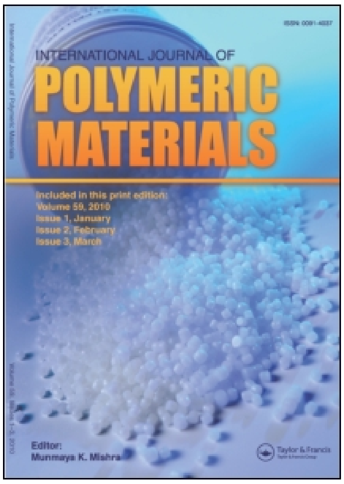

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Calorimetric Investigations of Anion Polymerization of Thienylmethylcyclotetrasiloxanes

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The kinetics of anionic polymerization of thienylmethylcyclotetrasiloxane with tetramethylammonium hydroxide has been studied. The polymerization mechanism is presented. It is shown that the kinetic curves are well described within the frames of the considered mechanism.

The numerical values of the reaction rate constants for different stages of polymerization are determined.

KEY WORDS Anionic polymerization calorimetry thienylmethylcyclotetrasiloxanes

EXPERIMENTAL

The kinetics of polymerization was studied using an isometric differential calorimeter DAK-I-I.

The heat change was measured by the registration of electromotive force using thermobatteries.

The calorimeter constants were $P/g = 6.3\ 10^{-2}$–$6.8\ 10^{-2}$ J/mole sec $M/g = 9.4$–11.3 J/mole.

The heat change was calculated by the Tiane formula:

$$W = B\Delta + c\frac{d\Delta}{dt}$$

The polymerization was carried out in a 50 mm length and 8.6 mm diameter glass tube. In addition a thin-wall glass ball full of catalyst was fastened to a special calorimeter syringe. This syringe is put into the glass tube containing the cycle and solvent.

The syringe with long pivot is extended out of the calorimeter, which allows us to break the glass ball after the temperature program is set and the calorimeter is in the working range. This allows us to fix the exact start of polymerization.

RESULTS AND DISCUSSION

In the present paper the kinetics of anionic polymerization of heptamethylthienylcyclotetrasiloxanes (D_3D^{Th}) and tetrathienyl-tetramethylcyclotetrasiloxanes (D_4^{Th}) by the calorimetric method is studied. The initial thienylmethylcyclotetrasiloxanes were synthesized using the method of Reference 1. The kinetics of polymerization of the obtained cycles was studied using the method of isothermal calorimetry by the apparatus DAK-I-I.

The kinetics of heat change in the process of polymerization in the presence of different quantities of initiator (tetramethylammonium hydroxide) is given in Figure 1.

The heat change during the polymerization process can be expressed in terms of the produced polymer:

$$Q = q_1(P) + q_2(P)$$

where Q is the experimentally observed heat change; q_1 is the heat effect of polymerization, p is the quantity of produced polymer and $q_2(P)$ is the heat effect of possible side reactions.

In order to find the values of q_1, and to estimate the values of $q_2(P)$, together with the calorimetric measurements (with different quantities of initiator) the quantities of produced polymer were determined.

Results are given in Table I. From Table I it is easy to see that the values of Q have a linear dependence on polymer quantities. This means that the effect of $q_2(P)$ in the polymerization process is negligible.

The kinetic curves of the degree of change *versus* time for different concentrations of initiator are given in Figure 2.

From these curves it is easy to see that the polymerization in the presence of

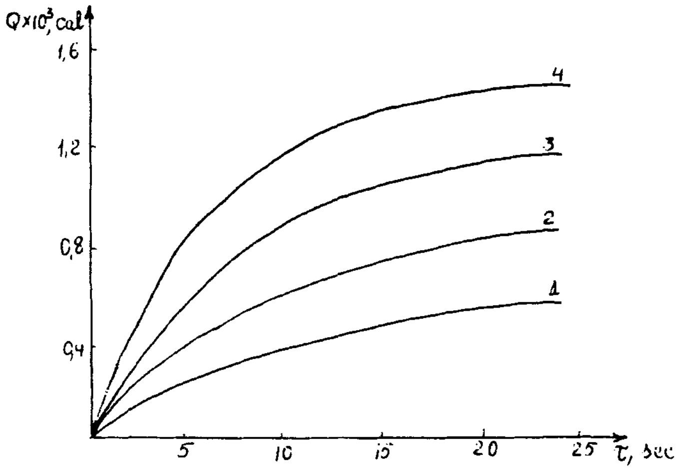


FIGURE 1 Kinetic curves of heat change for different initiator concentrations (mole/l): 1) 0.12; 2) 0.17; 3) 0.22; 4) 0.45; M_0 = 2 mole/l; T_0 = 60°C.

