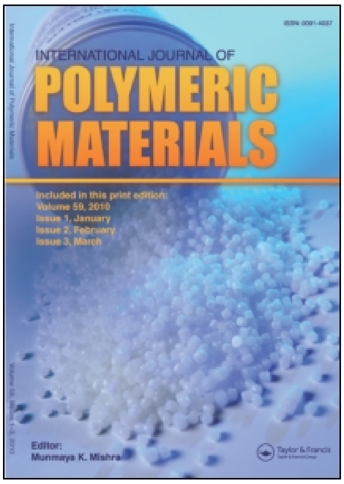

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Anionic Co-Oligomerization of Organic Cyclosiloxanes with 1, 3-Bis(3-Glycydoxypropyl) Tetramethyldisiloxanes and Investigation of Co-Oligomerization Products

L. M. Khananashvili[a]; N. I. Tsomaia[a]; D. U. Murachashvili[a]; D. A. Girdvliani[a]; M. G. Kharchkhadse[a]; R. Sh. Tkeshelashvili[a]
[a] Tbilisi State University, Tbilisi, Republic of Georgia

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Anionic Co-Oligomerization of Organic Cyclosiloxanes with 1,3-Bis(3-Glycydoxypropyl) Tetramethyldisiloxanes and Investigation of Co-Oligomerization Products

L. M. KHANANASHVILI, N. I. TSOMAIA, D. U. MURACHASHVILI,
D. A. GIRDVLIANI, M. G. KHARCHKHADSE
and R. SH. TKESHELASHVILI

Tbilisi State University, Chavchavadze ave. 3,
380028, Tbilisi, Republic of Georgia

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The co-oligomerisation of organic cyclosiloxanes with 1,3-bis(3-glycydoxypropyl) tetramethyl disiloxanes in the presence of dimethylformamide, initiated by the tetramethylammonium silanolate and co-oligomerisation reaction kinetics was investigated.

We found that the interaction of α, ω bis(3-glycydoxypropyl)methylvinylsiloxane with acetic acid proceeds through α- and β- junction reaction. The interaction of the same product with pyperazin gives only the products of β-junction.

Keywords: Organic cyclosiloxanes; 1,3-bis(3-glycydoxypropyl)tetramethyldisiloxanes; dimethylformamide; pyperazin; acetic acid

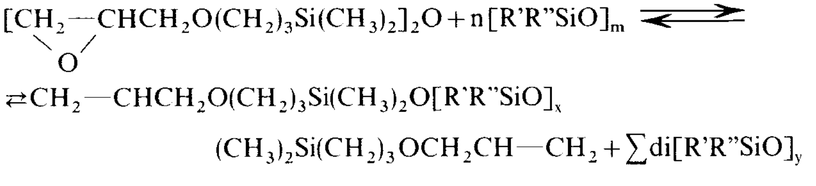
INTRODUCTION

Development of synthesis methods of oligoorganicsiloxanes with carbofunctional groups at the ends of molecules is of great scientific interest, because of the possibility of their utilization in various techniques for obtaining polymers with organic-inorganic chains of molecules [1–4].

The high reactivity of silicoorganic oligomers with epoxy groups at the ends is the reason for the great potential this group of silicon containing organic compounds has in synthesis of novel polymers. Therefore, the development of new methods of obtaining the α, ω-bis(3-glycydoxypropyl)oligoorganicsiloxanes is very timely and attractive.

The main method of obtaining of such oligomers is co-oligomerization of organic cyclosiloxanes (OCS) with 1,3-bis(3-glycydoxypropyl)tetramethyl disiloxanes (GTMDS) [5] in the presence of nucleofilic initiators: potassium- [6], tetramethylamonium silanolate [7,8].

