Cross-Aggregation of Active Centers in a Model Anionic Polymerization System. The Kinetics of the Reactions of Silanolates with Cyclic and Linear Polysiloxanes[36]

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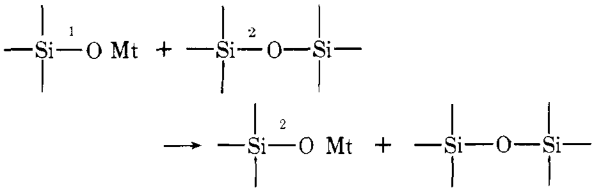
ABSTRACT: A general approach to the kinetic analysis of reactions involving reversible ion-pairs aggregation was developed for the case when both substrate A and product B form strong one-component aggregates and consequently they form also mixed two-component aggregates (cross-aggregates). A case in which the state of the aggregation is such that only aggregates $(A_{n-m}B_m)[m = 0, 1, 2, \ldots, n]$ of the same multiple n are to be considered may be related to an ideal case giving rise to first-order kinetics with respect to A. The value of the kinetic analysis for some more complex cases in terms of the first-order coordinates is also explained. The analysis may be extended to processes in which the concentration of aggregating species is not changed during the course of the reaction. The analysis has been successfully applied to the reaction of potassium phenyldimethylsilanolate with cyclic or linear polysiloxane oligomers which may serve as models of the component reactions of anionic polymerization of siloxanes. The results provide evidence of the interaction of the siloxane chain with an alkali metal counterion in free polysiloxanolate and in polysiloxanolates which are a part of aggregates. The analysis has also been applied in studies of the rate of the propagation step in anionic polymerization of siloxanes in the presence of mixtures of sodium and potassium siloxanolates.

All component processes in anionic polymerization of siloxanes may be, in principle, brought to a simple reaction between silanolate and siloxane groups.[1,2,3]



$$-\overset{|}{\underset{|}{\mathrm{Si}}}{}^{1}-\mathrm{O\,Mt} + -\overset{|}{\underset{|}{\mathrm{Si}}}{}^{2}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}{}^{2}-\mathrm{O\,Mt} + -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- \qquad (1)$$

Mt = alkali metal

The role of the silanolate group is versatile. This group at the end of a growing polysiloxane chain acts as an active propagation center in the opening of the siloxane bond in a monomer and it participates in chain transfer or depolymerization when the siloxane bond constitutes a part of a polymer chain. Reaction 1 may also represent the initiation step when a simple low molecular weight silanolate is used. Silanolate groups are known to be strongly self-associated in media in which the polymerization is usually carried out.[4–7] This ion pair aggregation determines the kinetics of the anionic polymerization of siloxanes and if this phenomenon is ignored in the kinetic analysis of the process it may lead to a serious misinterpretation of the kinetic data. The studies done so far lead to the conclusion that free silanolate groups are active while silanolate in the aggregate constitutes a dormant center.[4–6] The reaction presented by (1) is thus a complex process composed of rapidly established equilibria of aggregate formation followed by the rate-determining step of opening of the siloxane bond by a free silanolate ion pair. When two different ion-pair species are involved (e.g., a silanolate group in the initiator and a silanolate group at the end of the macromolecule), the reaction may take a more complicated course as cross-aggregates appear. The kinetic analysis of these kinds of processes has been worked out only in part.[4] A more general approach would be of value because the processes involving cross-aggregation include some component reactions of many important polyreaction systems like anionic polymerization of diene and vinyl monomers initiated with a lithium catalyst[8–10] and anionic polymerization of oxiranes and some other heterocycles.[11–13] We hope that the approach we have developed using the reaction of silanolate with siloxanes as a model may gain some more general application as it permits the molecular interpretation of the kinetic results.

Approach to the Kinetic Analysis

Reaction Involving an Ideal Series of Cross-Aggregates. Among various states of aggregation involving two ion-pair species A and B we distinguish simple ones in which a series of strong aggregates $(A_{n-m}B_m)[m = 0, 1, 2, \ldots, n]$ of the same multiple n dominate over other aggregates. If uncomplexed substrate A_1 is the only reactive species, the reaction $A \rightarrow B$[26] proceeds according to the following scheme:

$$\begin{array}{lr} nA_1 \overset{\binom{n}{0}K_0}{\rightleftarrows} (A_n) & \\ \vdots & \\ (n-m)A_1 + mB_1 \overset{\binom{n}{m}K_m}{\rightleftarrows} (A_{n-m}B_m) & \begin{array}{l}[A_1] \ll [A] \\ [B_1] \ll [B]\end{array} \\ \vdots & \\ nB_1 \overset{\binom{n}{n}K_n}{\rightleftarrows} (B_n) & \end{array} \qquad (2)$$

$$A_1 + M \xrightarrow{k} B_1 \qquad \text{(rate determining)}$$

M = second substrate which appears in excess

Any case of a reaction involving a simple system of cross-aggregates may be related to a particular one which we call "ideal". This ideal system occurs when the exchange of one molecule of A for one molecule of B in each aggregate of the $(A_{n-m}B_m)$ series is accompanied by the same change of free enthalpy $\Delta\Delta G_{A\rightarrow B}$,[27] which is equivalent to (3) and (4)

$$K_m = (K_{m-1} \cdot K_{m+1})^{1/2} \qquad (3)$$

$$\Delta G_{(A_{n-m}B_m)} = \tfrac{1}{2}\{\Delta G_{(A_{n-m+1}B_{m-1})} + \Delta G_{(A_{n-m-1}B_{m+1})}\} \qquad (4)$$

Reaction 2 involving the ideal cross-aggregation system follows eq 5 of the first internal order and external order $1/n$ with respect to $[A]_0$.[4,8]

$$-\frac{d[A]}{dt} = \frac{k[M]}{(nK_0)^{1/n}} \frac{[A]}{[A]_0{}^{(n-1)/n}} \qquad (5)$$

$$[A] + [B] = [A]_0$$

Good examples are provided by the cross reaction of lithium styryl with an excess of 1,1-diphenylethylene in hexane (eq 6)[8] and by initiation of the polymerization of 2,2,5,5-tetra-

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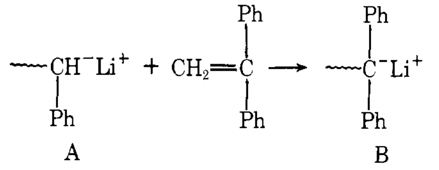
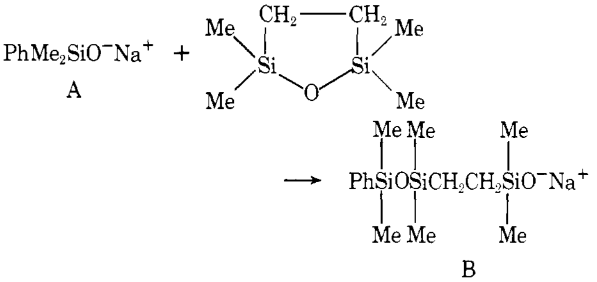
methyl-1-oxa-2,5-disilacyclopentane with sodium phenyldimethylsilanolate in heptane–dioxane 95:5 v/v solvent mixture (eq 7).[4] Both of them comply with eq 5 showing $n = 2$ and $n = 4$, respectively



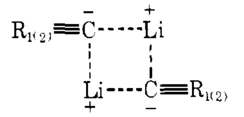
$$\sim\underset{\text{Ph}}{\text{CH}}{}^-\text{Li}^+ + \text{CH}_2{=}\underset{\text{Ph}}{\overset{\text{Ph}}{\text{C}}} \longrightarrow \sim\underset{\text{Ph}}{\overset{\text{Ph}}{\text{C}}}{}^-\text{Li}^+ \qquad (6)$$

A B

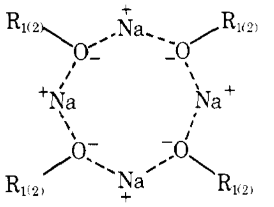


(7)

The bonding parts of aggregates forming the ideal series are expected to have the same structure and these will be of high degree of symmetry (eq 8). The change of A for B is then equivalent to change of substituents on the aggregate skeleton. These are conditions under which the formation of the series of $(A_{n-m}B_m)$ aggregates may be subjected to the linear free enthalpy relationship as required by the ideal cross-aggregation model.