TABLE I

The influence of initial conditions of polymerization on the values of heat change, reaction rate and polymer quantities

Monomer	Catalyst concentration mole/l	Initial reaction rate mole/l, min	Polymer quantity $P \times 10^3$ mole	Q 10^3, Cal	Heat effect of polymer Cal/mole
D^3D^{Th}	0.38	0.78	1.2	1.07	900 ± 200
	0.3	0.72	1.09	0.96	
	0.22	0.64	0.91	0.80	
	0.15	0.56	0.61	0.55	
	0.08	0.4	0.42	0.43	
	0.05	0.3	0.14	0.14	
	0.022	0.15	0.1	0.10	
D_4^{Th}	0.38	0.16	1.03	16	16,000 ± 1000
	0.22	0.125	0.87	13.7	
	0.08	0.07	0.54	8.1	
	0.022	0.024	0.255	4.2	

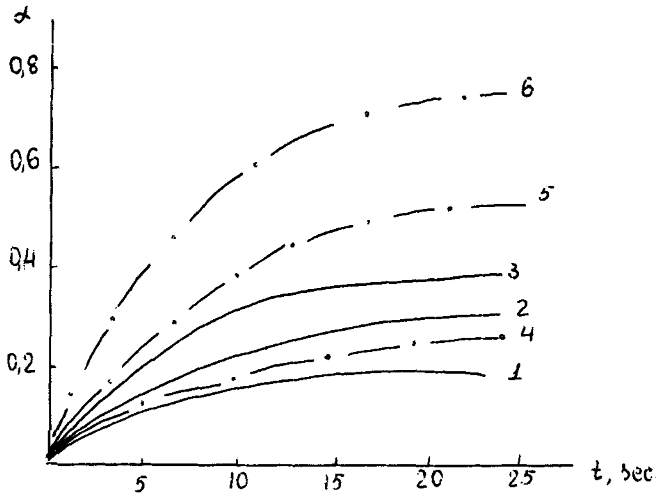


FIGURE 2 Kinetic curves of polymerization of D^3D^{Th} (curves 1, 2, 3) and D_4^{Th} (curves 4, 5, 6) for the different concentrations of initiator (mole/l): 0.08; 0.22; 0.33; T_0 = 60°C; M_0 = 1.34 mole/l.

tetramethylammonium hydroxide takes place without an induction period and an increase in catalyst concentration causes an increase in the initial rate of polymerization as well as the limit of the degree of conversion.

The observed maximal rates of polymerization at the beginnings of curves can be connected either with instant initiation, i.e., very quick production of active centers of polymerization (the time of active center production is shorter than the total time of polymerization) or with the fact that in the active centers of polymerization the quasistationary concentration in the presence of slow initiation is established.

The dependence of the reaction rate of polymerization *versus* the initiator concentration is given in Figure 3.

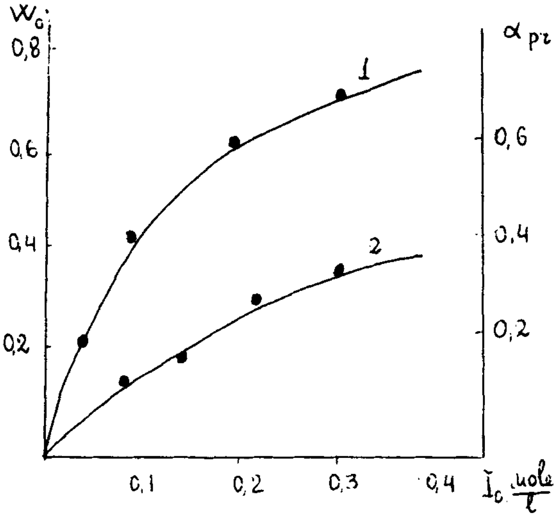
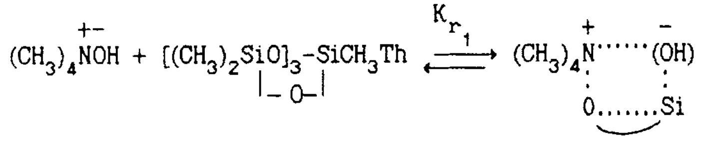


