Si}-M & \underset{M}{|} & & \underset{M}{|} & \end{matrix}$$

The subsequent process of chain growth is probably associated with coordination of the terminal silicon and oxygen atoms of the cyclic product, followed by ring cleavage and formation of a linear α,ω-dichlorodimethylsiloxane according to the reaction:



$$\begin{matrix} M-\mathrm{Si}-O-\mathrm{Si}-M & \overset{M}{|} & & \overset{M}{|} \\ & \underset{|}{\overset{|}{O}} & +\mathrm{Cl}-\mathrm{Si}-\left[(-O-\mathrm{Si}-)_4\right]^n-\mathrm{Cl}\rightarrow & \underset{M}{|} \\ M-\mathrm{Si}-O-\mathrm{Si}-M & \underset{M}{|} & & \end{matrix}$$



$$\begin{array}{ccccc}
 & M & & M & \\
 & | & & | & \\
M-\mathrm{Si}-O-\mathrm{Si}-M & \mathrm{Cl} & M & \left[(-O-\mathrm{Si}-)_4\right]_n & -\mathrm{Cl}\rightarrow \mathrm{Cl}-\left[(-O-\mathrm{Si}-)_4\right]_{n+1}-\mathrm{Cl}\\
 & | & \cdots & | & \\
 & O & & \mathrm{Si} & \\
 & | & & | & \\
M-\mathrm{Si}-O-\mathrm{Si}-M & & M & & \\
 & | & & & \\
 & M & & &
\end{array}$$

At the present time this reaction is being studied using other inorganic rings bearing organic groups as examples, and other reagents that cleave the molecular chain are also being investigated.

Experimental Part

For the syntheses, octamethylcyclotetrasiloxane with b.p. 174–176° (mol. wt. 296.6) and dimethyldichlorosilane with Cl content 55.7% (mol. wt. 129.08) were used.

Reaction of octamethylcyclotetrasiloxane with dimethyldichlorosilane. Into a dry stainless-steel autoclave of 0.5 l capacity there was charged a mixture of 55.7 g (0.435 mole) of dimethyldichlorosilane and 258 g (0.87 mole) of octamethylcyclotetrasiloxane. In the course of 1 hour the apparatus was heated to 250° and kept at this temperature for 3 hours. At the beginning of heating the pressure in the apparatus rose to 8–10 atm, and then fell to 2–3 atm. After cooling the apparatus, in one of the experiments 293 g of product were discharged; this product was distilled from a column with a packed dephlegmator, first at atmospheric pressure and then in vacuum at 3 mm. The experimental data are given in Table 2.

Table 2

Fraction No.	B.p., °C/mm	Number of Si atoms	Chlorine content, calc.	Chlorine content, found*	Yield, g	Yield, % of mixture
1	up to 200°	–	–	–	32.9	11.2
2	200–220°	5	16.68	16.48	49.4	16.7
3	130–140°/3	–	–	13.95	6.0	2.0
4	140–155°/3	–	–	12.65	16.0	5.5

Fraction No.	B.p., °C/mm	Number of Si atoms	Chlorine content, calc.	Chlorine content, found*	Yield, g	Yield, % of mixture
5	155–170°/3	–	–	11.39	9.4	3.2
6	170–210°/3	9	9.83	9.69	58.0	20.0
7	210–220°/3	–	–	8.27	8.9	3.0
8	220–230°/3	–	–	7.41	9.2	3.1
9	230–260°/3	13	6.96	6.81	22.6	7.7
Losses					4.9	1.9
Total					293	100

* Average data from 2 determinations are given.

From fractions Nos. 2, 6, 9 (Table 2), by double distillation, pure products of composition Cl–$[Si(CH_3)_2O]$ $Si(CH_3)_2$–Cl were isolated, where $n = 4, 8$, and 12; their physical properties are given in Table 1, and the analytical data in Table 3.

Table 3

$$Cl[(CH_3)_2SiO]_n - (CH_3)_2SiCl$$

Compound	B.p., °C/mm	Cl, % calc.	Cl, % found	H, % calc.	H, % found	C, % calc.	C, % found	Si, % calc.	Si, % found
$Cl[(CH_3)_2SiO]_4(CH_3)_2SiCl$	220–221°	16.68	16.58	7.1	7.00	28.21	28.67	32.96	33.30
$Cl[(CH_3)_2SiO]_4(CH_3)_2SiCl$	220–221°	16.68	16.43	7.1	7.09	28.21	28.67	32.96	33.36
$Cl[(CH_3)_2SiO]_8(CH_3)_2SiCl$	176–178°/3	9.83	9.49	7.53	7.38	29.93	29.82	34.97	34.98
$Cl[(CH_3)_2SiO]_8(CH_3)_2SiCl$	176–178°/3	9.83	9.45	7.53	7.26	29.93	29.66	34.97	35.24
$Cl[(CH_3)_2SiO]_{12}(CH_3)_2SiCl$	246–248°/3	6.96	6.91	7.71	7.65	30.65	30.54	35.80	35.90
$Cl[(CH_3)_2SiO]_{12}(CH_3)_2SiCl$	246–248°/3	6.96	6.81	7.71	7.62	30.65	30.64	35.80	35.95

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

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