R_1 = H, Ph, polystyrene chain
R_2 = Ph, Ph, polystyrene chain



(8)

R_1 = PhMe$_2$Si–
R_2 = polyethylenesiloxane chain

Reactions Involving Simple Nonideal Series of Cross-Aggregates. Binary Aggregates. Nonideal cross-aggregation in the simple series $(A_{n-m}B_m)$ is expected when either the binding fragment is changed in the series of aggregates or some other perturbation resulting in deviation from the linear free enthalpy relationship appears. The reaction represented by eq 2 for a nonideal system involving binary complexes (A_2), (AB), (B_2) is described by eq 9[28]

$$R = -\frac{d[A]}{dt} = \frac{k[M]}{(2K_0)^{1/2}}([A] - [(AB)])^{1/2} \qquad (9)$$

$$[A] + [B] = [A]_0$$

$$[(AB)] = \frac{[A]_0 - ([A]_0{}^2 - 4(1 - \xi)[A]([A]_0 - [A]))^{1/2}}{2(1 - \xi_1)} \qquad (9a)$$

$$\xi_1 \neq 1$$

Parameter ξ_1 is equal to the equilibrium constant of the formation of simple aggregates (A_2) and (B_2) from the cross-aggregate (AB) (eq 10) multiplied by a statistical factor 4 to allow for preferential formation of the cross-aggregates. For the ideal series $\xi_1 = 1$

$$2(AB) \overset{\xi_1/4}{\rightleftarrows} (A_2) + (B_2) \qquad (10)$$

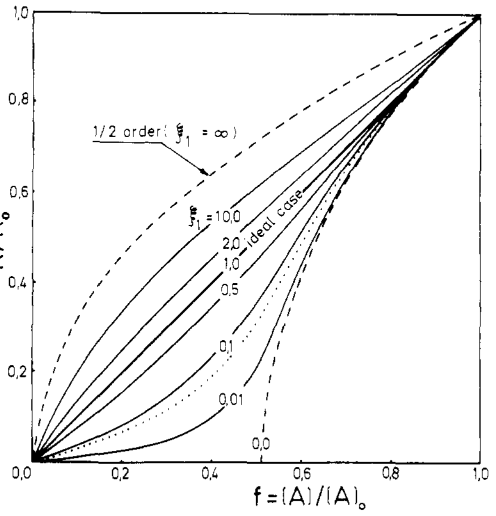


Figure 1. Variation of the relative rate (in relation to the initial rate) with change of the substrate fraction $f = [A]/([A] + [B]) = [A]/[A]_0$ for the reaction A → B involving the simple series of binary aggregates (A_2), (AB), (B_2). Curves illustrate also the variation of the relative concentration of uncomplexed species $[A_1]/[A_1]_0$ with the variation of the molar fraction $[A]/([A] + [B])$ in the (A_2), (AB), (B_2) aggregates system.

$$\xi_1 = K_0 \cdot K_2/K_1{}^2 \qquad (10a)$$

Parameter ξ_1 may serve as a convenient factor for characterization of the deviation from the ideal case and tendency for cross-aggregation. It unequivocally defines the shape of the kinetic curve in normalized plots, which is illustrated in Figures 1 and 2. The first of them represents the plot of the relative rate $R_{\text{rel}} = R/R_0$ vs. the fraction of unconverted substrate f. This function $R_{\text{rel}}(f)$ is described by eq 12, which was obtained by dividing eq 9 by eq 11 expressing the initial rate R_0 and by substituting $[A]/[A]_0 = f$, $[(AB)]/[A]_0 = [(AB)]_{\text{rel}}$

$$R_0 = k[M]([A]_0/2K_0)^{1/2} \qquad (11)$$

$$R_{\text{rel}}(f) = (f - [(AB)]_{\text{rel}})^{1/2} \qquad (12)$$

$$[B]_0 = 0, \quad \xi_1 \neq 1$$

$$[(AB)]_{\text{rel}} = \frac{1 - (1 - 4(1 - \xi_1)f(1 - f))^{1/2}}{2(1 - \xi_1)} \qquad (12a)$$

The function $R_{\text{rel}}(f)$ is important for two other reasons: (1) it corresponds to the relative concentration of uncomplexed species $[A_1]/[A_1]_0$ ($[A_1]_0$ is the concentration of uncomplexed A corresponding to the initial concentration of A and the concentration of B equal zero) as a function of the molar fraction $f = [A]/([A] + [B])$ and may be used in kinetic analysis of reactions involving cross-aggregation of the substrate with a component which does not appear in the stoichiometric equation; (2) it constitutes a base for simulation of the kinetic curves in other systems of coordinates.

Equations 9 and 12 have no analytical solution.[29] It may however be solved numerically to simulate kinetic curves in the normalized first-order plot. The normalization is done by multiplying the time scale by the initial first-order rate constant observed $(k_{\text{obsd}}{}^{\text{I}})_0 = k[M]/(2K_0[A]_0)^{1/2}$. The values of the integral $-\int_{f_0}^{f} df/R_{\text{rel}}(f)$ were calculated as a function of f (for each value of ξ_1 assumed). According to eq 13 derived from eq 9 or 12, the scale of the integral corresponds to the normalized time scale, so the dependence of the integral on f can be easily transformed to the first-order dependence ln $1/f$ vs. time scale in a normalized form. Simulated curves for various ξ_1 are shown in the Figure 2. The course of the reaction presented in this normalized plot is independent of the initial

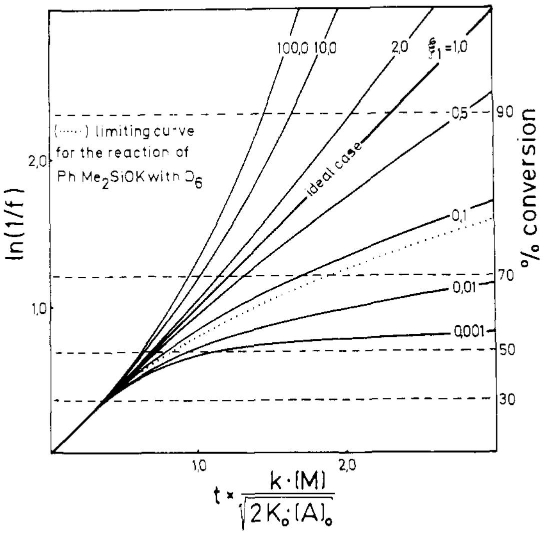


Figure 2. Simulated first-order kinetic curves with normalized time scale for the reaction A → B involving aggregates (A_2), (AB), (B_2).

specific rate and of the initial concentration of the substrate A

$$-\int_{f_0}^{f}\frac{df}{R_{rel}(f)} = \frac{k[M]}{(2K_0[A]_0)^{1/2}}\cdot t = (k_{obsd}{}^{I})_{t=0}\cdot t \qquad (13)$$

The characteristic feature of this plot is that the first portion of each curve, up to about 30% of conversion, is linear and to a good approximation superimposed on the line for the ideal case. Strong tendency to cross-association (equilibrium 10 lies to the left) which seems to be a common case[14–16,30] leads to $\xi_1 < 1$ and compared with the first-order run the reaction slows down as it proceeds. When $\xi_1 < 1$ the final parts of the first-order plot are also linear, as the reaction at high conversion of A approaches eq 14, which corresponds to eq 15 describing the process carried out with a large initial excess of the product B, e.g., $[B]_0 \gg [A]_0$

$$R = -\frac{d[A]}{dt} = \frac{kK_2{}^{1/2}[A]}{2^{1/2}K_1[A]_0{}^{1/2}}[M] \qquad (14)$$

if $[A]/[A]_0 \to 0$ and $[B]_0 = 0$

$$R = \frac{kK_2{}^{1/2}}{2^{1/2}K_1}[M]\frac{[A]}{[B]_0{}^{1/2}} \qquad (15)$$

if $[B]_0 \gg [A]_0$

Comparison of eq 14 and 13 (allowing for (10a)) leads to the conclusion that the ratio of slopes of the last portion and the first portion of the curve is equal to $r_{II}/r_I = \xi_1{}^{1/2}$. Hence ξ_1 may be easily determined from two experiments: one at $[B]_0 \gg [A]_0$ and one at $[B]_0 = 0$.