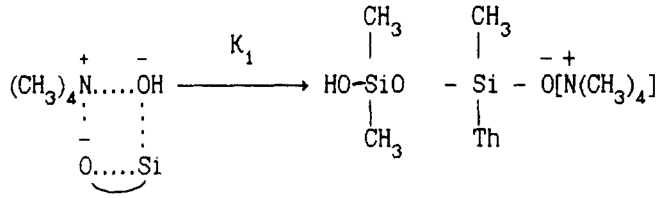
FIGURE 3 The dependence of initial polymerization rate of D^3D^{Th} versus initial concentrations of initiator (curve 1) and the dependence of initial concentration of initiator on the limit depth of conversion (curve 2).

From Figure 3 one can see, that the formal order of reaction depends on initiator concentration and varies from 1 to 0.

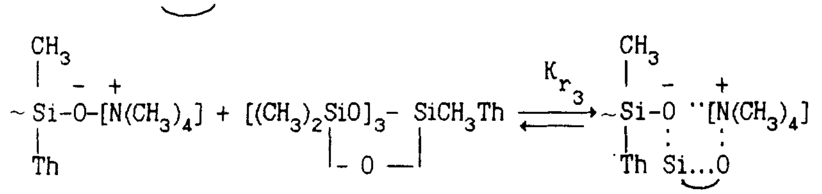
So, based on the results, the mechanism of thienylmethylcyclotetrasiloxane polymerization with tetramethylammonium hydroxide can proceed by the reactions:



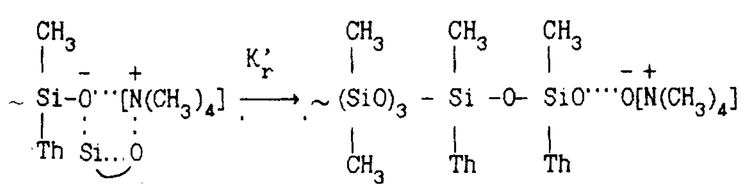
$$(CH_3)_4\overset{+-}{N}OH + \underset{|-O-|}{[(CH_3)_2SiO]_3\text{-}SiCH_3Th} \overset{K_{r_1}}{\rightleftarrows} \underset{O\ldots\ldots Si}{(CH_3)_4\overset{+}{N}\cdots\cdots\overset{-}{(OH)}} \qquad (1)$$



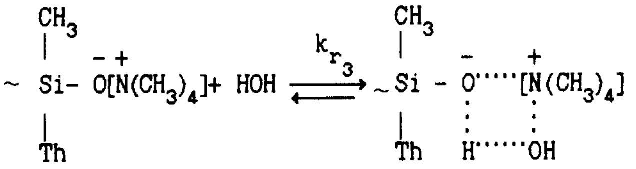
$$\underset{\overset{-}{O}\ldots\ldots Si}{(CH_3)_4\overset{+}{N}\ldots\ldots\overset{-}{O}H} \xrightarrow{K_1} HO\text{-}\underset{CH_3}{\overset{CH_3}{Si}}O - \underset{Th}{\overset{CH_3}{Si}} - \overset{-+}{O[N(CH_3)_4]} \qquad (2)$$



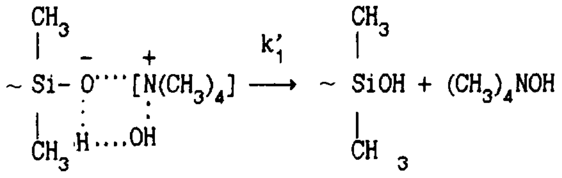
$$\sim\underset{Th}{\overset{CH_3}{Si}}\text{-}\overset{-\ +}{O\text{-}[N(CH_3)_4]} + \underset{|-\ O\ -|}{[(CH_3)_2SiO]_3\text{- }SiCH_3Th} \overset{K_{r_3}}{\rightleftarrows} \sim\underset{Th\ \ Si\ldots O}{\overset{CH_3}{Si}\text{-}\overset{-}{O}\cdots\overset{+}{[N(CH_3)_4]}} \qquad (3)$$



