

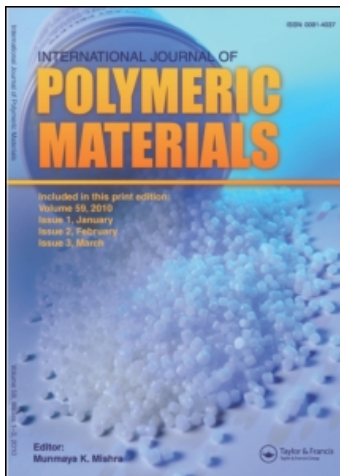
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## International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

### Ethylsiloxane Oligomers Containing Organocyclosiloxane Fragments as a Lateral Group

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**To cite this Article** Mukbaniani, Omari V. , Khananashvili, Lotari M. , Esartia, Izabella G. and Khaduri, Samson D.(1994) 'Ethylsiloxane Oligomers Containing Organocyclosiloxane Fragments as a Lateral Group', *International Journal of Polymeric Materials*, 24: 1, 131 – 139

**To link to this Article:** DOI: 10.1080/00914039408028559

**URL:** <http://dx.doi.org/10.1080/00914039408028559>

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# Ethylsiloxane Oligomers Containing Organocyclosiloxane Fragments as a Lateral Group

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The reaction and kinetic regularities of catalytic dehydrocondensation of oligoethylhydridsiloxane containing trimethylsiloxy end groups with hydroxyorganocyclosiloxanes in the presence of platinumchlorohydric acid or anhydrous powdered potassium hydroxide has been studied.

Ethylsiloxane oligomers containing various amounts of organocyclosiloxane fragments as lateral groups, completely soluble in organic solvents, has been synthesized.

Reaction order, activation energy and dehydrocondensation rate constants were found. Thermogravimetric, thermomechanical and x-ray diffraction studies of synthesized oligomers were carried out.

**KEY WORDS** Ethylsiloxane oligomers, thermogravimetric, thermomechanical properties

## INTRODUCTION

It is known<sup>1,2</sup> that catalytic dehydrocondensation between  $\text{=Si—H}$  containing compounds and hydroxyl containing organic compounds in the presence of alkaline catalysts proceeds with the elimination of hydrogen.

Catalytic dehydrocondensation of hydridorganosilanes with hydroxyorganosilanes and siloxanes proceeds similarly.<sup>3–6</sup> At the same time there are no references to catalytic dehydrocondensation of hydroxyorganocyclosiloxanes with ethylhydridsiloxane oligomers.

## EXPERIMENTAL PART

The organic solvents were purified by drying and distillation. The initial hydroxyorganocyclotri(tetra)siloxanes were synthesized by well-known methods.<sup>7,8</sup>

The ethylhydridsiloxane ( $\text{K}^*-94$ ) was used as a hydride containing ethylsiloxane. The purity of the obtained hydroxyorganocyclosiloxanes was verified by gas-liquid chromatography "LKhm-8MD" with SKTF-100 (10%) on NAW chromosorb, using a 2 M column, and He as carrier gas. Diffraction patterns were taken on a roentgenograph "DRON-2."  $\text{A—Cu}_\alpha$  without a filter, the angular velocity of the counter being  $\omega = 2$  deg/min.

The thermomechanical curves were taken on a custom made installation. The test conditions were:  $V = 5$  deg/min.  $\sigma = 0,1$  kg/cm<sup>2</sup>.

Thermogravimetric investigations were carried out on a "Paulic-Paulic-Erday" derivatograph model MOM-102. The test conditions were temperature increasing at a rate  $V = 5$  deg/min, weight = 100 mg.