Ternary Complexes and Complexes of Higher Multiples. This approach may be extended to reaction involving simple series of aggregates with a multiple n larger than 2. The kinetic equation includes $n - 1$ parameters ($\xi_1, \xi_2, \ldots, \xi_{n-1}$) determining the shape of the kinetic curve in normalized first-order kinetic plots.[31] For example, the reaction involving ternary complexes (A_3), (A_2B), (AB_2), (B_3) follows eq 18 including two parameters ξ_1 and ξ_2 corresponding to constants of equilibria 16 and 17, respectively, each of them being multiplied by a statistical factor of 3.

$$2(A_2B) \overset{\xi_1/3}{\rightleftarrows} (A_3) + (AB_2) \qquad (16)$$

$$2(AB_2) \overset{\xi_2/3}{\rightleftarrows} (A_2B) + (B_3) \qquad (17)$$

if $[B]_0 = 0$ and $\xi_1 \neq 1$, $\xi_2 \neq 1$

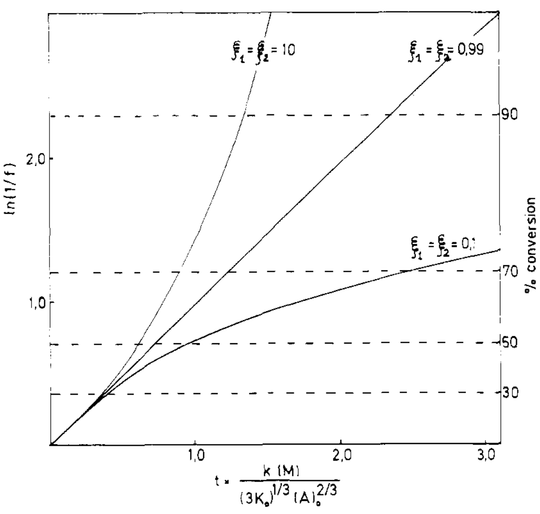


Figure 3. Simulated first-order kinetics curves with normalized time scale for the reaction involving ternary complexes in simple symmetrical cross-aggregation series (A_3), (A_2B), (AB_2), (B_3).

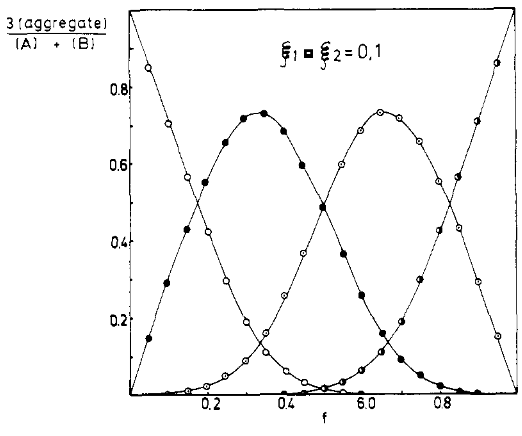


Figure 4. Relative concentration of complexes in the ternary system involving symmetrical cross-aggregation with $\xi_1 = \xi_2 = 0.1$: (◑) $3[(A_3)]/([A] + [B])$; (⊙) $3[(A_2B)]/([A] + [B])$; (●) $3[(AB_2)]/([A] + [B])$; (○) $3[(B_3)]/([A] + [B])$.

$$-\frac{df}{dt} = \frac{k[M]}{(3K_0)^{1/3}[A]_0{}^{2/3}}\{f - 2[(A_2B)]_{rel} - [(AB_2)]_{rel}\}^{1/3} = (k_{obsd}{}^{I})_0 R_{rel}(f) \qquad (18)$$

Relative concentrations of cross-aggregates (A_2B) and (AB_2) with respect to $[A]_0$ are determined by eq 19 and 20 which result from two balance equations (for A and B) and from equations for the constants of equilibria 16 and 17

$$\xi_1[(A_2B)]^2_{rel} - f\cdot[(AB_2)]_{rel} + 2[(AB_2)]_{rel}\cdot[(A_2B)]_{rel} + [(AB_2)]^2_{rel} = 0 \qquad (19)$$

$$\xi_2[(AB_2)]^2_{rel} - (1 - f)[(A_2B)]_{rel} + 2[(AB_2)]_{rel}[(A_2B)]_{rel} + [(A_2B)]^2_{rel} = 0 \qquad (20)$$

An analogous procedure to that used in the case of binary complexes allows the simulation of kinetic curves in a normalized first-order plot. Simulated curves for some pairs of ξ_1 and ξ_2 values are presented on Figures 3 and 5. Again the first portions of the lines are linear and to a good approximation superimpose on the lines for the case of ideal cross-aggregation.

Relative concentrations of the respective complexes as functions of the conversion of the reagent A are also calculated by this procedure. Some examples are presented in Figures 4 and 6.

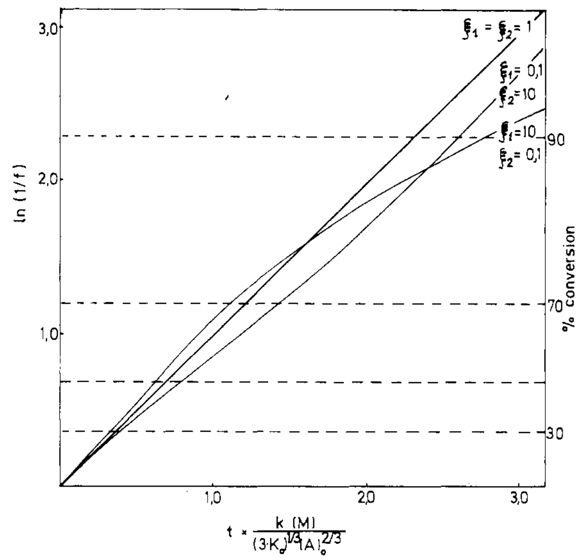


Figure 5. Simulated first-order kinetics curves with normalized time scale for the reaction involving ternary complexes (A_3), (A_2B), (AB_2), (B_3) with simple unsymmetrical cross-aggregation $\xi_1 \neq \xi_2$.

The procedure could be generalized to a reaction involving simple cross-aggregate series of any multiple n. The kinetics for the generalized case is as described by eq 21

$$-\frac{df}{dt} = \frac{k[M]}{(nK_0)^{1/n}[A]_0^{(n-1)/n}}\{f - (n-1)[(A_{n-1}B)]_{rel} \ldots - [(AB_{n-1})]_{rel}\}^{1/n} = (k_{obsd}{}^{I})_0 R_{rel}(f) \quad (21)$$

The criterion for the participation of the simple series of cross-aggregates in the reaction A → B is the independence of $R_{rel}(f)$ on the initial concentration of the substrate.