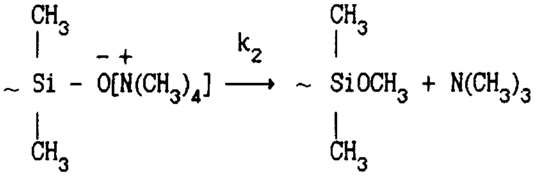
$$\sim\underset{Th\ \ Si\ldots O}{\overset{CH_3}{Si}\text{-}\overset{-}{O}\cdots\overset{+}{[N(CH_3)_4]}} \xrightarrow{K_r'} \sim(\underset{CH_3}{\overset{CH_3}{Si}}O)_3 - \underset{Th}{\overset{CH_3}{Si}}\text{ -O- }\underset{Th}{\overset{CH_3}{Si}}O\cdots\overset{-+}{O[N(CH_3)_4]} \qquad (4)$$



$$\sim \underset{\mathrm{Th}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\overset{-}{\mathrm{O}}[\overset{+}{\mathrm{N}}(\mathrm{CH_3})_4] + \mathrm{HOH} \overset{k_{r_3}}{\rightleftarrows} \sim \underset{\mathrm{Th}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\overset{-}{\mathrm{O}}\cdots[\overset{+}{\mathrm{N}}(\mathrm{CH_3})_4] \quad \mathrm{H}\cdots\mathrm{OH} \qquad (5)$$



$$\sim \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\overset{-}{\mathrm{O}}\cdots[\overset{+}{\mathrm{N}}(\mathrm{CH_3})_4] \quad \mathrm{H}\cdots\mathrm{OH} \xrightarrow{k'_1} \sim \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{SiOH}}} + (\mathrm{CH_3})_4\mathrm{NOH} \qquad (6)$$



$$\sim \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\overset{-}{\mathrm{O}}[\overset{+}{\mathrm{N}}(\mathrm{CH_3})_4] \xrightarrow{k_2} \sim \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{SiOCH_3}}} + \mathrm{N(CH_3)_3} \qquad (7)$$

where k_{r_1}, k_{r_2}, k'_r, k_{r_3}, K_1, K_2, and K_i are the rate constants of the corresponding reactions.

For convenience we will use the following notations: I = initiator, A^* = active center of polymerization, X = admixture (H_2O), M = monomer, A = deactivated form of the macromolecules, (IM), (A^*M) and (A^*X) the corresponding complex forms.

Using the principle of detailed equilibrium one has:

$$(IM) = k_{r_1} IM; \qquad (A^*M) = k_{r_2} A^*M; \qquad (A^*X) = k_{r_3} A^*X \tag{8}$$

Using Equation (8), the changes in monomer concentration, active macromolecules and initiator in reactions (1)–(7) can be written as:

$$\frac{dI}{dt} = -k_i IM + k_1 A^*X \tag{8'}$$

$$\frac{dA^*}{dt} = k_i IM - k_1 A^*X - k_2 A^* \tag{9}$$

$$\frac{dM}{dt} = k_r A^*M + k_i IM \tag{10}$$

In Equations (8)–(10) we have used the following notations: $k_i = k'_i k_{r_1}$; $k_r = k'_r k_{r_2}$; $k_1 = k'_1 k_{r_3}$.

Using the principle of quasistationary concentrations, from Equation (9) one gets:

$$A^* = \frac{k_i MI}{k_1 X + k_2} \tag{11}$$

Assuming, that the admixtures (water) gets into the polymerization system mainly with the initiator, i.e., their quantities are proportional to the initial concentration of initiator $(I_0)_x = \beta I_0$ from Equation (11) we have

$$A^* = \frac{k_i MI}{k_1 \beta I_0 + k_2} \tag{11'}$$

where β is the proportionality coefficient.

