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Heterogeneous Catalyzed Copolymerization of Octamethylcyclotetrasiloxane with 1,3,5,7-Tetravinyl-1,3,5,7-tetramethylcyclo-Tetrasiloxane

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HETEROGENEOUS CATALYZED COPOLYMERIZATION OF OCTAMETHYLCYCLOTETRASILOXANE WITH 1,3,5,7-TETRAVINYL-1,3,5,7-TETRAMETHYLCYCLOTETRASILOXANE

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ABSTRACT

For the introduction of vinyl groups at the Si atom of the siloxanic chain, copolymerization of octamethylcyclotetrasiloxane (D_4) with 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V_4) was performed. Vionit CS-34 C, a styrene-divinylbenzene copolymer with SO_3H groups, was used as catalyst. To estimate the reactivity ratios by the Mayo-Lewis scheme, the reaction was stopped at maximum 10% conversion. The probabilities of triads existence were calculated from ^{29}Si NMR, then the microstructure parameters of the formed copolymers were estimated. It was noticed that the dimethylsiloxy units have a higher tendency to form blocks.

INTRODUCTION

The properties of silicone products depend on the nature of the organic substituents attached to the silicon atom. Thus, polyorganosiloxane with methyl groups (the most used silicone rubber) allows an excellent combination of chain stability and flexibility. In order to obtain a silicone product with certain properties, the corresponding groups are introduced in well-determined ratios, more simply by copolymerization of the corresponding cyclosiloxane mixtures rather than by homopolymerization of only one type of monomer (mixed rings) [1]. Thus, the phenyl groups affect crystallinity, modifying flexibility at low temperature and enhancing the radiation resistance and thermal stability. The trifluor-propyl groups decrease polysiloxane swelling in common solvents. Vinyl siloxane units are introduced in small ratios in order to improve curing with peroxides and the compression set. Crosslinking can also be done through a hydrosilation reaction in the presence of Si—H groups besides the vinyl ones. Siloxane copolymers with a high vinyl groups content are used to obtain silicone foams [2].

The properties of siloxane copolymers are also determined by the comonomer sequences distribution in the chain. The sequences distribution in a copolymer can be determined by using the kinetic parameters of copolymerization, usually obtained with the Mayo-Lewis scheme [3], which assumes that no depropagation reactions occur and also that the rate constants depend only on the final unit in the growing chain [1].

During cyclosiloxanes polymerization initiated with strong acids or bases, two equilibria also occur, consisting in the redistribution of siloxane units between rings and chains [4, 5]. The equilibria for D_x homopolymerization can be represented as [1]:

$$-D_n^* + D_x \rightleftarrows -D^*_{(n+x)}$$

$$-D_n^- + -D_m^- \rightleftarrows -D^-_{(n+y)} + -D^-_{(m-y)}$$

where D is a bifunctional siloxane unit and n, x, m, and y are integer values. At equilibrium, each unit of the system really participates in the process, no matter whether it is placed in a ring or in a siloxane chain [3, 6]. Thus the kinetic parameters (the reactivity ratios) are different, depending on the conversion degree.

Recently, an alternative to the Mayo-Lewis scheme based on the reaction reversibility has been proposed. It predicts the microstructure at different stages of the reaction and determines the manner in which the microstructure is influenced by kinetic factors [1, 7]. The conclusions reached are based on high resolution ^{29}Si-NMR analysis of pentad and triad sequence signal intensities of the copolymers obtained [8, 9].

A model for equilibrium copolymerization, similar to the Mayo-Lewis scheme, was proposed [3] in which the competitive rate constants are nevertheless replaced by equilibrium constants, while the total concentrations of the siloxane units are considered, whatever their places are, in rings or in linear chains:

$$\begin{array}{ll}
-D^* + D \overset{K_{DD}}{\rightleftharpoons} -DD^* & \\
 & r_D = K_{DD}/K_{DV} \\
-D^* + V \overset{K_{DV}}{\rightleftharpoons} -DV^* & \\
 & \\
-V^* + V \overset{K_{VV}}{\rightleftharpoons} -VV^* & \\
 & r_V = K_{VV}/K_{VD} \\
-V^* + D \overset{K_{VD}}{\rightleftharpoons} -VD^* &
\end{array}$$

where D and V are the dimethyl- and vinylmethylsiloxane units, respectively; r_D and r_V can be estimated from the diads probabilities [10] which, in their turn, may be calculated from the run number [11].