The main feature of the approach presented here is that the knowledge of values of the constants of aggregate formation ($K_0, K_1, \ldots, K_n$) are not necessary to describe the kinetics of reaction when cross-aggregation occurs. Instead, the parameters used ($\xi_1, \xi_2, \ldots, \xi_{n-1}$) are related to constants of the equilibria between aggregates.

More Complicated Systems of Cross-Aggregates. System (A_3), (A_2), (AB), (B_2) Tending to the System (A_2), (AB), (B_2) with Dilution. The reactions A → B involving complicated cross-aggregation systems are those which do not comply with the reaction 2. They may be easily distinguished from those involving simple systems as the course of the reaction in the normalized first-order kinetics plot depends here on the initial concentration of the substrate A. Aggregates of different multiples must be considered, which makes it impossible to relate such a case directly to the ideal one. However, it often happens that a complicated system tends to the simple one with dilution and kinetic analysis allowing comparison with the ideal system may be developed. An example of this approach will be given here for the system of aggregates (A_3), (A_2), (AB), (B_2) tending to the binary system (A_2), (AB), (B_2) with dilution.

The reaction A → B follows reaction 22

$$2A_1 \overset{K_0}{\rightleftarrows} (A_2) \overset{\xi'^{1/3}}{\rightleftarrows} \tfrac{2}{3}(A_3) \quad (22a,a')$$

$$A_1 + B_1 \overset{2K_1}{\rightleftarrows} (AB) \qquad \begin{matrix}[A_1] \ll [A] \\ [B_1] \ll [B]\end{matrix} \quad (22b)$$

$$2B_1 \overset{K_2}{\rightleftarrows} (B_2) \quad (22c)$$

$$A_1 + M \xrightarrow{k} B_1 \quad \text{(rate determining)} \quad (22d)$$

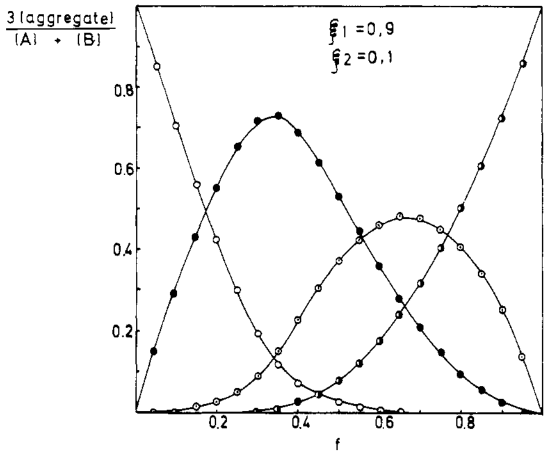


Figure 6. Relative concentration of complexes in the ternary system involving simple unsymmetrical cross-aggregation $\xi_1 = 0.9$, $\xi_2 = 0.1$: (◑) $3[(A_3)]/([A] + [B])$; (⊙) $3[(A_2B)]/([A] + [B])$; (●) $3[(AB_2)]/([A] + [B])$; (○) $3[(B_3)]/([A] + [B])$.

M denotes the second reagent used in excess of rA, $[M] \gg [A]_0$. Under the condition $[B]_0 = 0$ we can write three balanced equations

$$\alpha\{[A] - [(AB)]\} = 3[(A_3)] \quad (23a)$$

$$(1 - \alpha)\{[A] - [(AB)]\} = 2[(A_2)] \quad (23b)$$

$$[(AB)] + 2[(B_2)] = [A]_0 - [A] \quad (23c)$$

$$\alpha = \frac{3[(A_3)]}{3[(A_3)] + 2[(A_2)]} \neq 1$$

Taking into account equilibria 22 and eq 23b and substituting $[A]/[A]_0 = f$ and $[(AB)]/[A]_0 = [(AB)]_{rel}$ we obtain the kinetic eq 24

$$R = -\frac{df}{dt} = \frac{k[M]}{(2K_0[A]_0)^{1/2}}(1 - \alpha)^{1/2}(f - [(AB)]_{rel})^{1/2} \quad (24a)$$

$$\alpha \neq 1$$

$$[(AB)]_{rel} = f - \frac{8}{9}\cdot\frac{\alpha^2}{(1 - \alpha)^3\xi'[A]_0} \quad (24b)$$

From the balanced eq 23a–c and allowing for equilibria 22a′ and 10 we obtain eq 25

$$9\xi_1{}^3\xi' \cdot [(AB)]^6{}_{rel} - \frac{8\alpha^2}{[A]_0}\cdot\{(1 - f) - [(AB)]_{rel}\}^3 \cdot \{f - [(AB)]_{rel}\}^2 = 0 \quad (25)$$

$[(AB)]_{rel}$ and α are functions of the substrate fraction f and eq 24b and 25 express the relation between these quantities. The shape of the kinetic curve in the first-order plot for a given initial concentration of the reagent A is determined by two parameters: ξ_1 for the corresponding simple binary system of aggregates and ξ' that allows for the equilibrium 22a′. Assuming a pair of values for ξ_1 and ξ' it is possible to simulate by numerical calculations kinetic curves for chosen values of $[A]_0$. An example is given in Figure 7. Again the first and the final portions of these curves are linear. Taking into account that the reaction in its final stage must obey eq 14 the ratio of final to initial slopes is equal to $\{\xi_1/(1 - \alpha_0)\}^{1/2}$ (α_0 refers to the initial moment of the reaction). α_0 decreases with dilution so the ratio of the slopes decreases with decreasing $[A]_0$ reaching the limiting values $\xi_1{}^{1/2}$ for $\alpha = 0$, when only binary aggregates exist.

Equations 24b and 25 have also been used for simulation of the dependence of the ratio of the slopes, r_{II}/r_I, on the initial concentration of the substrate $[A]_0$. A nomogram of this de-

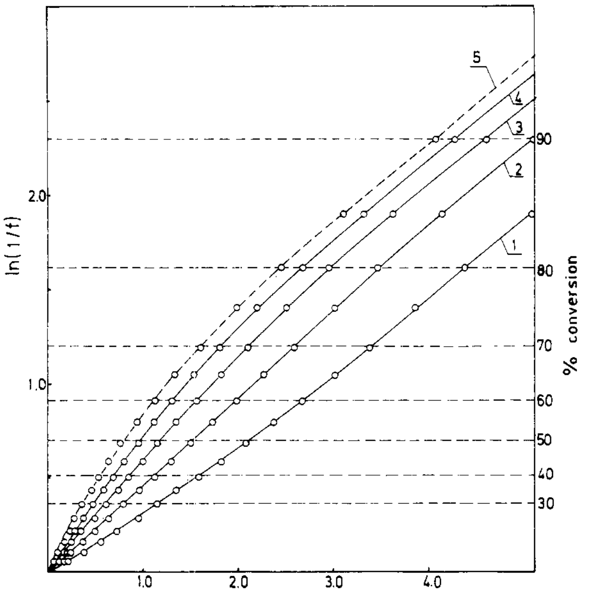


Figure 7. Simulated normalized first-order kinetics curves for the reaction A → B involving the cross-aggregation system (A_3), (A_2), (AB), (B_2), $\xi_1 = 0.15$. $[A]_0$ = (1) 10^{-1}, (2) 10^{-2}, (3) 10^{-3}, (4) 10^{-4} mol dm^{-3} (5) limiting curves $\alpha_0 = 0$ when (A_3) is not formed (dashed line).