The reaction proceeds by the following scheme:



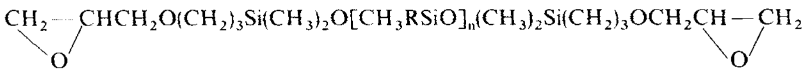
$$[\underset{\diagdown O \diagup}{CH_2-CH}CH_2O(CH_2)_3Si(CH_3)_2]_2O + n[R'R''SiO]_m \rightleftarrows CH_2-CHCH_2O(CH_2)_3Si(CH_3)_2O[R'R''SiO]_x (CH_3)_2Si(CH_2)_3OCH_2CH-CH_2 + \sum di[R'R''SiO]_y$$

The co-oligomerisation of GTMDS with 1,3,5-trimethyl-1,3,5-trivinyl (D_3^{vin}), cis- and trans-1,3,5-trimethyl-1,3,5-triphenyl (A_3), 1,1,3,3,5,5-pentamethyl-5-naphthyl-(D_2H) cyclotrisiloxanes, 1,3,5,7-tetramethyl-1,3,5,7-tetravinyl (D_4^{vin}), and 1,1,3,3,5,5,7,-heptamethyl-7-naphthyl-(D_3H) cyclotetrasiloxanes in the presence of TMAS was studied.

The method of gel-permeation chromatography showed [8], that in anionic co-oligomerisation of GTMDS with octamethylcyclotetrasiloxane in the presence of polar addition of DMFA reaction proceeds quicker, then without the polar addition.

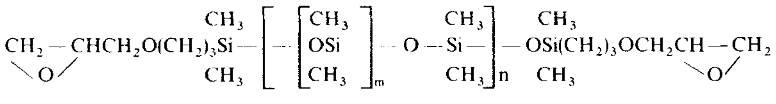
In the present paper in all reactions of co-oligomerisation a polar addition of DMFA (1 mass %) was used.

The organosiloxanes of following structure were synthesized:



$$\underset{\diagdown O \diagup}{CH_2-CH}CH_2O(CH_2)_3Si(CH_3)_2O[CH_3RSiO]_n(CH_3)_2Si(CH_2)_3OCH_2\underset{\diagdown O \diagup}{CH-CH_2}$$

$R=CH_2=CH-$, $n = 6$(I), $n = 8$(II); $R = C_6H_5$, $n = 6$ cis — A_3 (III) trans — A_3(IV);



$$\underset{\diagdown O \diagup}{CH_2-CH}CH_2O(CH_2)_3\overset{CH_3}{\underset{CH_3}{Si}}-\left[-\left[\begin{matrix}CH_3\\ OSi\\ CH_3\end{matrix}\right]_m-O-\overset{CH_3}{\underset{CH_3}{Si}}-\right]_n-\overset{CH_3}{\underset{CH_3}{OSi}}(CH_2)_3OCH_2\underset{\diagdown O \diagup}{CH-CH_2}$$

$m = 2$, $n = 2$(V); $m = 3$, $n = 2$ (VI).

EXPERIMENTAL

In co-oligomerisation reactions we used chromatographically pure 1,3-bis(3-glycydoxypropyl)tetramethyldisiloxane, D_3^{vin}, D_4^{vin}, cis- and trans-A_3, D_2H, and D_3H.

Co-oligomerisation was carried out at the temperature of 80°C, in argon, with addition of 1 mass % of DMFA, and stirring until the equilibrium was achieved.

After the reaction was finished, the obtained products were filtered and kept at 140–150°C for 2–3 hours. To extract the low-molecular cyclosiloxanes, the reaction mixture was cooled, and then vacuumed at the temperature of 130°C and pressure 133Pa.

The reaction process was controlled by following the content of organocyclosiloxanes in the reaction mixture by the method of gas-liquid chromatography using the chromatograph LXM-80 (model 2). The tube was 3000 * 4mm, nozzle – chromosorb W, phase – silicon organic polymer SE-30, carrier gas-helium, and by the change of 1% solution of reaction mixture in toluene at the temperature 20°C, which was measured by the Ubelode viscosimeter.

