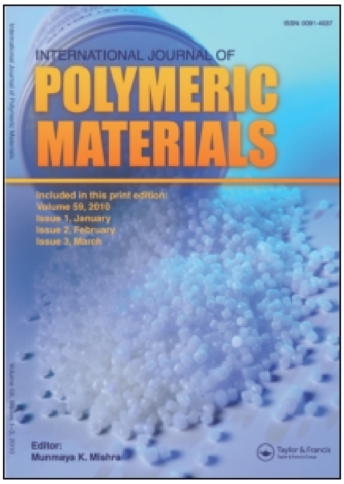

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Co-Oligomerization of Thienylcontaining Organic Cyclosiloxanes with 1,3-bis-(3-glycydoxypropyl)tetramethyldisiloxanes

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Co-Oligomerization of Thienylcontaining Organic Cyclosiloxanes with 1,3-bis-(3-glycydoxypropyl)tetramethyldisiloxanes

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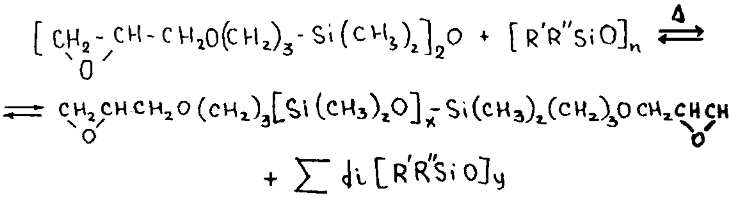
The co-oligomerization of thienylcontaining organic cyclosiloxanes with 1,3-bis(3-glycydoxypropyl)tetramethyldisiloxanes initiated by the siloxane of tetramethilamonium is studied. It is found out, that the velocity of expenditure of thienylcontaining organocyclosiloxanes is described by the linear equations depending on its instant concentration. The constants of velocity of expenditure of organocyclosiloxanes is calculated and is shown, that they depend on the concentration of 1,3-bis(3-glycydoxypropyl)tetramethyldisiloxanes in the reaction mixture. The velocity limitation is reached, when the Si—O—Si bound in 1,3-bis(3-glycydoxypropyl)tetramethyldisiloxanes is splitted. Using the method of gel permeable chromatography it is shown, that in the presence of polar admixture (dimethilphormamide) the system reaches the equilibrium much faster, producing the oligomeres of given molecular mass.

KEY WORDS Co-oligomerization, thienyl-cyclosiloxanes, glycydoxypropyl-tetramethyldisiloxanes.

INTRODUCTION

The investigation of methods of synthesis of oligoorganocyclosiloxanes with carbonfunctional groups bounded with silicon atom is of great interest and is widely investigated by many scientists. This interest is due to the fact, that these compounds can be used to obtain the block co-polymeres, which can be used in different fields of technics.[1-3]

Big reacting ability of siliconorganic compounds with epoxy groups at the ends is the reason of great interest of investigators, and namely, to the oligomeres α,ω-bis(3-glycydoxypropyl)diorganodisiloxanes. The main method of obtaining of such oligomeres is co-oligomerization of organocyclosiloxanes with 1,3-bis(3-glycydoxypropyl)tetramethyl-disiloxanes (I) in the presence of nucleophilic initiator—silanolate of tetramethylamonium (II).[4]



$$[\underset{\diagdown O \diagup}{CH_2-CH}-CH_2O(CH_2)_3-Si(CH_3)_2]_2O + [R'R''SiO]_n \xrightleftharpoons{\Delta}$$

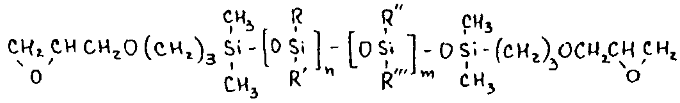
$$\rightleftharpoons \underset{\diagdown O \diagup}{CH_2CH}CH_2O(CH_2)_3[Si(CH_3)_2O]_x-Si(CH_3)_2(CH_2)_3OCH_2\underset{\diagdown O \diagup}{CHCH_2} +$$

$$+ \sum d_i[R'R''SiO]_y$$

The kinetics of anionic co-polymerization of cyclosiloxanes containing dimethyl, methylphenyl and triftorpropyl groups to the silicon atoms are described in References 5–7. The investigations searching for the possibility to improve the properties of polyorganic siloxanes by the change of part of alkyl- and arysiloxane pieces by other organic siloxane pieces are also of great interest. In particular the synthesis of organosiloxane oligomeres, containing thienyl group bounded to silicon atom, together with organic radicals, is very interesting.[8]

