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### Silicone Rubbers. Ix. Contributions to Polydimethylsiloxane- $\alpha,\omega$ -Diols Synthesis by Heterogeneous Catalysis

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## **SILICONE RUBBERS. IX. CONTRIBUTIONS TO POLYDIMETHYLSILOXANE- $\alpha,\omega$ -DIOLS SYNTHESIS BY HETEROGENEOUS CATALYSIS**

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### **ABSTRACT**

The cationic polymerization of a cyclosiloxane mixture (hexamethylcyclotrisiloxane-D<sub>3</sub>, octamethylcyclotetrasiloxane-D<sub>4</sub>, decamethylcyclopentasiloxane-D<sub>5</sub>, dodecamethylcyclohexasiloxane-D<sub>6</sub> and tetradecamethylcycloheptasiloxane-D<sub>7</sub>) in the presence of water as adjusting-control agent for molecular weight is studied in heterogeneous catalyst system using an ion-exchange VIONIT CS-34C with sulphonic groups. Thus poly(dimethylsiloxane)- $\alpha,\omega$ -diols for room temperature vulcanization (RTV) silicone rubbers, were obtained.

### **INTRODUCTION**

The first poly(dimethylsiloxane) synthesis reaction was made by Patnode [1] by cationic polymerization of corresponding cyclosiloxanes using sulphuric acid as catalyst. Any reagent which can break the siloxane bond by the electrophilic attack, initiates the polymerization of cyclosiloxanes. It can be a protonic acid or a Lewis acid. Frequently sulphuric acid or its derivatives are used [1-7].

The advantage of using an ion-exchange catalyst with proton generating groups or acid activated clay in the cyclosiloxanes polymerization reaction is the possibility of removing the electrophilic reagent by filtration. Porous materials as activated clays, catalyse the cyclosiloxane polymerization reaction even at room temperature. Thus poly(organo-H-siloxanes) were obtained using acid activated clays [8, 9]. Tichy [10] obtained low molecular weight poly(organosiloxane)- $\alpha,\omega$ -diols by  $D_4$  polymerization with black montmorillonitic earth and water as molecular weight adjusting agent. The same catalyst was used by Schatz [11] who polymerized  $D_4$  with glycols, di(*tert*-butyl)siloxane-diols and diphenylsilane-diols, obtaining poly(siloxane)- $\alpha,\omega$  - diols. Pike and contributors [12] obtained viscous oils by polycondensation of  $HO[(CH_3)_2SiO]_{20}OH$  type compounds using zeolites. Westhoff [13] made cyclosiloxane polymerization, using Amberlyst-15 and Dowex as catalyst in order to obtain poly(organosiloxanes). The equilibration reactions of siloxanes were investigated by Braun and Hamann, who used sulphonic cationit Wofatit type. They concluded that both, sulphuric acid and cationit, mechanisms were the same [14].

This paper presents the polymerization of cyclodimethylsiloxane-mixtures using VIONIT CS-34C as catalyst to obtain low-molecular weight poly(dimethylsiloxanes), (40000-70000) for silicone rubbers RTV type.

## EXPERIMENTAL

The dimethylcyclosiloxane-mixture for poly(dimethylsiloxane)- $\alpha,\omega$  -diols synthesis has the following composition (determined by chromatography):  $D_3=3.06\%$ ,  $D_4=76.23\%$ ,  $D_5=18.12\%$ ,  $D_6=2.39\%$ ,  $D_7=0.20\%$ ;  $n_D^{25}=1.3939$ ;  $\eta^{20}=2.6$  cSt and 0.01% wt. humidity.

The catalyst was VIONIT-CS-34C, a macroporous sulphonate styrene-divinylbenzene copolymer with the following characteristics:

granulation: 0.3-1.25 mm;

exchange capacity: 1.7-1.9 mval/ml (4.2 mval/g);

specific surface: 35 m<sup>2</sup>/g;  
humidity: 60% wt.;  
porosity: 39-42%;  
average pore diameter: 450 Å;  
delivery form: H<sup>+</sup>.

The cationit was air dried at 110°C, 4 hours to 4.7 % wt. humidity then 1 hr. at 110°C and 20 mm Hg to 3.3-3.4 % wt. humidity.