α,ω-bis[3-(2-hydroxy-3-acetoxy)propyl] oligo methyl vinyl siloxane (VII,VIII)

8.78g (0.01 mole) of compound I, 4.80g (0.04 mole) acetic acid, and TMAS (10 mole % of epoxy groups of compound I) was loaded in a four neck flask. After the reaction was finished, the excess of acetic acid was extracted on rotor extractor. 9.481 g (95%) of compounds VII and VIII were obtained.

Experimental % C = 45,69; H = 7.82; Si = 22.44; OH = 3.41.
calculated % C = 45,55; H = 7.70; Si = 22.71; OH = 3.66.

α,ω-bis[3-(2-hydroxy-3-piperazinpropoxy)propyl]oligo methyl vinyl siloxane (IX).

8.78 g (0.01 mole) of compound I, 6.88 g (0.08 mole) piperazine was loaded in four neck flask. The reaction mixture was mixed with dry dioxane (30ml) at the temperature 60°C. After the reaction was finished the mixture of hexane and toluene (mass ratio 1:1) was added to the obtained product. The flask was cooled by liquid nitrogen and then heated by warm water (procedure was repeated several times). The excess of piperazine was extracted by filtration and then reaction product was vacuumed. 9.66 g (92%) of compound IX was obtained.

Experimental %C = 48.00; H = 8.57; Si = 21.33; N = 5.33; OH = 3.23.
Calculated %C = 48.85; H = 8.5; Si = 21.5; N = 5.38; OH = 3.35.

The molecular mass of obtained products was measured by ebullioscopic method and by the concentration of epoxy groups at the ends of molecules.

The PMR spectra of compounds were obtained on spectrometer Bruker WP-250 in $CDCl_3$

The IR spectra of compounds were obtained on spectrofotometer UR-20.

RESULTS AND DISCUSSION

The value of η_{sp} in the process of co-oligomerization of 1,3-bis(3-glycydoxypropyl)tetramethyl disiloxane with organic cyclosiloxanes, initiated by TMAS in the presence of DMFA, passes through a maximum (Fig. 1) Directly after the addition of TMAS the growth of η_{sp} begins, achieving it's maximal value, and then decreasing till the equilibrium state is reached.

Figure 1 shows, that when the constant expenditure of organic cyclosiloxanes is achieved, the molecular masses of produced oligomers are higher than at equilibrium. This fact shows, that the reacting ability of 1,3-bis(3-glycydoxypropyl)tetramethyl disiloxane is lower, than that of organic cyclosiloxanes.

The decrease of η_{sp} after reaching maximum, indicates the decrease of molecular masses of reaction products. As the contents of cyclic products are not changed, the observed decrease of molecular masses of reaction products is due to the decrease of weight average of

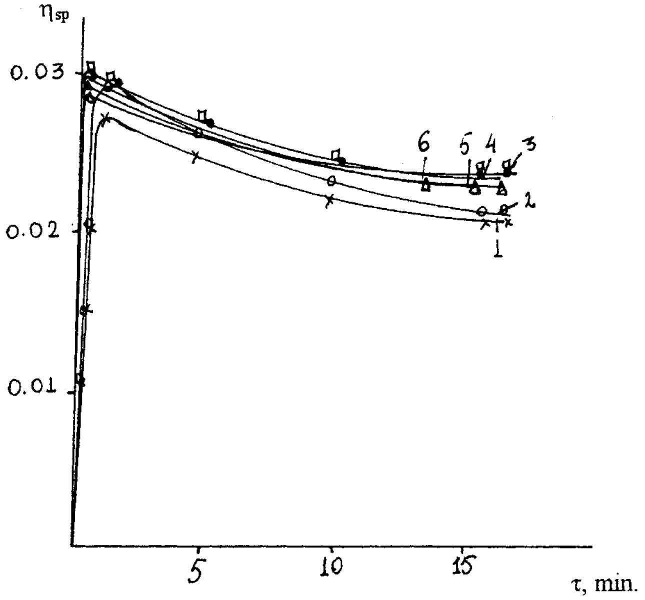


FIGURE 1 Time dependence of specific viscosity in the reaction of co-oligomerization of GTMDS with D_4^{vin} (1), D_3^{vin} (2), D_2H (3), D_3H (4), cis-A_3(5), trans-A_3 (6), in the presence of TMAS with addition of DMFA.

molecular masses, while their number average is preserved due to the reaction of 1,3-bis(3-glycydoxypropyl)tetramethyl disiloxane with the produced silicon chains.