In the present paper we have investigated the influence of concentration of initiator (II) and dimethylformamid (DMFA) used as aproton addition, on the content of products and the speed of reaction of co-oligomerization (I) with 1,3,5-trimethyl-1,3-divinyl-5-thienyl (D_2D^{Th})cyclotrisiloxanes, and also 1,3,5,7-tetramethyl-1,3,5-trivinyl-7-thienyl-($D_3^{vin}D^{Th}$), 1,1,3,3,5,7-hexamethyl-5,7-dithienyl($D_2D_2^{Th}$) and 1,3,5,7-tetramethyl-1,3,5,7-tetrathienyl(D_4^{Th})cyclotetrasiloxanes.

The organosiloxanes of following structure were synthesised:



$$\underset{\diagdown O \diagup}{CH_2CH}CH_2O(CH_2)_3\underset{CH_3}{\overset{CH_3}{Si}}-[O\underset{R'}{\overset{R}{Si}}]_n-[O\underset{R'''}{\overset{R''}{Si}}]_m-O\underset{CH_3}{\overset{CH_3}{Si}}-(CH_2)_3OCH_2\underset{\diagdown O \diagup}{CHCH_2}$$

n = 4, m = 2, R = R″ = Me, R′ = Vin, R‴ = Th (III, III′)

n = 8, m = 2, R = R″ = Me, R′ = Vin, R‴ = Th (IV, IV′)

n = 4, m = 3, R = R″ = Me, R′ = Vin, R‴ = Th (V, V′)

n = 8, m = 3, R = R″ = Me, R′ = Vin, R‴ = Th (VI, VI′)

n = 8, m = 1, R = R′ = R″ = Me, R‴ = Th (VII, VII′)

n = 16, m = 1, R = R′ = R″ = Me, R‴ = Th (VIII, VIII′)

n = 16, m = 0, R = Me, R′ = Th (IX, IX′)

n = 32, m = 0, R = Me, R′ = Th (X, X′)

The oligomeres III′–X′ were obtained in the presence of 1 mole % DMFA.

EXPERIMENTAL

Co-polymerization was held at the temperature 80°C, in argon surround, by the thermostation of reaction mixture, containing (I) and $D_2^{vin}D^{Th}$, $D_3^{vin}D^{Th}$, D_2D^{Th} and D_4^{Th} correspondingly, and also initiator (II), by the stirring till the equilibrium was achieved.

After the reaction was finished, the obtained products were filtered and warmed till 140–150°C, during 2–3 hours. To extract the lowmolecular cyclosiloxanes, the reaction mixture was cooled, and then vacuumed at the temperature 130°C and pressure 266 Pa.

The reaction process was controlled by the change of content of thienylcontaining organosiloxanes in the reaction mixture by the method of GC using the chromatograph LXM-80 (model 2). The tube was 3000 × 4 mm, nozzle-chromosorbe W, phase 5 mass %, SE-30 (gas carrier was helium), and by the change of 1% solution of reaction mixture in toluol at temperature 20°C, which was measured by the viscosimeter of Ubbelode.

The oligomeric products were investigated by the method of gas vapour chromatography (GVC) on liquid chromatograph "Knauer" (the lichrosorb tube was Si-60 and Si-300, the solvent was methilethilketon (MEK) (1 ml/min), and detector was the differential refractometer $c = 0.02$ g/min).