### Synthesis:

The cationic polymerization of dimethylcyclosiloxanes was made in a three necked round bottom flask equipped with reflux condenser and thermometer. 120 ml cyclosiloxanes and 0.48 ml water were added, this mixture was heated at 110°C and 3g VIONIT CS-34C prepared as above were introduced and stirred for 90 min.

Then the reaction mixture was filtered by vacuum. The filtrate was distilled at 160°C and 20 mm Hg to separate the unreacted cyclosiloxanes.

### Techniques:

The resulting polymers were characterized by M<sub>v</sub> determination [16]:

$$[\eta] = 8.28 \cdot 10^{-3} \cdot M^{0.72}$$

and (-OH) determination by the acylation method [17]. M<sub>n</sub>, M<sub>w</sub> and I (polydispersity index) were determined. The GPC curves of the polymers were obtained with a WATERS ASSOCIATED 440 apparatus equipped with a differential refractometer R<sub>401</sub> and Styragel columns. The calibration was made with poly(styrene) standard.

## RESULTS AND DISCUSSION

By the working manner described above we intend to show:

- a) the influence of the polymerization time on the molecular weight and conversion in 15-180 minutes ranges;
- b) the influence of the temperature on the molecular weight and conversion using different temperatures from 50°C to 110°C;
- c) the influence of catalyst concentration on the molecular weight and conversion using 0.5 to 3.5% wt. amounts;
- d) the influence of the water/cyclosiloxane ratio on the molecular weight and conversion.

The influence of reaction time on the polymer molecular weight and cyclosiloxane conversion is shown in TABLE 1. In this case, increasing the polymerization time leads to increasing molecular weight and conversion. Finally a polymerization-depolymerization equilibrium is established. During the reaction time, the active centers attack the Si-O bonds in cyclosiloxanes and linear polymers [18] and a cyclosiloxane-mixture (including starting cyclosiloxanes) was formed. One can write the following equilibrium equation:



The equilibrium reaction mixture (after 90 min) contains D<sub>4</sub>, D<sub>5</sub>, D<sub>6</sub>, D<sub>7</sub> and D<sub>8</sub> (TABLE 2) in good correspondence with literature [19]. The equilibrium quantity of D<sub>3</sub> is about 1% corresponding to [19-21] but D<sub>4</sub> and D<sub>5</sub>, thermodynamically more stable, are at maximum amounts.

The water content in the reaction mixture decreases from 0.01% to 0.001% wt. being consumed as adjusting chain control agent. The values of polydispersity, I, are a little greater but the content of functional groups for the same molecular weight is according to the data from literature [22].

The influence of temperature on the molecular weight and cyclosiloxane conversion is presented in TABLE 3. Increasing the temperature, the conversion

TABLE 1.

The variation of molecular weight and conversion versus reaction time

Nr.	Reac. time (min)	$M_v$	Conv. (%)	$M_n$	$M_w$	I	OH gr. cont. (%)	
							experim.	liter.
1.	15	53500	83	38500	57100	1.48	0.06	0.06
2.	30	61500	89	42000	72400	1.72	0.06	0.06
3.	45	68000	93	47200	53800	1.39	0.04	0.06
4.	60	67000	91	55900	73000	1.31	0.05	0.05
5.	75	66900	92	53800	71500	1.33	-	0.05
6.	90	72800	91	48000	63100	1.32	-	0.05
7.	120	84000	90	61900	75300	1.22	-	0.04
8.	180	77200	91	37600	55800	1.48	-	0.04

TABLE 2.

The composition of cyclosiloxanes unreacted in different stages of reaction and reformed as a result of the reaction (eq. 1)

No.	Time min.	D <sub>3</sub>	D <sub>4</sub>	D <sub>5</sub>	D <sub>6</sub>	D <sub>7</sub>	D <sub>8</sub>	H <sub>2</sub> O %
1.	0	3.06	76.23	18.12	2.39	0.20	-	0.0100
2.	15	0.25	61.11	31.37	6.19	1.08	-	0.0068
3.	30	0.35	58.47	34.53	5.90	0.75	-	0.0010
4.	45	0.22	58.47	38.16	5.81	0.82	-	0.0010
5.	60	0.24	50.80	37.01	10.11	1.64	0.20	0.0010
6.	75	0.24	56.75	33.11	8.27	1.34	0.29	0.0075
7.	90	0.40	45.56	38.65	12.75	2.18	0.46	0.0051
8.	120	0.24	49.66	37.54	10.07	2.02	0.47	0.0046
9.	180	0.29	45.88	39.18	11.63	2.44	0.58	0.0010

TABLE 3.