Although cyclosiloxanes copolymerization is a reversible process, this was neglected in some studies, either by restricting conversion to low values [12, 13] or by using strained rings and mild catalysts, which do not rapidly induce redistribution of the siloxane rings [14–16].

The present paper discusses the copolymerization of dimethyl- and vinylmethylcyclosiloxanes with four siloxane units, the most largely applied industrially rings. The reaction's reversibility is restricted by the utilization of an ion exchanger with SO_3H groups as catalyst and by stopping the reaction at less than 10% conversion.

EXPERIMENTAL

Materials

Monomers: Octamethylcyclotetrasiloxane, $[-(CH_3)_2SiO-]_4$, (D_4), of 99.5% purity with $n_D^{20} = 1.3950$ and $d_4^{20} = 0.9593$; 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, $[-(C_2H_3)CH_3SiO-]_4$, (V_4), of 99.0% purity with $n_D^{20} = 1.4342$ and $d_4^{20} = 0.9892$.

Catalyst: Vionit CS-34 C—an ion exchanger with sulfonic groups. It has the following characteristics:

Exchange capacity: 4.2 meq/g
Porosity: 39–42%
Granulation: 0.4–0.65 mm
Specific surface: 35 m^2/g

Procedure

Polymerization was performed in bulk in the presence of water as both cocatalyst and chain transfer agent.

In a reaction vessel, equipped with stirrer, reflux condenser, and nitrogen inlet, monomers were added in various molar fractions, f_1 and f_2 calculated by

$$f_1 = \frac{[-(CH_3)_2SiO-]_4}{[-(CH_3)_2SiO-]_4 + [-(C_2H_3)CH_3SiO-]_4} \quad (1)$$

$$f_2 = \frac{[-(C_2H_3)CH_3SiO-]_4}{[-(CH_3)_2SiO-]_4 + [-(C_2H_3)CH_3SiO-]_4} = 1 - f_1 \quad (2)$$

When the desired temperature (70°C) was reached, the catalyst (2.5% wt) was added. The reaction was performed for 30 minutes and was stopped by filtering the catalyst. The copolymer was purified through precipitation with methanol from toluene solution and vacuum drying at 110°C. The cyclic compounds were separated from the toluene-methanol solution by distillation.

RESULTS AND DISCUSSION

The copolymers' compositions are expressed (Table 1) as molar fractions of the dimethylsiloxanic units (F_1) and of the vinylmethylsiloxanic units (F_2), respectively, in the copolymer as follows:

$$F_1 = \frac{[-(CH_3)_2SiO-]}{[-(CH_3)_2SiO-] + [-(C_2H_3)CH_3SiO-]} \quad (3)$$

$$F_2 = \frac{[-(C_2H_3)CH_3SiO-]}{[-(CH_3)_2SiO-] + [-(C_2H_3)CH_3SiO-]} = 1 - F_1 \quad (4)$$

where $[-(CH_3)_2SiO-]$ and $[-(C_2H_3)CH_3SiO-]$ are the concentrations of the dimethyl- and vinylmethylsiloxanic units, respectively, in the chain. They have been calculated from the intensities of the ^{1}H-NMR integral signals corresponding to the protons in the methyl and vinyl groups, respectively. The results have been confirmed by ^{29}Si-NMR and ^{13}C-NMR spectra interpretations. Spectra of the C_{18} copolymerization mixture are presented in Figs. 1 to 3.