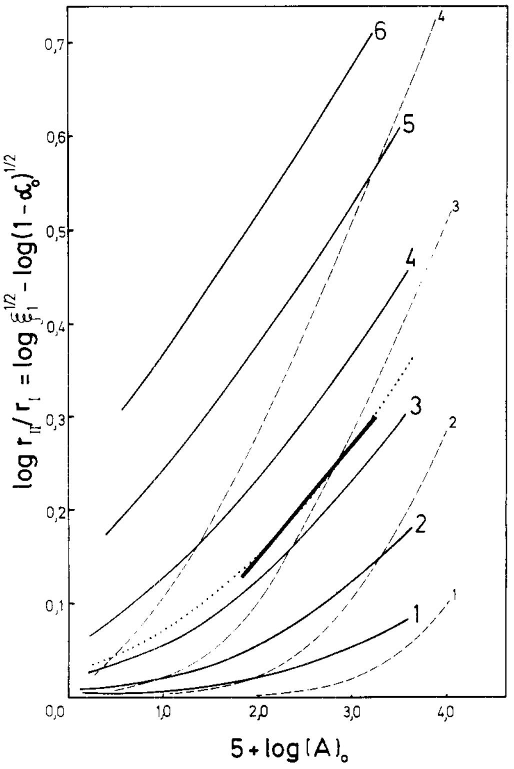


Figure 8. Dependence of the shape of first-order kinetics curves (in terms of log final to initial slopes ratio) on log initial concentration of the substrate for the reaction A → B involving the aggregate systems: (A_3), (A_2), (AB), (B_2) tending to the binary system (A_2), (AB), (B_2) with dilution (continuous lines); (A_4), (A_2), (AB), (B_2) tending to the binary system (A_2), (AB), (B_2) with dilution (dashed lines). Curves are simulated for various values of ξ' (for the system involving quaternary complex (A_4),$\xi' = [(A_4)]/[(A_2)]^2$) and the ordinate scale is normalized by assuming $\xi_1 = 1$. The dotted line corresponds to the reaction of I with excess of polysiloxanes in heptane–dioxane 95:5 v/v, 30 °C. The boldfaced line comes from experiments (date transformed from Figure 12), and its position in relation to the ordinate scale was established by the best fit to the simulated curves.

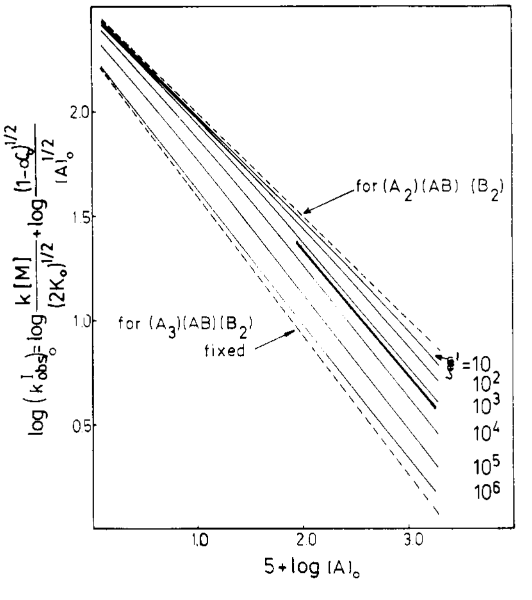


Figure 9. The dependence of the observed first-order rate constant on the initial concentration of substrate for the reaction A → B involving the aggregate system (A_3), (A_2), (AB), (B_2) tending to the binary system (A_2), (AB), (B_2) with dilution. Curves are simulated for various values of parameter $\xi' = [(A_3)]^2/[(A_2)]^3$ and the ordinate scale is normalized by assuming $k[M]/(2K_0)^{1/2} = 1$. The boldfaced line represents the experimental line for the reaction of I with an excess of polydimethylsiloxane (in heptane–dioxane 95:5 v/v, 30 °C, [-Si(CH$_3$)$_2$O-] = 0.45 mol dm^{-3}) and corresponds to $\xi' = 2 \times 10^3$ mol^{-1} dm^3.

pendence for assumed value of the parameter $\xi_1 = 1$ consisting of curves for various values of parameter ξ' is presented in Figure 8 (continuous lines).

$$\log (r_{II}/r_I) = \log \xi_1^{1/2} - \log (1 - \alpha_0)^{1/2} \qquad (26)$$

According to eq 26 corresponding curves for other values of the parameter ξ_1 can be obtained by shifting the scale on the axis of $\log (r_{II}/r_I)$ by the value $\log \xi_1^{1/2}$. Thus the nomogram is of general applicability for evaluation of the parameters ξ' (determining the shape of the curve) and ξ_1 (determining the position of the curve along the ordinate). First, ξ' is determined by selection of the curve on the nomogram which corresponds to the experimental dependence r_{II}/r_I vs. $[A]_0$. Then, having a known numerical value of r_{II}/r_I for a given concentration $[A]_0$, the true value of ξ_1 is found by appropriate shift of the scale along the ordinate.

A similar analysis was developed to prepare the analogous nomogram corresponding to the system of aggregates (A_4), (A_2), (AB), (B_2) leading to the system (A_2), (AB), (B_2) with dilution (Figure 8, dashed lines). Knowing r_I and r_{II} over a relatively wide range of $[A]_0$, the latter case may be distinguished from the former.

Equations 24b and 25 also permit the prediction of the dependence of the initial first-order rate constant observed $(k_{obsd}{}^I)_0$ on the initial concentration of the substrate $[A]_0$. A nomogram consisting of curves for various values of parameter ξ' is presented in Figure 9. The scale of the ordinate is normalized by assuming $k[M]/(2K_0)^{1/2} = 1$.

The upper limiting straight line with slope ½ represents the case of the simple binary complex system ($\alpha_0 = 0$), while the lower limiting straight line with slope ⅓ represents the fixed system (A_3), (AB), (B_2) ($\alpha = 1$), which does not become a simple binary system with dilution. The system under consideration is represented by curves lying between these limiting lines. In the analysis of experimental data they may be approximated to straight lines. This nomogram may be used to check the value of the parameter ξ' obtained from the nomogram in Figure 8.

The Kinetics of the Process Involving Cross-Aggregation of the Substrate with Another Reagent (the Concentrations of Both do not Appear in the Stoichiometric Equation). The kinetic analysis presented above is in principle concerned with a dynamic system of aggregates in the sense that the concentration of both aggregating species is changed during the course of the reaction. It may however be readily adopted to reaction systems involving cross-aggregating species which do not appear in the stoichiometric equation. Polymer chain propagation on an active center, which in the process aggregates and forms a dormant center, in the presence of a nonreactive agent that is able to undergo aggregation and cross-aggregation constitutes a good example. In the simplest case of polymerization in a living system when binary complexes are formed the reaction proceeds according to the scheme:

$$\begin{aligned} &A_1 + A_1 \overset{K_0}{\rightleftarrows} (A_2) \\ &A_1 + C_1 \overset{2K_1}{\rightleftarrows} (AC) \qquad [A_1] \ll [A] \\ &C_1 + C_1 \overset{K_2}{\rightleftarrows} (C_2) \qquad [C_1] \ll [C] \qquad (27) \\ &\sim\!\!(M_n)A_1 + M \rightarrow \sim\!\!(M_{n+1})A_1 \text{ (rate determining)} \end{aligned}$$

$(M_n)A_1$ and $(M_{n+1})A_1$ are kinetically indistinguishable. This is a static system of aggregates in the sense that the concentration of aggregating species is unchanged during the reaction. The rate at constant [M] is constant. The state of aggregation equilibria is the same here as it would be in the corresponding dynamic system in the reaction A → C described by reaction 2 ($n = 2$) when in the same condition as at the moment when adequate amounts of A have been transformed to C (the global concentration of the aggregating species in the dynamic and static systems being equal). In a series of kinetic experiments involving the static cross-aggregation system performed under the same conditions at the same total concentration of aggregating species $[A] + [C] = [A]_0$ and variable fraction $[A]/([A] + [C]) = f_{st}$, the rate $(R/R_0)_{st}$ related to the rate when $[C] = 0$, $[A] = [A]_0$ is expressed by eq 28 analogous to eq 12.