RESULTS AND DISCUSSIONS

When the concentration of initiator (II) is less than 5×10^{-2} mole/l, the co-oligomerization of compound (I) with thienylorganocyclosiloxanes proceeds slowly and the final conversion with respect to cyclosiloxanes is lower than of the equilibrium one ($P_{eq} = 95$–96%). That's why the further investigation of reaction was held for the concentration of initiator (II) equal to 5×10^{-2} mole/l.

In the process of co-oligomerization of thienylorganocyclosiloxanes with compound (I), incited by (II), the conversion with respect to organocyclosiloxanes reaches 90–94% after 30–60 min (Figure 1a). At the same time the maximum value of η_{sp} is achieved (Figure 3a), which is preserved during the 10–12 hours, and then decreases till the constant value. The velocity of expenditure of $D_2^{vin}D^{Th}$, $D_3^{vin}D^{Th}$, D_2D^{Th} and D_4^{Th} is described by the linear equations depending on its current concentration (Figure 1b, Table I).

The constants of velocity of co-oligomerization of thienylcontaining organosiloxanes with compound (I), increases according to the following scheme: $D_3^{vin}D^{Th} < D_2^{vin}D^{Th} < D_2D_2^{Th}$. The higher values of velocities of co-oligomerization of D_4^{Th} and $D_2D_2^{Th}$ in comparison with $D_2D_4^{Th}$ and $D_3^{vin}D^{Th}$ can be explained by the difference in number of thienyl-groups in these compounds. During the co-polymerization of compound (I) with $D_2^{vin}D^{Th}$ and $D_3^{vin}D^{Th}$, incited by (II), the ionic pairs are produced, when silicon bounds of cyclosyloxanes are splitted by the initiator.

The epoxigroups of compound (I) can act as aproton ester groups, resulting the improvement of activity of initiator (II). The comparison of constants of velocities for oligomeres III–X and III′–X′ shows, that they depend on partial content of initial