The ^{29}Si-NMR spectra of cyclosiloxane mixtures separated from the reaction mixture did not show the appearance of new cyclic species as a result of depropagation. Thus, the irreversibility condition for the Mayo-Lewis equation can be ac-

TABLE 1. Compositions of the Initial Mixtures (f) and of the Copolymers Obtained (F)[a]

	Composition								
	C_{22}	C_{21}	C_{20}	C_{19}	C_{18}	C_{16}	C_{17}	C_{24}	C_{23}
f_1	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
F_1	0.22	0.37	0.52	0.64	0.73	0.80	0.85	0.89	0.97
F_2	0.78	0.63	0.48	0.36	0.27	0.20	0.15	0.10	0.03

[a] f_1 = molar fraction of dimethylsiloxy units in the initial mixture. F_1 and F_2 = molar fractions of dimethylsiloxy and vinylmethylsiloxy units, respectively, in the copolymer.

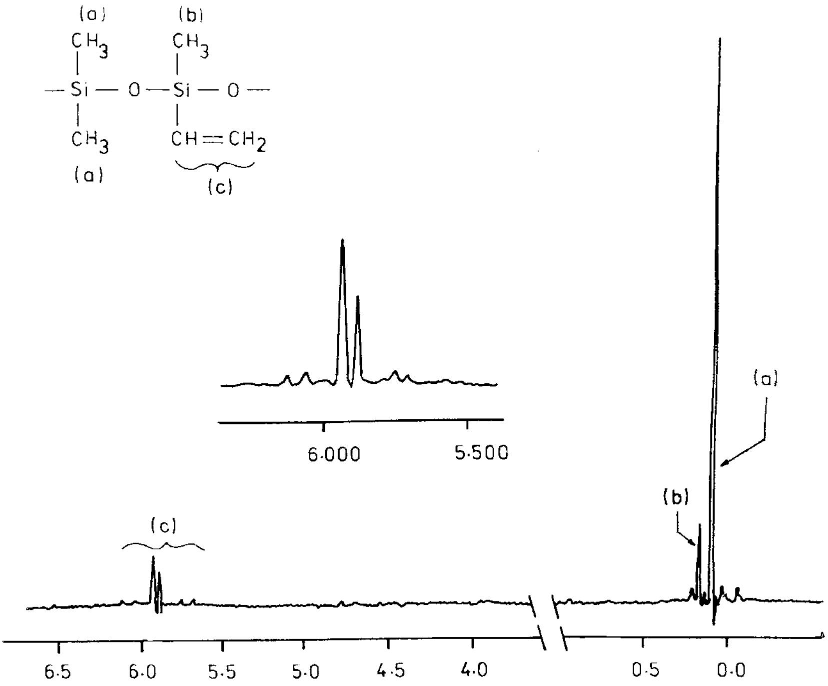

FIG. 1. ^{1}H-NMR spectrum of the C_{18} mixture (f_1 = 0.5) copolymerization after removing the catalyst.

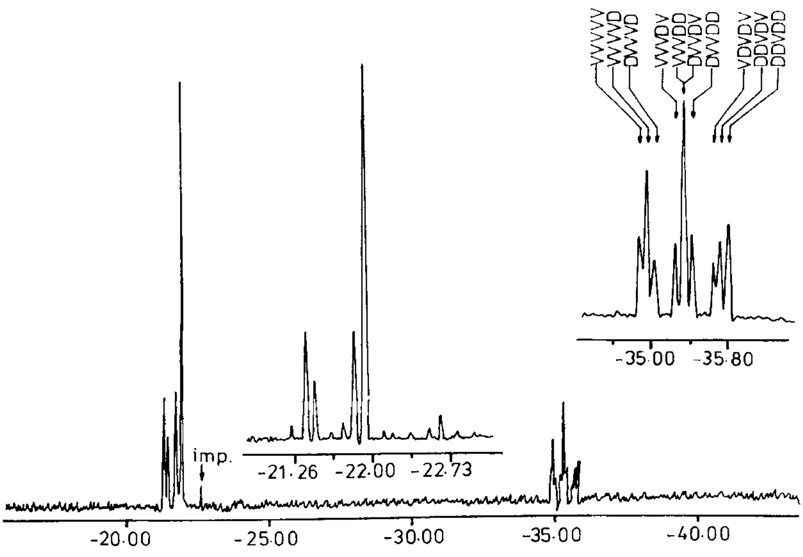

FIG. 2. ^{29}Si-NMR spectrum of the C_{18} mixture (f_1 = 0.5) copolymerization after removing the catalyst.