Molecular weight and conversion  
variation versus temperature.

No.	Temp. °C	M <sub>v</sub>	Conversion %
1.	50	88600	58
2.	70	83900	86
3.	80	81600	89
4.	90	70800	90
5.	110	66100	91

increases and the molecular weight decreases. Increasing the catalyst amount leads to conversion and molecular weight variations, too (TABLE 4).

TABLE 4.

The influence of catalyst quantity on  
molecular weight and conversion.

No.	Catal. % wt.	M <sub>v</sub>	Conversion %
1.	0.5	31900	44
2.	1.0	43300	89
3.	1.5	55800	89
4.	2.0	50800	90
5.	2.5	66100	91
6.	3.0	69500	92
7.	3.5	80500	93

If the quantity of water in the reaction mixture varies (0.1-0.8% relative to the cyclosiloxane amount) the molecular weight decreases from 91700 to 50700 at 90-91% conversion (TABLE 5). The work prescription is the one mentioned in the experimental part.

TABLE 5.

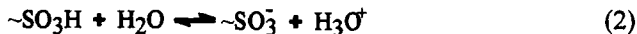
Effect of water amount added in the  
reaction mixture on the molecular  
weight and conversion

No.	Water amount %	M <sub>v</sub>	Conversion %
1.	0.1	91600	91
2.	0.2	84200	91
3.	0.3	88500	90
4.	0.4	66100	91
5.	0.5	66600	91
6.	0.6	63500	91
7.	0.7	54000	91
8.	0.8	50700	90

To determine the catalyst activity after different thermic investigations and to discover the role of the water in this reaction, we carried out a series of tests whose results are presented in TABLE 6. As one can see from this table, water addition leads to higher molecular weights and especially higher rates of conversion. From this results we conclude

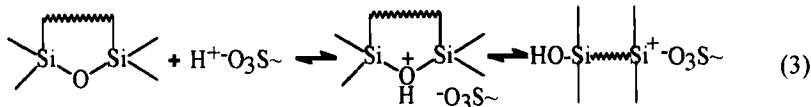
that the sulphonic groups existing in

the catalyst pearl, hydrolyse in the presence of water [23] according to the following equation:

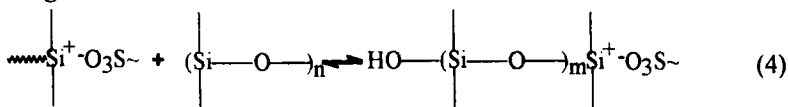


The water involved in this process is either added to the reaction mixture or is included in the catalyst and cyclosiloxanes. The lowest degree of humidity (even after 4 hrs. at 110°C in air and 1 h in vacuum drying) was 3.38 % wt. This humidity and that of the cyclosiloxanes (0.01 % wt.) are enough to create OH terminal groups of the macromolecules which have molecular weight 60000 and a good conversion ( $M_v=63000$ ,  $\text{conv.}=82\%$ ). Increasing the water amount results in a better conversion. Since the water is present, it can be presumed that the reaction is catalysed by the dissociated sulphonic groups, [15] solvated protons. Taking into account the general scheme of a classical ion pairs cationic polymerization [26], one can write:

- initiation:

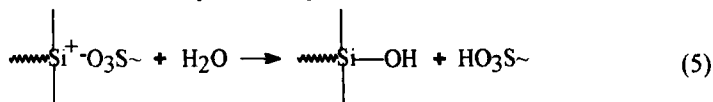


- chain growth:



- the interruption may be:

**Partially interruption** (without stopping the kinetic chain). In this case the chain transfer reaction to water is important (equation 5).