### Heterofunctional Condensation (HFC) of Ethylhydridsiloxane (K\*-94) with Trimethylchlorsilan

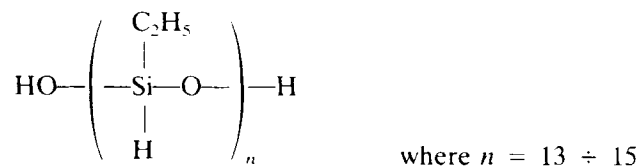
A solution of 30.3 g (0.279 mol) of trimethylchlorsilane in 50 ml of anhydrous toluene was added to a solution of 105 g (0.093 mol) of ethylhydridsiloxane (K\*-94) and 14.7 g (0.186 mol) of pyridine in 700 ml of anhydrous toluene, at room temperature. The reaction mixture was stirred and heated for 3–4 h until the solvent boiled. The precipitate was filtered off, and the solvent was evaporated. The reaction product was thermostatted *in vacuo* up to a constant weight, at 100°C. 107 g of clear substance I was obtained.

*Dehydrocondensation reaction.* The catalytic dehydrocondensation reaction was carried out in a two-necked flask equipped with a catalyst inlet tube and a reflux condenser connected with a gasometer. Between the gasometer and the reflux condenser a cold trap and a wash bottle were installed.

The initial reagents were placed into the flask and dissolved in absolute toluene and thermostatted in an oil bath until constant temperature was achieved. Catalyst was then introduced. After which hydrogen evolution began. The hydrogen was collected in the gasometer. Hydrogen having ceased to be released, the solvent was eliminated (if potassium hydroxide was used as a catalyst, the reaction products were washed until neutral, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>).

## RESULTS AND DISCUSSION

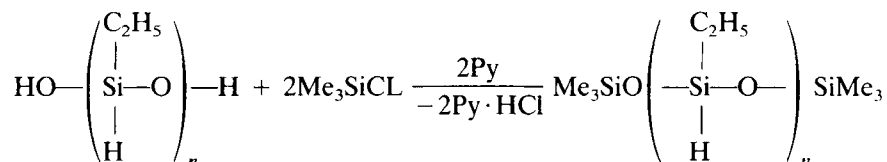
Commercially available oligoethylhydridsiloxane (K\*-94) was used as an initial product for the purpose of the synthesis of ethylsiloxane oligomers containing organocyclosiloxane fragments as lateral groups of the following structure:



Besides linear oligohydridethylsiloxanes, the product also contains cyclic ethylhydridsiloxanes.

In the first stage the reaction of HFC of K\*-94 with trimethylchlorsilan was carried out with a 1:3 ratio of the initial components. The reaction was carried out in anhydrous toluene solution in the presence of pyridine at room temperature. In the final stage the reaction mixture was heated for 3–4 h until the solvent boiled.

The precipitate was filtered off, washed with the water, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was driven off, and heated up to  $80\text{--}100^\circ\text{C}$  *in vacuo* ( $P = 1\text{ mmHg}$ ). In these conditions the cyclic hydridethylsiloxanes are largely removed from the reaction products. This is supported by the results of gas-liquid chromatographic analysis. HFC proceeds according to the following scheme:



where  $n = 15$ .

The reaction of catalytic dehydrocondensation of oligomer I with hydroxyheptamethylcyclotetrasiloxane ( $\text{D}_4^{\text{OH}}$ ) with the 1:15 ratio of the initial components was also carried out.

Preliminary heating of the toluene solution  $\text{D}_4^{\text{OH}}$  (concentration  $C = 0.2271$  mole/l) during 10 h in the presence of platinochlorohydric acid or KOH in the temperature range  $40\text{--}60^\circ\text{C}$  showed that both polymerization and polycondensation of hydroxycyclosiloxane under the experimental conditions does not take place and no changes for the methyl protons in NMR spectra of  $\text{D}_4^{\text{OH}}$  are observed. Detailed analysis of the solution by GLC demonstrated the presence of hydroxymethylcyclosiloxane and the absence of bicyclosiloxanoxide, the product of homofunctional condensation. Hence, in the case of the dehydrocondensation of blocked oligomer I with  $\text{D}_4^{\text{OH}}$  there will be no side processes of polymerization and condensation, which is in agreement with Reference 9. The dehydrocondensation reaction of the blocked oligomer I with  $\text{D}_4^{\text{OH}}$  is influenced by the type of catalyst used.