The chromatography method investigation of co-oligomerization mixture during the reaction shows, that the conversion of organocyclic siloxanes reaches 92–94% shortly after 10–30 min. from the beginning of process (Fig. 2), and then has a constant value during the whole process. This fact shows that the reaction achieves equilibrium condition relative to organic cyclosiloxanes. The velocity of expenditure of organic cyclosiloxanes is described by the linear equations depending on the current concentration.

Table I shows, that organocyclic ring of D_3^{vin} opens 1.19 times quicker then D_4^{vin}; D_3H is 1.23 times quicker than D_3^{vin}; D_2H is 1.25 times higher than D_3H; cis- and trans-A_3 are 2.0 and 2.1 times quicker than D_2H. High co-oligomerization rates for cis- and trans-A_3, D_2H and D_3H is caused by the negative inductive effect of phenyl and naphthyl groups.

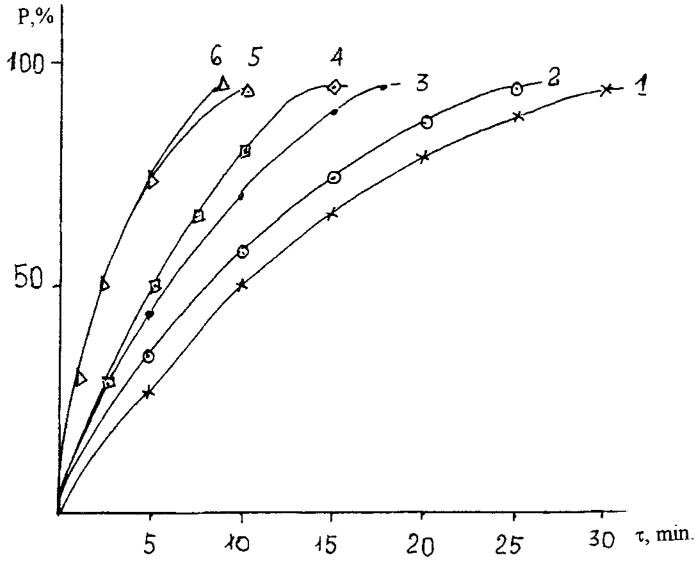


FIGURE 2 Time dependence of conversion in the reaction of co-oligomerization of GTMDS with D_4^{vin} (1), D_3^{vin} (2), D_2H (3), D_3H (4), cis- A_3 (5), trans- A_3 (6), in the presence of TMAS with addition of DMFA.

Decreasing values of reaction rate constants: cis-A_3 > trans-A_3 > D_2H > D_3H cannot be explained solidly by steric effect of phenyl and naphthyl groups.

After splitting of siloxane bond in TMAS in the process of co-oligomerization of GTMDS with cis and trans-A_3, D_2H, D_3H, D_3^{vin}, D_4^{vin} with initiator TMAS and in the presence of DMFA the ion pairs are formed. In the first case cis-and trans-A_3 are forming ion pairs with dimethyl phenyl methylnaphthyl and methylvinylsiloxane groups at the ends of growing chains. The reaction ability of the first pair is lower (inductive and stearic effects) then of the others.

The decrease of reaction constants for D_3^{vin}, D_4^{vin} is due to the positive I-effect of vinyl groups with Si—O—Si and as a result the deactivation of all bonds in respect to nucleophilic reagents takes place.