Using Equation (11) and taking into account that $M = M_0(1 - \alpha)$ (where M_0 is the initial concentration of monomer and α is the degree of conversion) from Equations (8) and (10) we will have:

$$\frac{dI}{dt} = \frac{k_i k_2 I M_0(1 - \alpha)}{k_1 \beta I_0 + k_2} \tag{12}$$

$$\frac{d\alpha}{dt} = k_i I(1 - \alpha) + \frac{k_r k_i I M_0(1 - \alpha)^2}{k_1 \beta I_0 + k_2} \tag{13}$$

From Equation (13) for the initial polymerization rate (i.e., for $t = 0$) one gets:

$$\left.\frac{d\alpha}{dt}\right|_{t=0} = W_0 = k_i I_0 + \frac{k_r k_i I_0 M_0}{k_1 \beta I_0 + k_2} \tag{14}$$

For the sake of comparison with experimental data we will rewrite Equation (14) in the following form:

$$\frac{I_0}{W_0} = \frac{k_1 \beta I_0}{(1 + k_r M_0)k_i} + \frac{k_2}{(1 + k_r M_0)k_i} \tag{15}$$

To find an equation describing the evaluation of the degree of conversion over time let us divide Equation (13) into Equation (12):

$$\frac{d\alpha}{dt} = \frac{k_i I(1 - \alpha)(k_1 \beta I_0 + k_2) + k_r k_i I_0(1 - \alpha)^2}{k_i k_2 I M_0(1 - \alpha)} \tag{16}$$

The first term in the numerator can be neglected, because the monomer quantity required on initiation is very small in comparison with the one required for the polymerization reaction. Using this fact, from Equation (16) one obtains:

$$1 - \alpha = \exp\left(-\frac{k_r}{k_2}[I_0 - I]\right) \tag{17}$$

Assuming, that the initiator is used mainly at the beginning of the reaction from Equations (12) and (17) we can find:

$$I = I_0 \exp\left(-\frac{k_2 k_i M_0}{k_1 \beta I_0 + k_2}\right) \tag{18}$$

Now using (18) from Equation (17) we get

$$1 - \alpha = \exp\left[-\frac{k_r}{k_2} I_0 \left(1 - \exp\left(-\frac{k_2 k_i M_0}{k_1 \beta I_0 + k_2} t\right)\right)\right] \tag{19}$$

To compare with the experimental data we have to rewrite Equation (19) in the following way:

$$-\ln\left(\frac{\ln(1 - \alpha)}{I_0 k_r / k_2} + 1\right) = \frac{k_2 k_i M_0}{k_1 \beta I_0 + k_2} t \tag{20}$$

And finally for the limit of degree of conversion, i.e., for $t \to \infty$ from Equations (17) and (19) we have:

$$-\ln(1 - \alpha_{pr}) = \frac{k_r}{k_2} I_0 \tag{21}$$

Now Equations (15), (20) and (21) obtained from reactions (1)–(7) can be compared with experimental data.

As seen from Figure 4, $\ln(1 - \alpha_{pr})$ is linearly dependent on the initial concentration of initiator and the value of k_r/k_2 is 0.6. Using this data for k_r/k_2, the value of the degree of conversion in the variables of Equation (20) can be compared with the kinetic curves for degree of conversion given in Figure 5.

From Figure 5, it can be seen that the kinetic curves of polymerization are in good agreement with Equation (20). All kinetic curves are cited on one line, because the change of initial concentration of monomer was very small and the change of initial concentration of initiator in the limits shown in Figure 5, influences very weakly the values of $k_2 k_i M_0/(k_1 \beta I_0 + k_2)$.

The value of $k_2 k_i M_0/(k_1 \beta I_0 + k_2)$ can be determined by the slope of the curve in Figure 5. It is equal to 0.036.