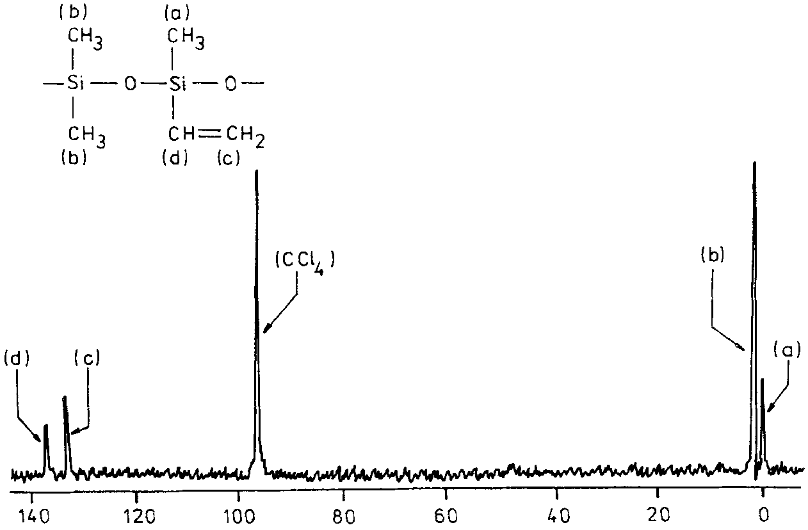

FIG. 3. ^{13}C-NMR spectrum of the C_{18} mixture ($f_1 = 0.5$) copolymerization after removing the catalyst.

cepted as being obeyed [17]. To determine the reactivity ratios, the Mayo-Lewis equation was transformed into

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \tag{5}$$

where r_1 and r_2 are reactivity ratios, f_1 and f_2 are the molar fractions of the two monomers (D_4 and V_4, respectively) in the initial mixture, and F_1 is the molar fraction of dimethylsiloxy units in the copolymer.

Determination of reactivity ratios involves use of the nonlinear least squares method. A computer program [18] based on f_1 and F_1 values was employed. It displayed the two values of the reactivity ratios ($r_1 = 2.698$ and $r_2 = 0.423$), a table of molar fractions (F_1), the experimental (F_{1e}) and calculated values (F_{1c}) (Table 2), as well as the value of the determination coefficient ($R^2 = 0.9985$).

A copolymerization diagram (Fig. 4) showing the experimental points was also plotted.

The ^{29}Si-NMR spectra of the copolymers show two groups of signals, corresponding to the two monomer units, D and V [3] (Table 3).

At the pentad level, nine visible signals can be attributed to each group and to ten different sequences [19] (Fig. 5).

TABLE 2. Experimental Values (F_{1e}) and Values Calculated from Eq. (5), (F_{1c})

F_{1e}	0.22	0.37	0.52	0.64	0.73	0.80	0.85	0.90	0.97
F_{1c}	0.213	0.383	0.520	0.631	0.722	0.797	0.861	0.914	0.960

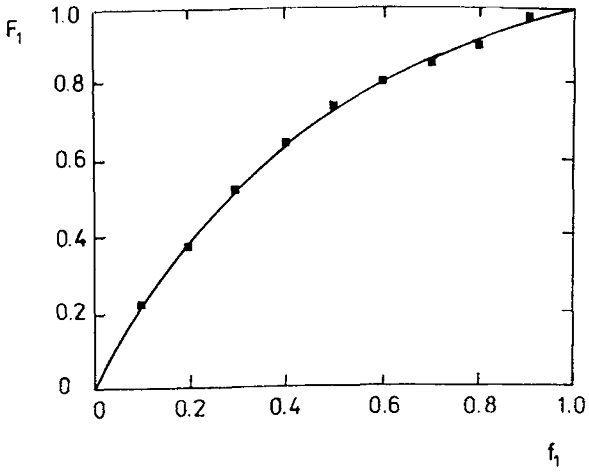

FIG. 4. Copolymerization diagram (based on data from Eq. 5 and Table 1).