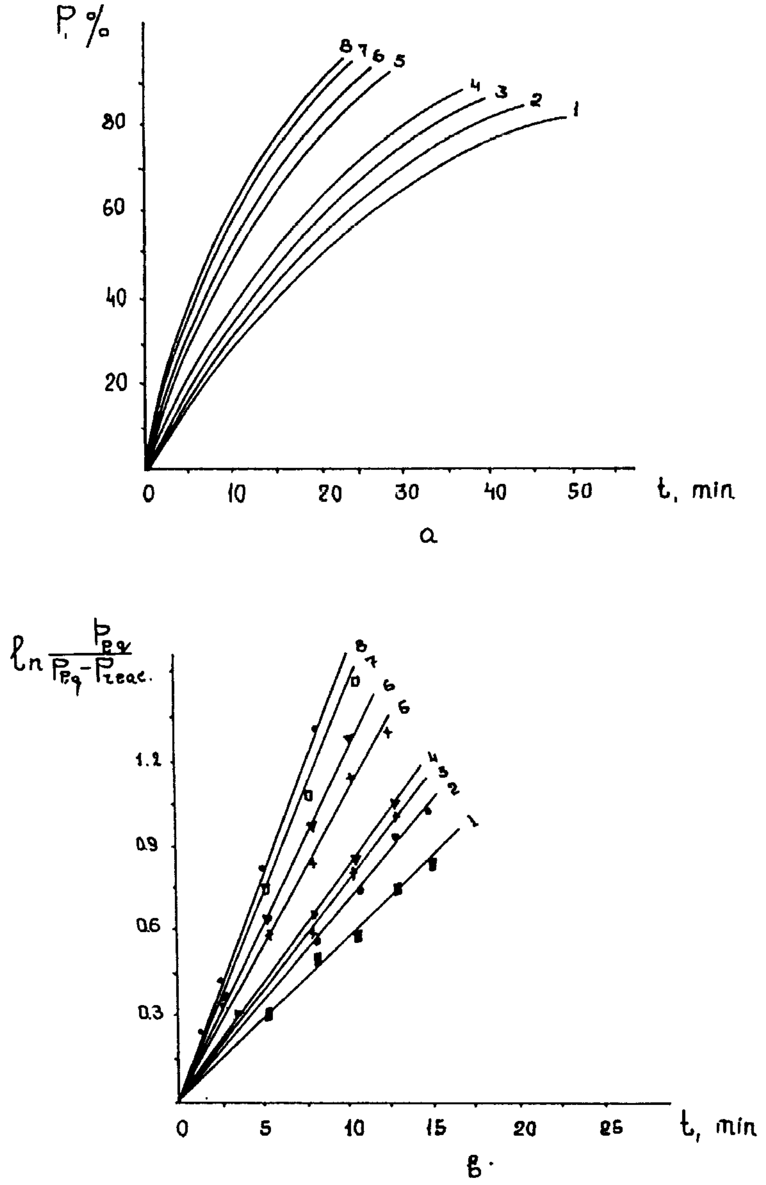


FIGURE 1 The dependence of conversion (a) and ln $P_{eq}/P_{eq} - P_{reac}$ (b) of siloxanes from the time of co-oligomerization of compound (I) with $D_3^{vin}D^{Th}$ (1, 2), $D_2^{vin}D^{Th}$ (3, 4), D_2D^{Th} (5, 6), D_4^{Th} (7, 8) in the rate 1:4 and 1:8 initiated by the compound (II) without an addition of DMFA.

reagents, and so, on concentration of compound (I). This fact proves, that the epoxigroups improve the activity of initiator (II).

The activity of initiator is improved even more in the presence of DMFA. That's why the co-oligomerization of thienilorganocyclosiloxanes with compound (I), incited by the compound (II), in the presence of 1 mass % of DMFA, proceeds much more quicker.

TABLE I

The conditions of synthesis, physical and chemical properties of oligosiloxanes and kinetic constants of the reaction of co-oligomerization

No	DMFA mass %	TIME hours	η_{sp}	M= $[\eta*5*10^{3}]^{[illegible]}$	M (ebulioscopy)	The concentration of epoxigrours mass %	Constants of velocity K min^{-1}	a	Corrrelation coefficient r^2
III	0	35	0.031	2081	2200	4.01	0.051	0.037	0.997
III'	1	13	0.029	1881	1900	4.52	0.278	-0.140	0.987
IV	0	35	0.048	4036	4200	2.15	0.049	0.035	0.998
IV'	1	12	0.042	3297	3400	2.52	0.243	-0.120	0.990
V	0	44	0.033	2288	2400	3.66	0.061	0.041	0.999
V'	1	13	0.031	2081	2200	3.91	0.350	-0.065	0.987
VI	0	45	0.050	4294	4400	2.00	0.058	0.053	0.999
VI'	1	12	0.047	3909	4000	2.15	0.307	-0.061	0.995
VII	0	30	0.035	2502	2500	3.44	0.084	-0.0002	0.997
VII'	1	12	0.330	2288	2300	3.74	0.430	-0.048	0.994
VIII	0	35	0.050	4294	4100	2.05	0.073	0.014	0.996
VIII'	1	11	0.048	4037	3950	2.18	0.380	-0.087	0.997
IX	0	32	0.041	3179	3200	2.70	0.110	-0.0005	0.982
IX'	1	10	0.038	2833	2900	2.97	0.720	-0.049	0.965
X	0	32	0.060	5660	5750	1.51	0.091	0.048	0.995
X'	1	11	0.057	5237	5400	1.59	0.667	-0.091	0.968

During the co-oligomerization of thienylorganocyclosiloxanes with the compound (I), in the presence of DMFA, the conversion of cyclosiloxanes reaches 93–94% already after 5–15 minutes from the beginning of reaction (Figure 2a). The velocity of expenditure of organocyclosiloxanes are also described by the linear equations depending on the current concentration (Figure 2b). The constants of velocities are given in Table I.

The change of η_{sp} of reacting mixture in the presence of DMFA has also an extremal character (see Figure 3b).

Directly after the addition of compound (II) the growth of η_{sp} begins, which achieves its maximal value and then decreases till the equilibrium state.

As can be seen from Figure 3b, when the constant expenditure of organosiloxanes is achieved, the molecular masses of produced oligomeres are higher, than an equilibrium one. This fact shows, that the reacting ability of compound (I) is lower, than of thienilorganocyclosiloxanes.