The comparison of the initial polymerization rates with Equation (15) is given

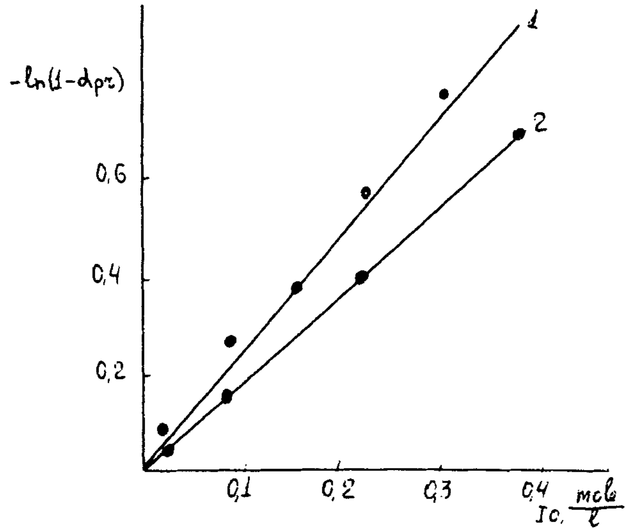


FIGURE 4 The dependence given in variables of Equation (29) for anion polymerization of D^3D^{Th} (curve 1) and D_4^{Th} (curve 2).

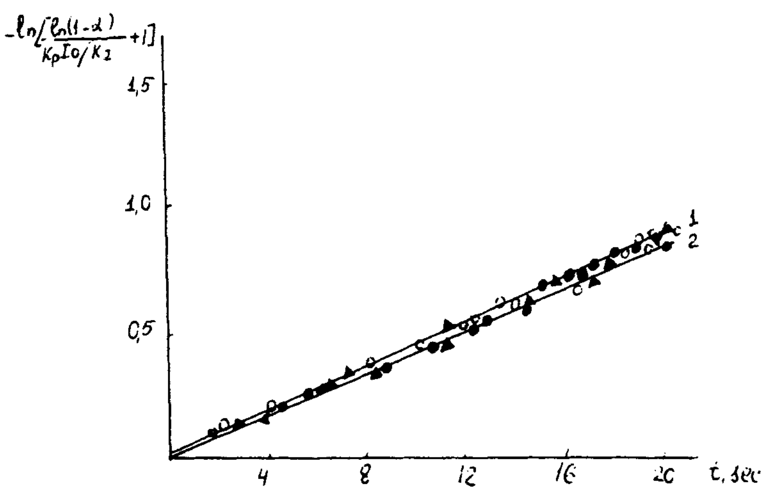


FIGURE 5 Linear dependence in variables of Equation (30) for anion polymerization of D^3D^{Th} (curve 1) and D_4^{Th} (curve 2).

in Figure 6. The values of $k_1\beta/(1 + k_rM_0)k_i$ and $k_2/(1 + k_rM_0)k_i$ determined from Figure 6 are 0.13 and 1. The comparison of

$$k_r/k_2, \quad \frac{k_2k_iM_0}{k_1\beta I_0 + k_2}, \quad \frac{k_1\beta}{1 + k_rM_0}, \quad \frac{k_2}{(1 + k_rM_0)k_i},$$

allows us to determine the values of constants: $k_i = 0.046$ (mole/l sec), $k_r = 0.0036$ (mole/l sec), $k_1 = 0.04$ (mole/l sec), $k_2 = 0.006$ (1/sec).

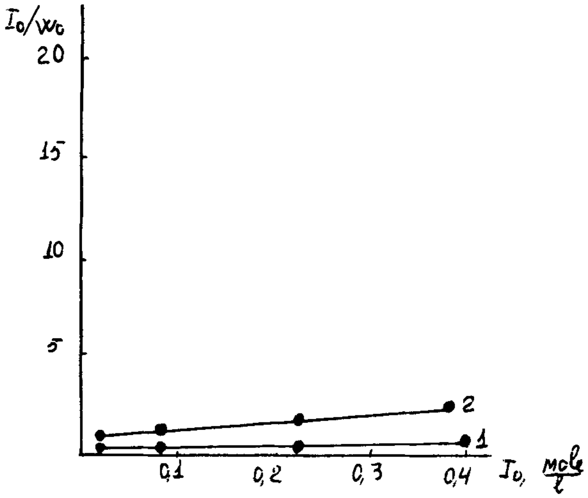


FIGURE 6 Linear dependence in variables of Equation (31) for anion polymerization of D^3D^{Th} (curve 1) and D_4^{Th} (curve 2).