The copolymer microstructure can be quantitatively described by calculating such parameters as copolymer composition (F_1, F_2), average length of the sequences ($\bar{l}_D$, $\bar{l}_V$), and the calculated (R_{th}) and experimental (R) run number values [8].

The ^{29}Si-NMR spectra of the C_{16}, C_{18}, C_{20}, C_{21}, and C_{24} samples were recorded on an AC-80-Bruker apparatus having the following characteristics:

Frequency: 19.20 MHz
Proton maximum decoupling
$CDCl_3$ as internal lock
Pulse width: 4.3 μs
Pulse delay: 5.720 s
Spectral width: 4760 Hz
Number of data points: 32 K
Samples: 30% in CCl_4
$Cr(AcAc)_3$ (0.8%) added as relaxation agent
TMS as internal reference standard
Room temperature recording

The microstructure parameters were calculated based on some statistical considerations and intensity measurements at the triad level [3, 11, 20]:

$$R_V = f_V F_2 \times 100 \tag{6}$$

$$R_D = f_D F_1 \times 100 \tag{7}$$

$$R = R_V = R_D \tag{8}$$

f_D and f_V are integral factors for D and V units, respectively, and may be calculated with

$$f_{D,V} = \frac{1}{0.5 + \frac{F_0^*}{F_1^*}} \tag{9}$$

TABLE 3. Experimental Chemical Shifts in Copolymers

	δ^b (ppm) for D-centered pentads					δ^b (ppm) for V-centered pentads				
Sequence[a]	C_{16}	C_{18}	C_{20}	C_{21}	C_{24}	C_{16}	C_{18}	C_{20}	C_{21}	C_{24}
22						−35.83	−35.79	−35.81		
21			−20.91	−20.87				−35.74	−35.72	
20			−20.99					−35.67		−35.64
12			−21.28		−21.30		−35.42	−35.45		
11		−21.37	−21.39	−21.38		−35.39	−35.34	−35.37	−35.34	
10	−21.41	−21.47	−21.47					−35.27		−35.19
02					−21.77					
01		−21.84	−21.87			−34.99	−34.95	−34.97	−34.95	
00	−21.97	−21.94	−21.95	−21.92				−34.90		−34.01

[a] Corresponding to Fig. 5.

[b] Chemical shift.

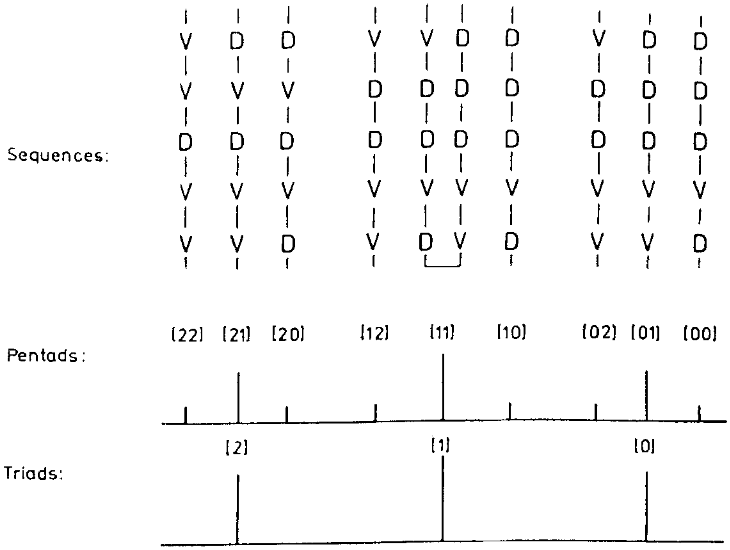

FIG. 5. ^{29}Si-NMR spectrum pattern for a vinylmethyldimethylsiloxanic copolymer [8].

or

$$f_{\mathrm{D,V}} = \frac{4}{2 + \dfrac{F_1^*}{F_2^*}} \tag{10}$$

where F_0^*, F_1^*, and F_2^* are integral fractions, corresponding to triads 0, 1, and 2, respectively (Fig. 5).