In the presence of platinochlorohydric acid the reaction proceeds at slowly  $60^\circ\text{C}$ , and over 6 hours the hydrogen conversion does not exceed 50%, while in the presence of powdered anhydrous KOH dehydrocondensation proceeds more vigorously. The reaction in the presence of potassium hydroxide (0.1% of the total amount of the initial components) was studied at 40, 50, and  $60^\circ\text{C}$  at a concentration of  $C = 0.2271$  mole/l. As is seen from Figure 1, with the increase in temperature from 40 to  $60^\circ\text{C}$  the hydrogen conversion increases from 65 to 85%; the dehydrocondensation reaction proceeds vigorously during the first 1.5–2 h and 5 h later the conversion changes only slightly.

In addition, these data are evidence that at an initial component ratio of 1:15 the reaction does not proceed completely and dehydrocondensation of all the active centers is impeded. A detailed analysis of the reaction mixture by GLC showed the presence of unreacted  $\text{D}_4^{\text{OH}}$ .

This may be explained by steric effects created by organocyclosiloxane fragments in the course of the formation of the macromolecular chain.

Dehydrocondensation proceeds according to the general scheme:

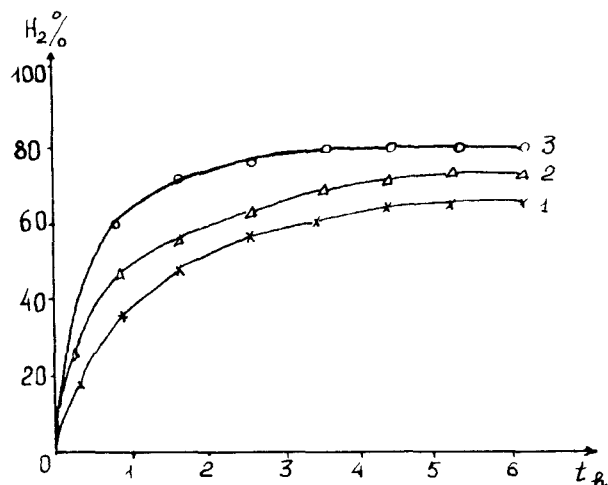
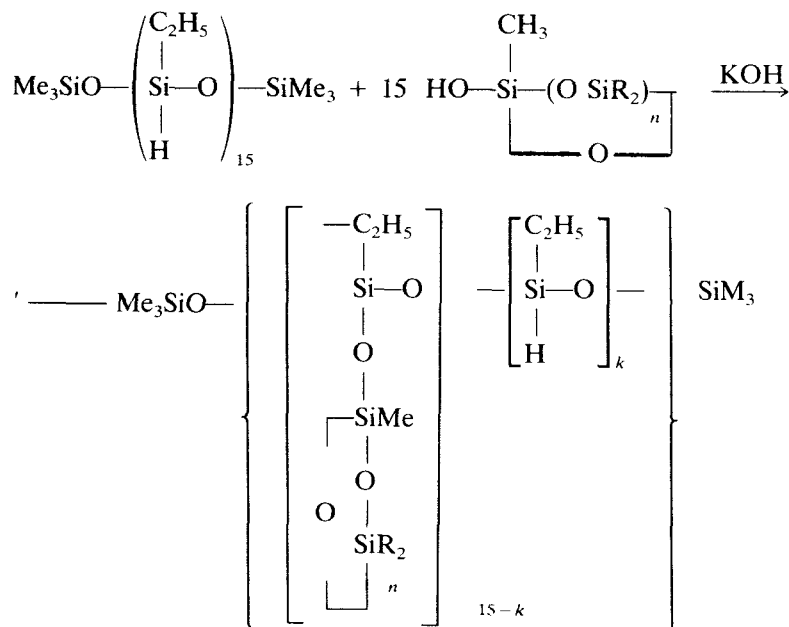