The structure of synthesized oligomers I–IV were determined by their molecular weights, content of epoxy groups (see table), IR and PMR (^1H and ^{13}C) spectroscopy.

TABLE I Synthesis conditions, characteristics and reaction rate constants of compounds I–VI

Compound N	*GTMDS* g.*	*OCS,*	*OCS, g.*	*Time of reaction, h*	η_{sp}	*Molecular mass***	*Contents of epoxy groups, %*	*Reaction rate cons., k, min^{-1}*	*yelled %*
I	3.62	D_4	6.88	16	0.022	1300	8.65	$9.2* \ 10^{-2}$	90
II	3.62	D_3	5.16	16	0.021	1250	7.81	$9.76*10^{-2}$	91
III	3.62	cis-A_3	8.16	10	0.024	1300	7.11	$3* \ 10^{-1}$	95
IV	3.62	trans-A_3	8.16	10	0.023	1200	7.01	$3.2* \ 10^{-1}$	96
V	3.62	D_2H	6.68	10	0.022	1200	7.85	$1.5* \ 10^{-1}$	94
VI	3.62	D_3H	8.16	12	0.024	1390	6.77	$1.2* \ 10^{-1}$	92

*In co-oligomerization reactions to 0.01 mole GTMDS was added 0.02 mole OCS.
**molecular mass has been determined by ebullioscopic method.

In the infrared spectra of oligomers I–IV the characteristic adsorption bands of oxyran rings in the range of 915, 3050–3070 and 4550 cm^{-1} are present.

The bands at 1585 and 1480 cm^{-1} indicate the presence of C—C bonds of aromatic rings. The bands at 690–705 cm^{-1} also indicates the aromatic rings. The weak bands at 1680–1945 cm^{-1} indicate the overtones.

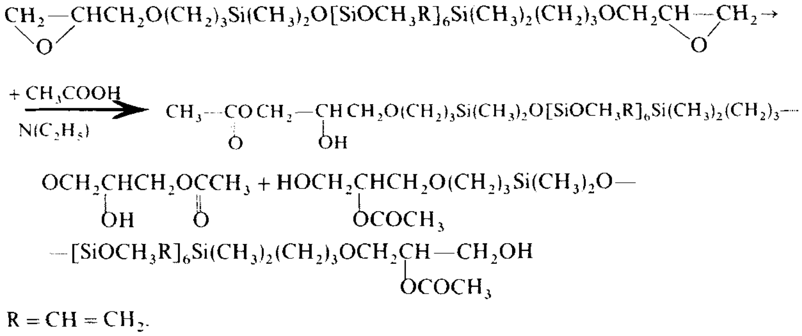
The resonance signals of fields at 6.9–7.1 md (the aromatic rings) can be detected in PMR spectra of compounds III and IV. The signals at 0.65 (V) and 1.17 md (V) belong to the Si—CH_3 groups with naphtyl subsitutes, and the signals with chemical shift 0.22 (V) and 0.39 md (VI) belongs to the Si—CH_3 groups adjacent to naphthyl groups. The signals at 0.42 (V), 0.27 and 0.57 md (VI) belong to the most remote Si—CH_3 groups.

Tree resonance signals at the signals at 0.9, 1.1 and 1.5 md (V,VI) are also present in the PMR^{13}C spectra.

The weak signal with chemical shift at 136.3 (V) and 137.2 md (VI) belongs to Si—C bond.

To investigate the reacting ability of synthesized oligomeres and to get oligoorganic compounds with carbofunctional groups at the ends of molecules we carried out the interaction of compound I with acetic acid and piperazin.