The decrease of η_{sp} after the reaching of maximum, shows that in this case the decrease of molecular masses of reacting products takes place. As the content of cyclic products is not changed, the observed decrease of molecular masses of reacting products is due to the fact of the decrease of average weight of molecular masses, with the preservation of average number of the later, due to the interaction of initial compound (I) with the produced silicon chains.

The investigation of products of co-oligomerization of D_4^{Th} and $D_2D_2^{Th}$ with compound (I), by the method of gas vapour chromatography shows, that during the whole process the bimodal distribution of reacting mixture is valid. One maximum corresponds to the lowmolecular organosiloxanes and initial compound (I). During the reaction its value decreases. Second maximum corresponds to the oligomeric products, and increases during the reaction (Figure 4).

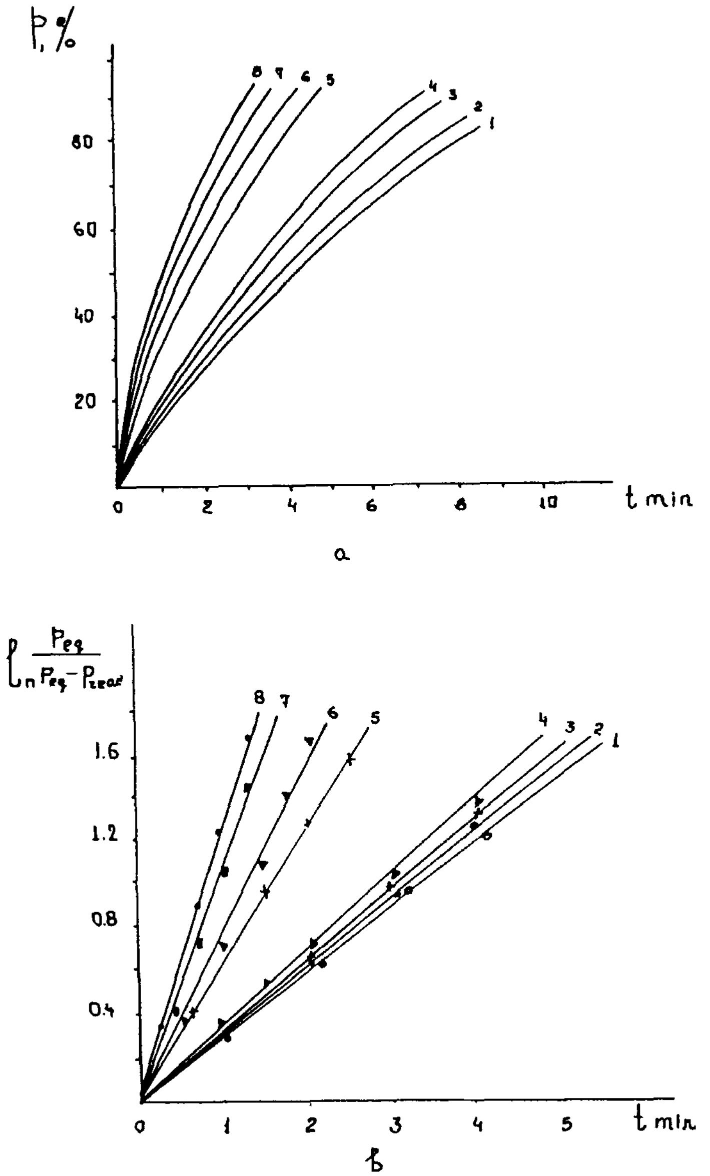


FIGURE 2 The dependence of conversion (a) and ln $P_{eq}/P_{eq} - P_{reac}$ (b) of siloxanes from the time of co-oligomerization of compound (I) with $D_3^{vin}D^{Th}$ (1, 2), $D_2^{vin}D^{Th}$ (3, 4), D_2D^{Th} (5, 6), D_4^{Th} (7, 8) in the rate 1:4 and 1:8 initiated by the compound (II) with an addition of DMFA.