FIGURE 1 Hydrogen conversion in the dehydrocondensation of oligoethylhydrosiloxanes blocked by trimethylsiloxy groups with hydroxyheptamethylcyclotetrasiloxane: curve I corresponds to a reaction temperature of 40°C, curve 2 at 50°C, curve 3 is at 60°C with a 1:15 ratio of the initial components.



where at  $R = \text{Me}$ ,  $n = 3$  II (40°C), III (50°C), IV (60°C).  
 at  $R = \text{Ph}$ ,  $n = 2$  V (60°C).

In the case of catalytic dehydrocondensation with a 1:7.5 ratio of the initial components the reaction proceeds further and faster (Figure 2). Thus, at a 1:15 ratio of the initial components the maximum conversion at 60°C is about 80% after 3.5 hours, while at a 1:7.5 ratio of components hydrogen conversion is about 98%

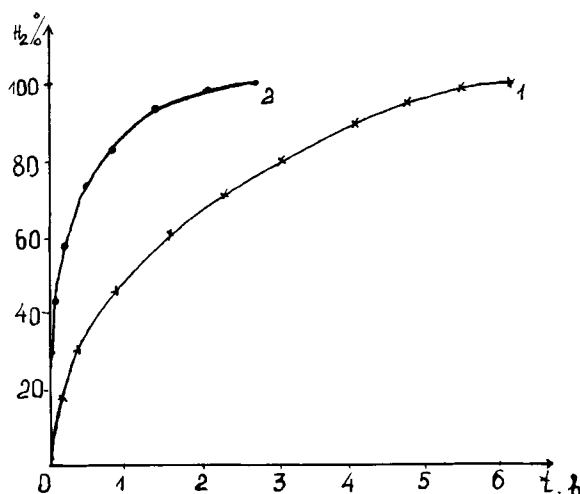


FIGURE 2 Hydrogen conversion in the dehydrocondensation of oligoethylhydrosiloxanes blocked with hydroxyheptamethylcyclotetrasiloxane at a 1:7.5 ratio; were curve 1 at 40°C, curve 2 at 60°C.

( $R = \text{Me}$ ,  $n = 3$  – oligomer-VII) during 2.5 hours and at 40°C the conversion is about 96% ( $R = \text{Me}$ ,  $n = 3$  – oligomer VI). After the end of dehydrocondensation the reaction products were washed with water until neutral to eliminate traces of potassium hydroxide, dried, the solvent evaporated to a constant mass and heated to 100°C *in vacuo* ( $P = 1 \text{ mmHg}$ ). The reaction products are transparent or slightly opalescent liquids depending on the surrounding groups, and are soluble in organic solvents.

Table I shows the results of elementary analysis, physical chemical properties and the yield of ethylsiloxane oligomers containing cyclic fragments as lateral groups.

In the IR spectra of the synthesized oligomers II–IV one can observe absorption bands characteristic of asymmetric stretching vibrations of the Si—O—Si bands in the region 1020 and 1080  $\text{cm}^{-1}$  characteristic of both linear siloxane links and Si—O—Si bonds in the cyclotetrasiloxane ring. One can also observe asymmetric stretching vibrations of Si—O—Si bands for oligomer V at 1020  $\text{cm}^{-1}$  where linear siloxane bond vibrations and those for the cyclotrisiloxane ring are superimposed.

In the spectra one can also observe the absorption bands for the Si—H bond at 2160  $\text{cm}^{-1}$ , for the Si—Me groups at 1270  $\text{cm}^{-1}$  and for symmetric stretching vibrations of the  $\text{CH}_2$  groups at 2800  $\text{cm}^{-1}$ .