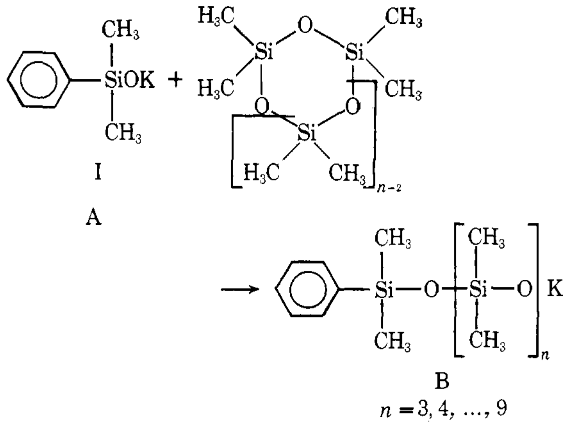
$$\left(\frac{R}{R_0}\right)_{st} = \left(f_{st} - \frac{[(AC)]}{[A]_0}\right)^{1/2} = (R_{rel})_{st}(f_{st}) \qquad (28)$$

When f_{st} is changed the rate follows one of the curves, representatives of which are drawn in Figure 1.

Kinetics of the Reaction of Potassium Triorganosilanolate with Polydimethylsiloxanes

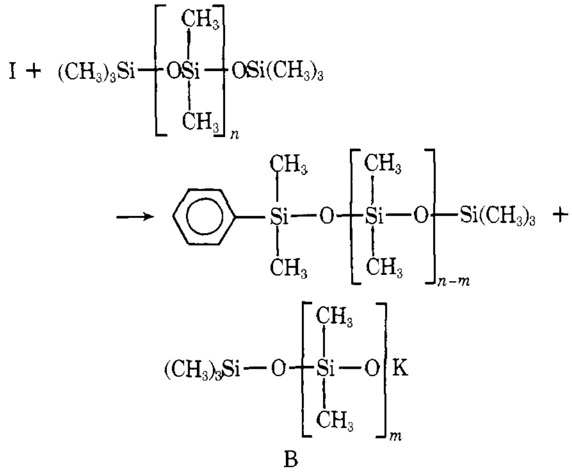
The reactions of potassium phenyldimethylsilanolate (I) with a series of cyclic polydimethylsiloxanes D_n and also with a series of linear polydimethylsiloxanes blocked with trimethylsilyl groups MD_nM[32] have been used as models.

Studies of these reactions are of interest also on account of the fact that the former constitutes a model of initiation and the latter is similar to chain transfer (chain redistribution) in anionic polymerization of siloxanes. This polyreaction is of considerable importance in the technology of silicon rubber.



(29)

$n = 3, 4, \ldots, 9$



(30)

$n = 0, 1, \ldots, 10$

The kinetics of reactions 29 and 30 carried out in heptane–dioxane 95:5 v/v was studied by UV spectrometry using the method described in ref 4. Vacuum techniques were applied throughout the silanolate synthesis and during the kinetic studies. A large excess of siloxane was used to ensure its constant concentration during the reaction. The problem of reactivity of different oligomers of the D_n and MD_nM siloxane series toward I has been dealt with in our previous publication[18] in which initial rates of I with various siloxanes of both these series were compared. In the present work we are interested in the rigorous examination and molecular interpretation of the kinetics of the process for a full range of silanolate conversion. The reaction of I with most oligomers studied followed a complicated conversion–time dependence.[33] The exception was the reaction with MM, MDM, and MD_2M which to a good approximation obeyed first-order internal kinetics similar to those observed in reaction 7.[4]

In order to check to what extent any perturbating processes and variations in the medium composition may affect the kinetics we performed a two-step experiment. First, I was allowed to react completely with D_6 (99% conversion after 3 h) under the conditions used for the kinetic studies. The solutions were allowed to react for another 7 h, that is until a considerable amount of living polymer with longer chains had been produced and there were other meaningful changes in the medium. Then a new portion of I was introduced and the conversion–time curve was monitored. It was compared with the corresponding portion of the kinetic curve obtained in a separate one-step run performed under exactly the same conditions of solvent, temperature, and D_6 concentration but using the concentration of I equal to the sum of the concentrations of silanolate used in each of the two steps of the experiment (Figure 10). The superposition is fairly good taking into account that variations in the medium during the two-stage experiment were certainly much larger than the variation which might appear during one run. We may thus assume to a good approximation that the shape of the kinetic curve is not perturbed by any other processes but is determined by fast established equilibria of aggregation. This conclusion was fully confirmed by kinetic analysis of the results obtained.

The shape of the kinetic curve in a first-order plot is characteristic for a reaction involving aggregation of substrate and

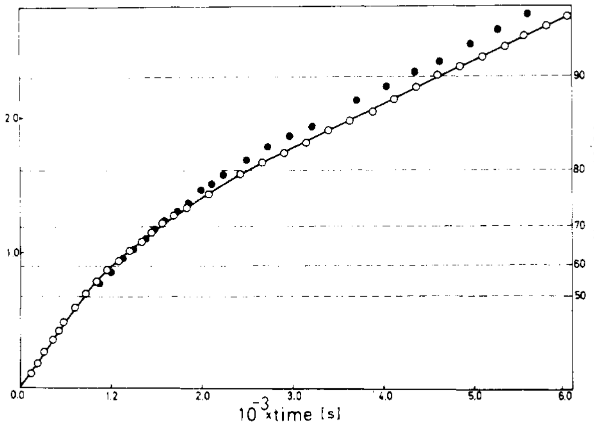


Figure 10. Comparison of conversion–time curves for one-step and two-step experiments of the reaction of I with D_6 in heptane–dioxane 95:5 v/v, 30 °C, $[\text{-Si(CH}_3)_2\text{O-}] = 1.0$ mol dm^{-3}: one-step run $[\text{I}]_0 = 9.5 \times 10^{-3}$ mol dm^{-3}; the second step of two-step run $[\text{I}]_0 = 4.7 \times 10^{-3}$ mol dm^{-3} + $[\text{LE}] = 4.7 \times 10^{-3}$ mol dm^{-3} ([LE] = concentration of living ends of polymers).

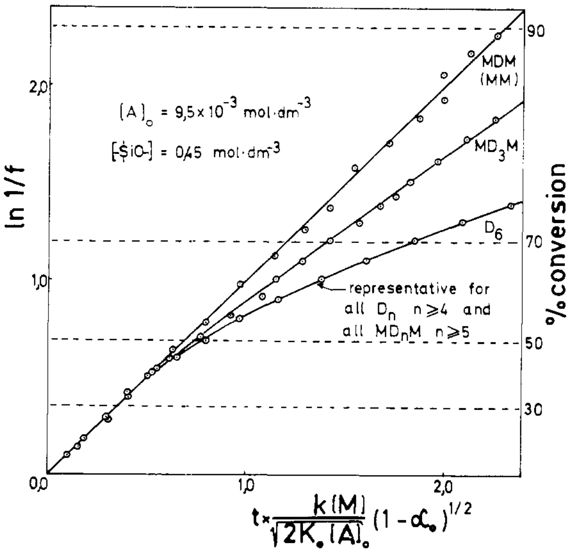


Figure 11. First-order kinetics plot with normalized time scale ($(1 - \alpha_0)$ is taken into account in the normalization factor) for the reaction of I with linear (MD_nM) and cyclic (D_n) siloxanes in heptane–dioxane 95:5 v/v, 30 °C. All experiments were performed at the same initial concentration of I and $[\text{-Si(CH}_3)_2\text{O-}] = [\text{M}]$.