For the oligomeres (III′) and (X′) the mass values M_n, M_W and M_r for oligomeric parts achieve the following values: 5425, 11393, 21077 and 4961, 9823, 17681, corresponding to the maximal value of η_{sp}, and then decreases till minimal value (4200, 7980, 14364 and 4100, 8155, 14516 correspondingly) with the constant value of η_{sp}.

The ratio of M_W/M_n for oligomeric components of reaction products as during the

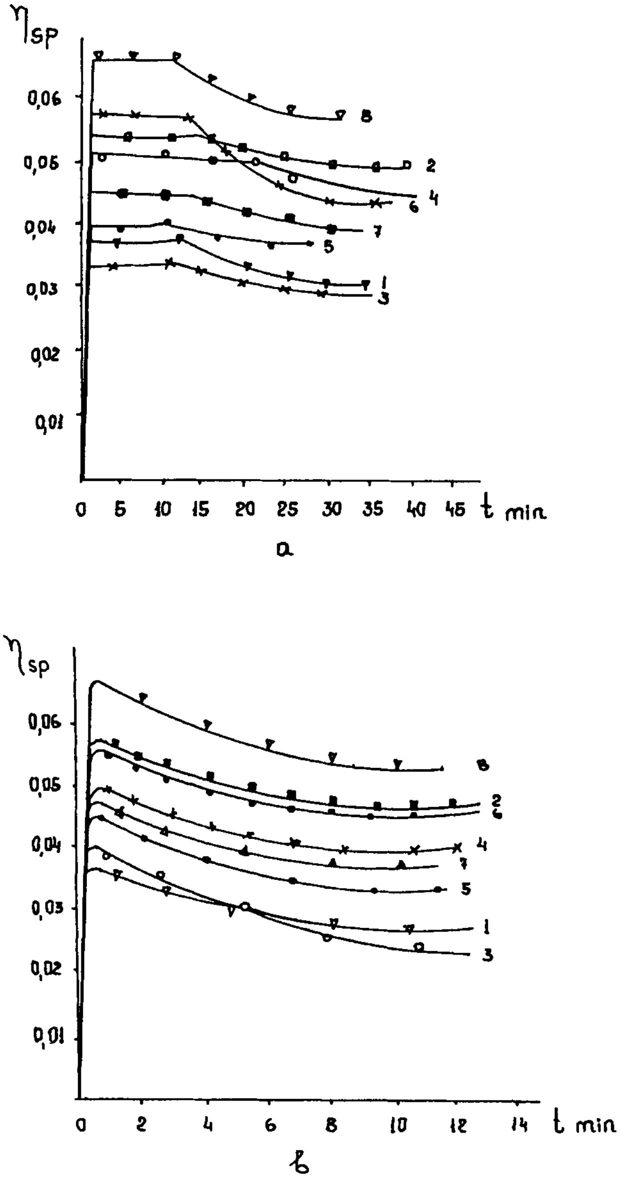


FIGURE 3 The dependence of η_{sp} from the time of co-oligomerization of compound (I) with $D_3^{vin}D^{Th}$ (1, 2), $D_2^{vin}D^{Th}$ (3, 4), D_2D^{Th} (5, 6), D_4^{Th} (7, 8) in the rate 1:4 and 1:8 without (a) and with (b) an addition of DMFA.

reaction process as after its end is close to two. This value is characteristic to the equilibrium reaction of oligomerization of organocyclosyloxanes with big contribution of interchain interactions.[9]

The analysis of gas vapour chromatography shows, that without an addition of DMFA, the total content of lowmolecular products, after the achievement of constant value of η_{sp} is equal to 30–35 mass %.