One can see that the catalytic dehydrocondensation reaction is of the second order. Figure 3 shows the time dependence of the inverse concentration. The reaction rate constants at various temperatures were calculated:  $K_{40^\circ} = 0.923 \times 10^{-1}$ ;  $K_{50^\circ} = 1.6 \times 10^{-1}$ ;  $K_{60^\circ} = 2.85 \times 10^{-1}$ . It was found that for each increase in temperature of 10°C the reaction rate constants increase approximately 1.7 times.

Figure 4 shows the dependence of the reaction rate logarithm on inverse temperature, from which the activation energy was calculated  $E_{\text{activ}} = 51.5 \text{ kJ/mol}$ .

A thermomechanical investigation of the oligomers was performed. As is evident from the table,  $T_{\text{vitr}}$  for oligomer III is  $-80^\circ\text{C}$ , for oligomer VI is  $-95^\circ\text{C}$  which indicates that for an increase in the amount of cyclotetrasiloxane fragments  $T_{\text{vitr}}$ .

TABLE I  
Elementary analysis, some physicochemical properties and the yield of oligomers

Oligomers	Yield	$d_1, \text{\AA}$	$d_2, \text{\AA}$	$\eta_{sp}/c$ : Solution in toluene at 25°C	$T_{\text{air}}$ °C	Elementary composition <sup>a</sup>			Conv. $H_2$ , %
						C	H	Si	
II	87	—	—	0.04	—	30.06	7.28	37.71	65
						30.24	7.19	37.59	
III	90	—	—	0.04	-80	29.95	7.24	37.72	72
						29.84	7.15	37.63	
IV	90	8.27	4.00	0.04	—	29.85	7.21	37.72	80
						29.78	7.11	37.67	
V	88	8.73	4.32	0.03	—	57.46	5.49	22.03	66
						57.29	5.30	22.26	
VI	90	—	—	0.05	-95	29.93	7.27	37.09	96
						29.79	7.20	37.16	
VII	91	7.97	3.87	0.05	—	29.93	7.27	37.09	98
						29.80	7.21	37.16	

<sup>a</sup>In the numerator there are calculated values; in denominator actual values.

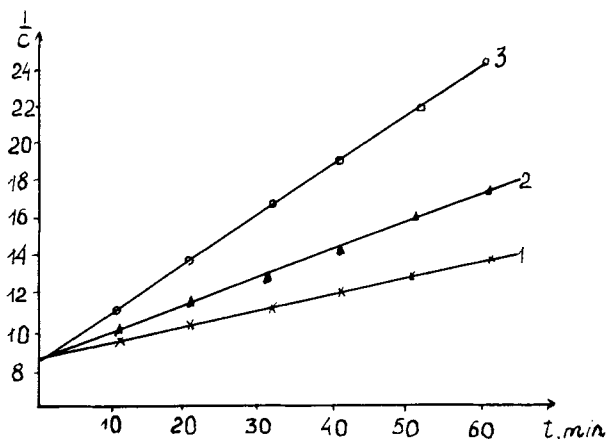


FIGURE 3 Time dependence of the inverse concentration of reagents in the reaction of catalytic dehydrocondensation at a 1:15 ratio; curve 1 at 40°C, curve 2 at 50°C, curve 3 at 60°C.

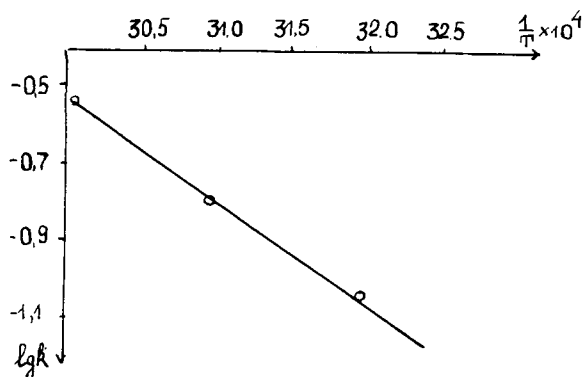


FIGURE 4 Dependence of the reaction rate constant logarithm on the inverse temperature at a 1:15 ratio.

also increases. This may be explained by the increase in the rigidity of the oligomer segments.