The theoretical run number, R_{th}, is calculated using Eq. (11):

$$R_{\mathrm{th}} = \frac{100F_1 \cdot 100F_2}{50} \tag{11}$$

Comparison of the R and R_{th} values permits some conclusions to be drawn on the way the two monomers are linked in the chain:

$R < R_{\mathrm{th}}$: tendency to form blocks
$R = R_{\mathrm{th}}$: random copolymerization
$R > R_{\mathrm{th}}$: tendency to alternate

Using R values, one can calculate the average length of the sequences:

$$\bar{l}_{\mathrm{D}} = \frac{2F_1 \times 100}{R} \tag{12}$$

$$\bar{l}_{\mathrm{V}} = \frac{2F_2 \times 100}{R} \tag{13}$$

and the conditional probabilities at the triad level [10]:

TABLE 4. Microstructure Parameters of Vinylmethyl-dimethylsiloxane Copolymers with Various Compositions, Calculated from ^{29}Si-NMR Spectra

Parameter	C_{21}	C_{20}	C_{18}	C_{16}	C_{24}
F_1[a]	37.66	50.68	71.11	79.18	90.47
F_2[a]	62.34	49.32	28.89	20.82	9.530
f_D[b]	0.416	0.571	0.734	0.720	0.796
f_V[b]	0.768	0.565	0.293	0.188	0.084
R_D[c]	28.92	28.63	20.83	14.88	7.590
R_V[c]	25.93	28.16	21.20	14.99	7.580
R_{th}[c]	46.95	49.99	41.08	32.97	17.24
$\bar{l}_D$[d]	2.746	3.570	6.769	10.61	23.87
$\bar{l}_V$[d]	4.547	3.474	2.750	2.789	2.510
$P_{(D/D)}$[e]	0.636	0.719	0.852	0.906	0.958
$P_{(V/D)}$[e]	0.364	0.281	0.148	0.094	0.042
$P_{(D/V)}$[e]	0.220	0.288	0.364	0.359	0.398
$P_{(V/V)}$[e]	0.780	0.712	0.636	0.641	0.602

[a] F_1 and F_2 = molar fractions of dimethyl- and vinylmethylsiloxane units, respectively in the copolymer.

[b] f_D and f_V = integral factors for D and V units, respectively.

[c] R_D, R_V, and R_{th} = run numbers.

[d] $\bar{l}_D$ and $\bar{l}_V$ = average lengths of the sequences.

[e] $P_{(D/D)}$, $P_{(V/D)}$, $P_{(D/V)}$, and $P_{(V/V)}$ = conditional probabilities.

$$P_{(D/D)} = \frac{100F_1 - \frac{R}{2}}{100F_1} \tag{14}$$

$$P_{(V/V)} = \frac{100F_2 - \frac{R}{2}}{100F_2} \tag{15}$$

$$P_{(V/D)} = \frac{R}{2F_1 \times 100} \tag{16}$$

$$P_{(D/V)} = \frac{R}{2F_2 \times 100} \tag{17}$$

The results obtained are presented in Table 4.

Since in each case $R < R_{th}$, we can recognize the tendency to form blocks during copolymerization. From the variation of the R values it can be noticed that the more the dimethylsiloxane groups content in the initial mixture increases, the higher the block character of the copolymer becomes. This means that the dimethylsiloxane units have a higher tendency to form blocks, while vinylmethylsiloxane block formation is less favourable because of the reduced reactivity of V_4 in acid medium. The electronegative effect of the vinyl substituent at the silicon atom of the cyclic tetramer leads to an increase of Si electropositivity in the siloxane unit of the monomer and a decrease of the electronic density on the oxygen atom [21]. A result of this effect is a decrease in V_4 reactivity compared to D_4 in acid medium. The steric factor probably also has some influence.

CONCLUSIONS

Nonequilibrium D_4 and V_4 copolymerization in heterogeneous acid catalysis was performed.

The reactivity ratios of the two monomers, r_1 and r_2, were calculated on the basis that the copolymerization reactions are irreversible.

The microstructure parameters of the obtained copolymers were determined from the ^{29}Si-NMR spectra at low conversions of the monomers, and they showed a strong tendency to form dimethylsiloxane blocks separated by vinylmethylsiloxane units.

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