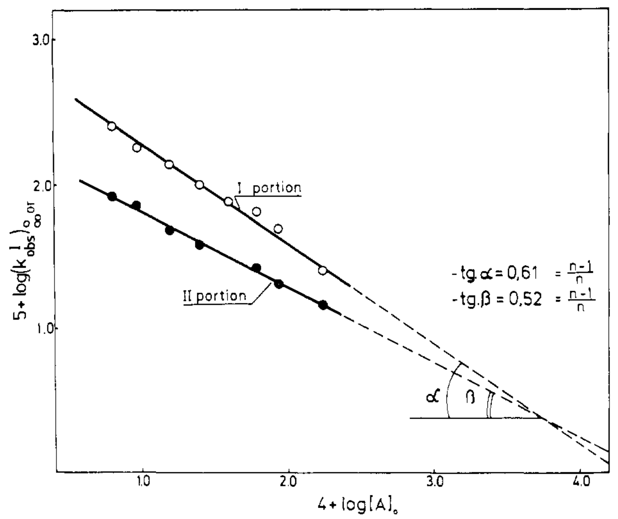


Figure 12. The variation of log first-order rate constant observed resulting from the initial portions of conversion–time curves $(k_{\text{obsd}}{}^{\text{I}})_0 = k[\text{M}]/(nK_0)^{1/n}[\text{A}]_0{}^{(n-1)/n}$ (○), and the first-order rate constant observed resulting from final portions of conversion–time curves (which corresponds to $(k_{\text{obsd}}{}^{\text{I}})_\infty = kK_2{}^{1/2}[\text{M}]/2^{1/2}K_1[\text{A}]_0{}^{1/2}$ (●) according to eq 12) with the log initial concentration of the silanolate for the reaction of I with D_6 in heptane dioxane 95:5 v/v, 30 °C; $[\text{-Si(CH}_3)_2\text{O-}] = 0.45$ mol dm^{-3}.

Table I
First-Order Rate Constants Observed for the Reaction of I with Some Cyclic D_n and Linear MD_nM Siloxanes Found from the Initial $(k_{\text{obsd}}{}^{\text{I}})_0$ and Last Portions $(k_{\text{obsd}}{}^{\text{I}})_\infty$ of the Kinetics Curves[c]

Siloxane	$(k_{\text{obsd}}{}^{\text{I}})_0 \times 10^3$,[a] s^{-1}	$(k_{\text{obsd}}{}^{\text{I}})_\infty \times 10^3$,[b] s^{-1}	$r_{\text{II}}/r_{\text{I}}$
D_3	2.86	1.49	0.52
D_6	0.39	0.17	0.43
D_7	6.30	2.01	0.38
D_8	6.00	2.46	0.41
MD_3M	0.20	0.14	0.66
MD_5M	1.20	0.47	0.39
MD_6M	2.04	0.88	0.43
MD_7M	2.08	0.82	0.39
MD_8M	2.42	1.02	0.42
$MD_{10}M$	4.07	1.68	0.42

[a] $(k_{\text{obsd}}{}^{\text{I}})_0 = [k[\text{M}](1 - \alpha_0)^{1/2}]/[(2K_0)^{1/2}[\text{A}]_0{}^{1/2}]$. [b] $(k_{\text{obsd}}{}^{\text{I}})_\infty = [kK_2{}^{1/2}/2^{1/2}K_1[\text{A}]_0{}^{1/2}][\text{M}]$. [c] Heptane–Dioxane 95:5 v/v, 30 °C, $\text{+Si(CH}_3)_2\text{O+} = 0.45$ mol dm^{-3}, $[\text{I}]_0 = 9.5 \times 10^{-3}$ mol dm^{-3}.

product as the first and the last portions of the line are linear. Reactions of I with all linear MD_nM ($n > 5$) polysiloxanes likewise with all cyclic D_n ($n > 4$) polysiloxanes, when carried out under the same conditions, follows the same the normalized first-order curve (Figure 11) in spite of large variation of the specific reaction rate, particularly within the series of cyclic oligomers. This is illustrated by the data in Table I where the shape of the kinetic curve is represented by the ratio of final slope to initial slope ($r_{\text{II}}/r_{\text{I}}$). All of these cases are treated as one general case, which corresponds to the aggregation involving silanolate groups situated at the end of the siloxane chain with silanolate groups of I.

The shape of the curve in the normalized first-order plot was found to be dependent on the initial concentration of I and the variations of the initial and the final slopes with $[\text{A}]_0$ are illustrated on Figure 12. This observation leads to the conclusion that the case does not fit reaction 2.

From the variation of initial slope with $[\text{A}]_0$ the external order of 0.39 was found, and this might be interpreted in terms of the coexistance of both binary (A_2) and ternary (A_3) complexes of the substrate. The product B, polysiloxanolate, forms only binary simple complexes (B_2), because the propagation step in anionic polymerization was shown in earlier works to be of the order ½ with respect to [⁓SiOK] groups.[19,20] This order was confirmed for the solvent and temperature used in this study by a series of dilatometric kinetic experiments the results of which are presented in Figure 13.

The variation of the final slope with $[\text{A}]_0$ indicates that the rate at higher conversion of the substrate is inversely proportional to the square root of the initial silanolate concentration, thus the reaction proceeds according to eq 14, which means that among cross complexes only the binary one (AB) is important.[34] Consequently the reaction follows eq 22, which tends to the scheme for a simple binary system on dilution.

The data were analyzed using the nomogram presented in Figure 8. The experimental line derived from the dependence of $r_{\text{II}}/r_{\text{I}}$ on $[\text{A}]_0$ (obtained from Figure 12) was fitted to the nomogram by shifting it up and down parallel to the axis log

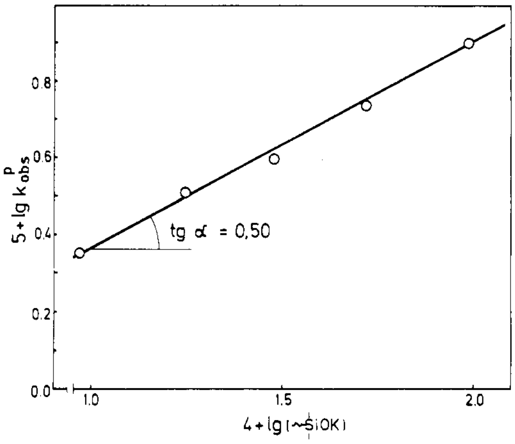


Figure 13. The dependence of rate constant observed of the propagation step in anionic polymerization of D_3 on the concentration of potassium silanolate groups: $[-Si(CH_3)_2O-] = 1.0$ mol dm^{-3}, heptane–dioxane 95:5 v/v, 30 °C.

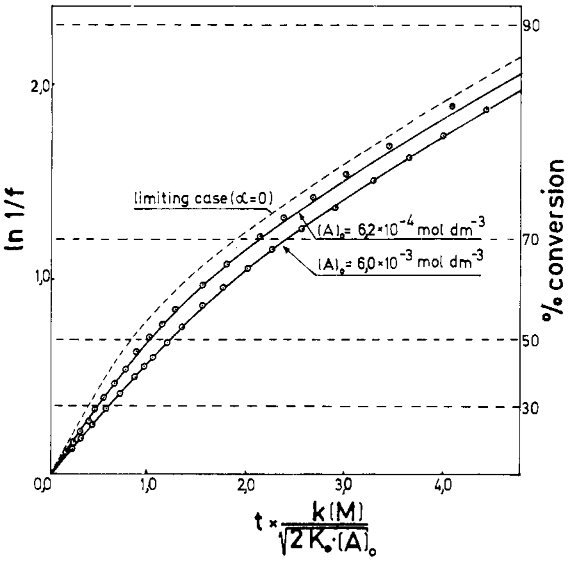


Figure 14. Comparison of curves simulated in a normalized first-order plot for the reaction involving aggregate system (A_3), (A_2), (AB), (B_2) tending to the system (A_2), (AB), (B_2) on dilution assuming values of parameters $\xi_1 = 0.07$, $\xi' = 2 \times 10^3$ mol^{-1} dm^3 found from Figures 8 and 9 (continuous line), with the experimental data (points) obtained for reaction of I with an excess of polydimethylsiloxane (D_6): heptane–dioxane 95/5 v/v, 30 °C; $[-Si(CH_3)_2O-] = 0.45$ mol dm^{-3}.