So the kinetics of anionic polymerization of heptamethylthienylcyclotetrasiloxane is well described quantitatively by the equations taking into account the reactions of initiation, growth, bimolecular conveying and monomolecular chain breaking.

Note, that polymerization of thienylmethylcyclotetrasiloxane in toluene leads to a lowering of the initial reaction rate and to growth in the degree of conversion. This fact shows, not only that bimolecular chain breaking exists, but also monomolecular, which is of physical nature.

So, based on the results, the general scheme of anionic polymerization of thienylmethylcyclotetrasiloxanes can be written as:

$$I + M \overset{k_{r_1}}{\rightleftarrows} (IM) \tag{22}$$

$$(IM) \xrightarrow{k_i'} A^* \tag{23}$$

$$A^* + M \xrightarrow{k_{r_2}} (A^*M) \tag{24}$$

$$(A^*M) \xrightarrow{k_r} A^* \tag{25}$$

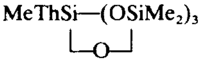
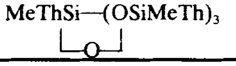
$$A^* + X \overset{k_{r_3}}{\rightleftarrows} (A^*X) \tag{26}$$

$$(A^*X) \xrightarrow{k_1'} A \tag{27}$$

$$A^* \xrightarrow{k_2} A \tag{28}$$

TABLE II

The values of kinetic constants for studied thienylmethylcyclotetrasiloxanes

Notations	Cycle	k_ik_r	$k_rk_r\beta_2$	$k_1k_{r_3}\beta$	k_2
D^3D^{Th}	 MeThSi—$(OSiMe_2)_3$	0.081	0.036	0.46	0.055
D_4^{Th}	 MeThSi—$(OSiMeTh)_3$	0.054	0.096	0.25	0.052

where I is the initiator, A^* is the active center of polymerization, X is admixture (H_2O), M is monomer and A is the deactivated form of the macromolecules.

Reaction (24) consists of two stages. The first is the monomolecular reaction of initial initiator restoration, and the second is the bimolecular reaction of silane group recombination.

From (22)–(28), assuming that the admixtures (water) get into the polymerization system mainly with the initiator, i.e., $(I_0)_x = \beta I_0$ we have:

$$-\ln(1 - \alpha_{pr}) = \frac{k_p k_{p_2}}{k_2} I_0 \tag{29}$$

$$\frac{I_0}{W_0} = \frac{k_i k_{p_3} \beta I_0}{(1 + k_p k_{p_2} M_0) k_i} + \frac{k_2}{(1 + k_p k_{p_2} M_0) k_i} \tag{30}$$

$$-\ln\left(\frac{\ln(1 - \alpha)}{k_r k_{r_2}/k_2} I_0 + 1\right) = \frac{k_2 k_i k_{r_i} M_0}{k_1 k_{p_3} \beta I_0 + k_2} t \tag{31}$$

where α_{nr} is the limit to degree of conversion, β is the proportionality coefficient, I_0 and M_0 are the initial concentrations of initiator and monomer, α is the degree of conversion and t is time.

As can be seen from Figures 4 and 5, for both cycles the dependence of limit of degree of conversion and initial polymerization rate on initial concentration is well described by Equations (26) and (27). Using the value of $k_r k_{r_2}/k_2$, we can compare the kinetic curves of polymerization obtained for different initial conditions with Equation (28). Figure 6 shows that Equation (28) describes well all these kinetic curves. The values of the kinetic constants of the reactions determined by the slope of the curves given in Figure 6 are given in Table II.

Note, that the results obtained allow us to conclude, that the mechanism of anionic polymerization of thienylmethylcyclotetrasiloxanes given here is quite general.

CONCLUSION

A calorimetric investigation of the anionic polymerization of thienylmethylcyclotetrasiloxane with the nucleophilic initiator $(CH_3)_4NOH$ is explored. The kinetic scheme of the process which describes quantitatively the kinetic curves quite well is proposed.

The values of the reaction constants are determined.

Reference

1. L. M. Khananashvili, E. A. Chernishev, Ts. N. Vardosanidze, E. G. Markarashvili, M. L. Kantaria and V. I. Savushkina, *Labartkava M.O.—J. of Organic Chem.*, **53**, 1575–1578 (in Russian).