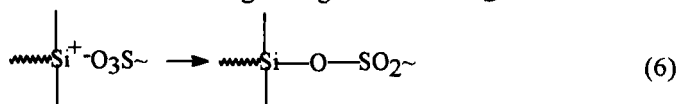


The presence of such a chain transfer is proved by the relative high polydispersity

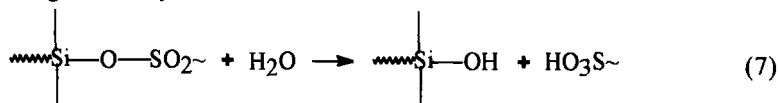


values ( $I=1.22-1.72$ ) for the resulting molecular weight. The chain transfer stabilizes the macromolecular chain and takes part in the catalyst regeneration.

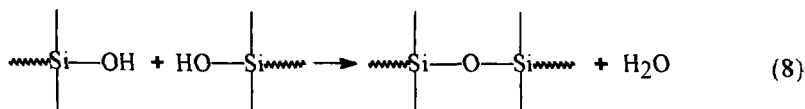
**Interruption by stopping the kinetic chain.** Because of its high nucleophilic character the counterion reacts with the growing center forming a bond:



We presume that this bond suffers from a hydrolytic attack in the presence of water building the catalyst:



The reaction is getting complicated with the concomitance of the inter- or intramolecular acidolytic condensation reactions:



Different from the polymerization with sulphuric acid when the hydrolysis reaction leads to a decrease of molecular weight because of the macromolecules splitting into smaller molecules in this case macromolecules detach only from the catalyst surface so that the molecular weight remains unaffected. This was confirmed experimentally by the data from TABLE 6. Adding water to the reaction mixture (after 1.5 hrs.) containing a highly dried cationit, one can observe an increase of conversion. This is the result of the active centers deblocking through the detached macromolecules in the presence of water.

If the reaction represented by equation 7 did not take place, active centers which have initiated the polymerization, would remain blocked being included in the

TABLE 6.

The catalyst drying time and water quantity influence on the conversion and molecular weight. (In every case, air drying was performed at 110°C and vacuum drying at 110°C and 20 mm Hg)

No.	Water amount add.	Catalyst amount *	Catalyst drying conditions	Reaction time	M <sub>v</sub>	Conversion
	%	% wt.		min.		%
1.	-	2.5	-	90	22700	52
2.	-	2.5	4h. air, 1h. vacuum	90	63000	82
3.	-	2.5	4h. air, 2h. vacuum	90	52300	73
4.	-	2.5	-	90	8600	45
5.	-	2.5	4h. air	90	69900	90
6.	-	2.5	4h. air, 1h. vacuum	90	63000	82
7.	-	2.5	4h. air, 2h. vacuum	90	52400	73
8.	-	2.5	4h. air, 3h. vacuum	90	64000	75
9.	-	2.5	4h. air, 4h. vacuum	90	49500	72
10.	0.4% after 75 min.	2.5	4h. air, 1h. vacuum	90	60300	77
11.	-	2.5	4h. air, 1h. vacuum	75	58800	72
12.	0.4% after 75 min.	2.5	4h. air, 4h. vacuum	90	62800	75
13.	-	2.5	4h. air	90	49500	72
14.	0.4% start	2.5	4h. air, 1h. vacuum	90	59800	92
15.	0.4% start 0.4% after 90 min.	2.5	4h. air, 1h. vacuum	105	62800	92

\*The catalyst amount does not take humidity into account.

~Si-O-SO<sub>2</sub>~ bond, on one side, and on the other free active centers became unavailable because the macromolecules formed on the catalyst surface prevent the approach of the monomer molecules.

Based on this experimental data we presume that in the absence of water the reaction did not take place. Large quantities of water lead to an intensive chain transfer and to lower molecular weights.

### CONCLUSIONS

1. We studied the influence of the parameters: time, temperature, catalyst concentration, chain transfer agent, on the molecular weight and conversion.
2. Based on the experimental data and by analogy with the sulphuric acid polymerization reaction the authors proposed a different mechanism. Water has the role of a cocatalyst and chain transfer agent supplying the terminal OH-groups of the macromolecules.

This reaction only takes place with high conversion in the presence of water (even traces). So it is possible to determine an optimal quantity of water corresponding to a maximal molecular weight and a maximal conversion.

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