The synthesized oligomers were analyzed by the X-ray method. It was shown, that the interchain distance for oligomer IV and VI is different, since the interchain distance increases from 7.97 Å (for oligomer VI) to 8.27 Å (for oligomer IV), this may be explained by an increase in the number of cyclic fragments (Figure 5).

It was shown by thermogravimetric investigations that (Figure 6) the oligomers are characterized by higher thermaloxidative stability. According to Figure 6 mass losses for oligomers at 240–250°C do not exceed 5%. The main destruction process proceeds in the temperature range of 300–550°C. Above 600°C the curves of mass loss does not change.

The final mass losses for oligomer IV is 67%, and for oligomer VI – 64%. The thermoxidative stability of the oligomers also increases with an increase in the number of cyclic fragments in the lateral chain, because this increase of cyclic lateral fragments prevents the chain transfer in the case of depolymerization.<sup>10</sup>



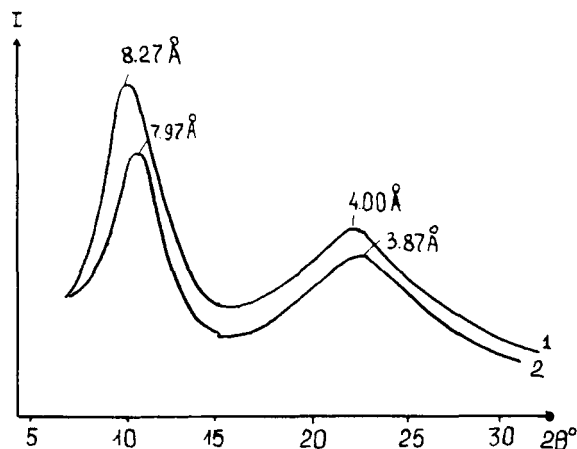


FIGURE 5 Diffractograms of oligomers, where curve 1 is for oligomer VI, 2 is for oligomer IV.

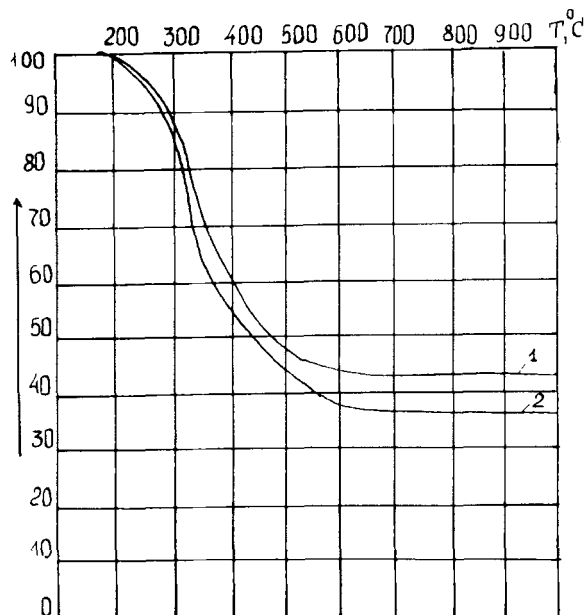


FIGURE 6 Thermogravimetric curves for oligomers, where curve 1 is for oligomer VI, curve 2 is for oligomer IV (in air, the rate of temperature increase is 5 deg/min).

Thus, we have for the first time shown a possibility to obtain organosiloxane oligomers with cyclic fragments in the lateral chain by catalytic dehydrocondensation of oligohydridethylsiloxane blocked by trimethylsiloxane groups, with hydroxyorganocyclosiloxanes.

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