The interaction between compound I with acetic acid in the presence of TEA proceeds by the reactions of α- and β-jointing (see scheme).



$$\underset{\diagdown O \diagup}{CH_2-CH}CH_2O(CH_2)_3Si(CH_3)_2O[SiOCH_3R]_6Si(CH_3)_2(CH_2)_3OCH_2\underset{\diagdown O \diagup}{CH-CH_2} \rightarrow$$

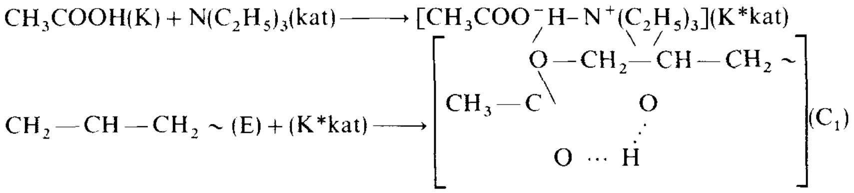
$$\xrightarrow[N(C_2H_5)]{+CH_3COOH} CH_3-\underset{\overset{\|}{O}}{C}OCH_2-\underset{\overset{|}{OH}}{C}HCH_2O(CH_2)_3Si(CH_3)_2O[SiOCH_3R]_6Si(CH_3)_2(CH_2)_3-$$

$$OCH_2\underset{\overset{|}{OH}}{C}HCH_2O\underset{\overset{\|}{O}}{C}CH_3 + HOCH_2\underset{\overset{|}{OCOCH_3}}{C}HCH_2O(CH_2)_3Si(CH_3)_2O-$$

$$-[SiOCH_3R]_6Si(CH_3)_2(CH_2)_3OCH_2\underset{\overset{|}{OCOCH_3}}{C}H-CH_2OH$$

$R = CH = CH_2$.

As we can see from the scheme, the epoxy groups at the ends of molecules transform to hydroxyl – ester groups. Seven signals in area 65–75 md in PMR spectra of compounds VII and VIII belongs to these groups. We were unable to separate the compounds VII and VIII. The mechanism of interaction of compound I with acetic acid in the presence of TEA involves two parallel reactions. The result of first reaction is a complex acid-amine-epoxy group compound (1) and the second reaction of the product gives ionic-adduct of amine with epoxy group (2).



$$CH_3COOH(K) + N(C_2H_5)_3(kat) \longrightarrow [CH_3COO^-H-N^+(C_2H_5)_3](K^*kat)$$

$$CH_2-CH-CH_2 \sim (E) + (K^*kat) \longrightarrow \left[\begin{array}{c} O-CH_2-CH-CH_2\sim \\ CH_3-C \qquad\quad O \\ O \cdots H \end{array}\right] (C_1)$$

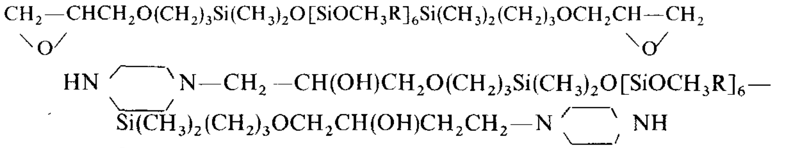
$$(C1) \longrightarrow CH_3COOCH_2CH(OH)CH_2\sim + (kat)$$

$$(E) + (kat) \longrightarrow (C_2H_5)N^+ \, CH_2CH(OH)CH_2\sim$$

$$(C) + (K) \longrightarrow CH_3COO^-(C_2H_5)N^+CH_2CH(OH)CH_2\sim \quad (C_2)$$

$$(C_2) \longrightarrow (Pr) + (kat)$$

The interaction between compound I and piperazin proceeds mainly by the reaction of α-junction by following scheme:



$R = CH = CH_2$

The signals of C(1–3) at 52.4, 69.7 and 74.1 md in PMR spectra of compound IX prove that compound I has the proposed structure.

The signals of epoxy ring at 4550, 3060 and 915 cm^{-1} were not detected in infrared spectra of compounds (VII–IX), while the detected intensive adsorption stripes at 3400^{-1}, shows the presence of hydroxyl group. Adsorption bands at 1740 cm^{-1} (VII, VIII) show the presence of carbonyl groups.

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