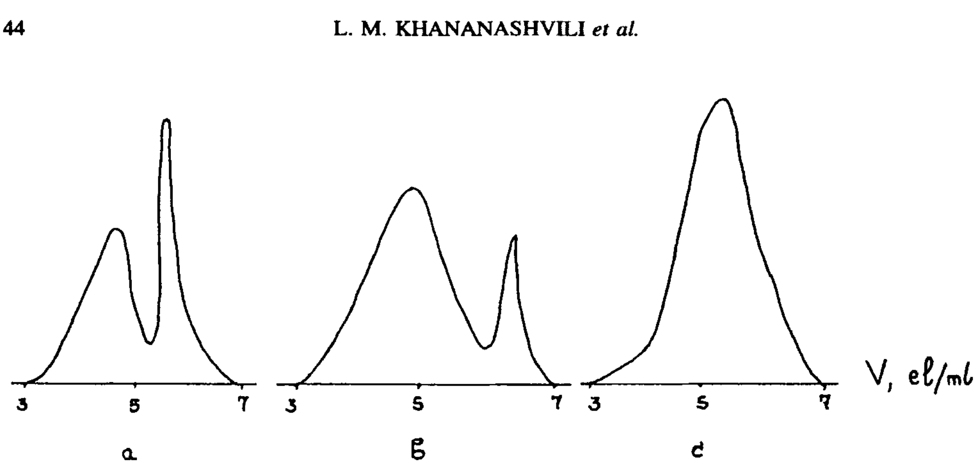


FIGURE 4 The change of molecular mass distribution of co-oligomerization of products D_2D^{Th} (rate 1:8) initiated by the compound (II) with an addition of DMFA. The reaction time is 1 min (a), 5 min (b), 8 hours (c).

After the addition of DMFA the content of lowmolecular products is only 15–17 mass %, which is almost the value of the state of equilibrium. This fact indicates that the reaction mixture achieves the equilibrium state when the polar admixture is used.

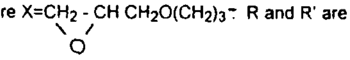
The values of molecular masses of oligomeres obtained as well as in the presence of DMFA, so without it, after the extraction of lowmolecular components, was determined by the ebulioscopic method, by the presence of cyclic epoxi groups[10] (see Table I).

The reaction of co-oligomerization with the consideration of all stages of process can be described as:

$$\sim Si(CH_3)_2O\,N(CH_3)_4 + XSi(CH_3)_2OSi(CH_3)_2X \rightleftarrows$$
$$\rightleftarrows \sim Si(CH_3)_2OSi(CH_3)_2\text{-}X + XSi(CH_3)_2ON(CH_3)_4 \qquad 1.$$

$$XSi(CH_3)_2ON(CH_3)_4 + p[RR'SiO]_n \rightleftarrows$$
$$\rightleftarrows XSi(CH_3)_2O[SiRR'O]_mN(CH_3)_4 + a[RR'SiO]_t \qquad 2$$

$$XSi(CH_3)_2O[SiRR'O]_{m+1}Si(CH_3)_2\text{-}X + XSi(CH_3)_2ON(CH_3)_4 \rightleftarrows$$
$$\rightleftarrows XSi(CH_3)_2O[SiRR'O]_{m-q}\text{-}Si(CH_3)_2\text{-}X +$$
$$+ XSi(CH_3)_2[SiRR'O]_{q+1}\text{-}N(CH_3)_4$$


were $X=CH_2\text{-}CH\,CH_2O(CH_2)_3\text{-}$ (with CH_2–CH bridged by O) R and R' are given below.

In the infrared spectrum of synthesised compounds III–X and III′–X′ the characteristic adsorption stripes of epoxy groups in the range of 3060 and 915 cm^{-1} are present. The strong stripes at 705 and 1220 cm^{-1}, medieval stripes at 1500, 1520, and 1800 cm^{-1}, week stripe at 3035 cm^{-1}, characterises the presence of C—S bounds (thienil groups).

Strong adsorption stripes at 1080–1060 cm^{-1}, indicates the presence of SiOSi bounds in compounds III–X and III′–X′.

In the PMR spectra of compounds III–X and III′–X′ the resonance signals can be detected at 7.06–7.78 m.d. (the thyenil group).

As for the proton signals of epoxy cycle, they show as complex multiples in the area 2.4–2.9 m.d. The signals in the area 5.2–6.1 m.d. belongs to the protons of vinyl groups.

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