(r_{II}/r_I). The best fit is represented by the boldfaced line in Figure 8. Since α_0 as a function of $[A]_0$ is known, the procedure gives us values of both parameters $\xi_1 = 0.07$ and $\xi' = 2 \times 10^3$ dm^3 mol^{-1}. It was found that the experimental dependence of log (r_{II}/r_I) on log $[A]_0$ cannot be fitted to the nomogram in Figure 8 for the system (A_4), (A_2), (AB), (B_2), which confirms our conclusion that appart from the binary complex (A_2), the ternary complex of the substrate $(PhMe_2SiOK)_3$ is mainly formed under the conditions used. The attempt to find agreement of the data with the system involving quaternary complexes of I is justified by the fact that the external order 0.39 in $[A]_0$ does not exclude the possibility of the participation of aggregates of higher multiple than 3. This might be expected as our cryoscopic studies of the state of aggregation of $PhMe_2SiOK$ carried out in dioxane at concentrations 5×10^{-2}–5×10^{-1} mol dm^{-3} showed an average multiple of aggregates closed to 4 (3.5/4.0).

On the grounds of estimated values of ξ_1 and ξ' normalized first-order kinetics plots were simulated and compared with experimental data (Figure 14). The agreement seems to be very good. The confidence in the unequivocal character of the interpretation of the kinetics data may stem from the fact that fitting only two parameters gives us a family of an infinit number of curves of very characteristic shapes. The most important seems to be the knowledge of parameter ξ_1, as it determines the shape of the kinetic line for the limiting case $\alpha = 0$ where only binary complexes (A_2), (AB), and (B_2) are formed. This is the case of simple cross-aggregation which can be related to the ideal case of cross-aggregation. The kinetic curve for this limiting case is compared with simulated ones in Figures 1 and 2 (dotted lines).

Table II
Results of the Series of Kinetic Run of the Polymerization of D_3 at a Constant Total Concentration of Silanolates $[\sim\!\!\!\overset{|}{\underset{|}{S}}iOK] + [\sim\!\!\!\overset{|}{\underset{|}{S}}iONa] = 5 \times 10^{-3}$ mol dm^{-3} and at Variable Ratio of the Potassium to the Total Amount of Counterion (f)[b]

	f[c]	$k_f \times 10^4$, s^{-1}[a]	$R/R_0 = k_f/k_{f=1}$
1	1	3.0	
2	0.80	2.3	0.77
3	0.68	1.7	0.57
4	0.50	0.95	0.32
5	0.40	0.51	0.17
6	0.30	0.30	0.10

[a] k_f is first-order rate constant of the propagation $k_f = k_p[LE]^{1/2}/(2K_2)^{1/2}$. [b] Heptane–Dioxane 95:5 v/v, 50 °C, $[-Si(CH_3)_2O-] = 3.3$ mol dm^{-3}. [c] $f = [\sim\!\!\!\overset{|}{\underset{|}{S}}iOK]/[\sim\!\!\!\overset{|}{\underset{|}{S}}iOK] + [\sim\!\!\!\overset{|}{\underset{|}{S}}iONa]$.

Propagation of the Polymerization of Hexamethylcyclotrisiloxane (D_3) on Potassium Siloxanolates in the Presence of Sodium Siloxanolates

The polymerization of hexamethylcyclotrisiloxane (D_3) in n-heptane–dioxane 95:5 v/v solution in the presence of the mixture of potassium and sodium polydimethylsiloxanolates has been studied for experimental verification of the extention of our kinetic analysis of the reaction with cross-aggregation to the processes involving the static cross-aggregation system. The other purpose was to obtain information on the tendency to cross-aggregation between sodium and potassium silanolate groups when both are situated at the end of the siloxane polymer chain. Also it should give a more comprehensive interpretation of the known phenomenon of polyelectrolytic inhibition of anionic polymerization of siloxanes.[21,22,35] This manifests itself in decrease of the reactivity of the $\sim\!\!\!\overset{|}{\underset{|}{S}}iOK$ groups in the presence of $\sim\!\!\!\overset{|}{\underset{|}{S}}iONa$ groups.

The reactivity of sodium silanolate as a propagating center is much less than that of potassium siloxanolate, so to a good approximation it can be assumed that the sodium affects the polymerization rate only by changing the concentration of potassium active centers as a result of cross-aggregation. Both sodium and potassium polysiloxanolates are known to form binary complexes in nonpolar media,[5,23,24] so the reaction should fit eq 27 with A denoting the $\sim\!\!\!\overset{|}{\underset{|}{S}}iOK$ species and C denoting the $\sim\!\!\!\overset{|}{\underset{|}{S}}iONa$ species. A series of kinetic runs of the polymerization of D_3 at a constant total concentration of silanolates $[\sim\!\!\!\overset{|}{\underset{|}{S}}iOK] + [\sim\!\!\!\overset{|}{\underset{|}{S}}iONa]$, and with a variable ratio of the potassium to the total amount of counterion, has been performed. Results are given in Table II, and they are also represented by circles in Figure 15. They fit well to the curve simulated for $\xi_1 = 5 \times 10^{-2}$.

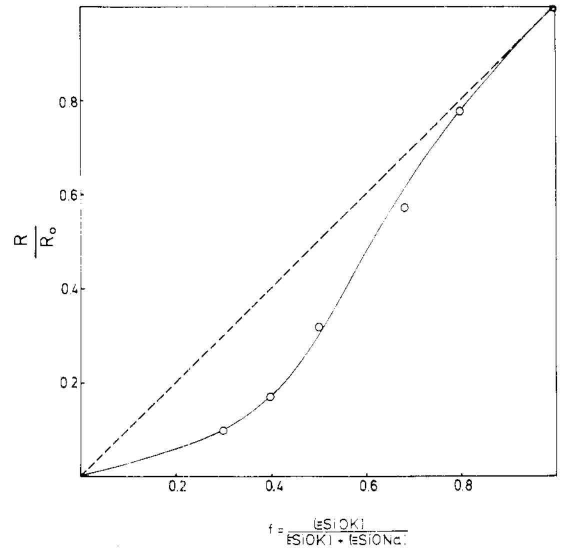


Figure 15. The relative rate of the polymerization of D_3 on potassium silanolate active center $\sim$SiOK (A) in the presence of sodium silanolate $\sim$SiONa (C) at variable fractions of potassium silanolate. [$\sim$SiOK] + [$\sim$SiONa] = 5×10^{-3} mol dm^{-3}, [-Si(CH$_3$)$_2$O-] = 3.3 mol dm^{-3}, heptane–dioxane 95:5 v/v, 50 °C.

The possibility of fitting the experimental results to one of the curves in Figure 1 gives support to the correctness of our approach since the curves in Figure 1 are of very characteristic shape. We believe that this approach may be applied to other polymerization systems involving cross-aggregation of active centers with another component. The data point also to the large tendency to cross-aggregation between sodium and potassium polysiloxanolates.

Structure of Aggregates of Active Centers in the Siloxane Polymer

The binding parts of aggregates involving siloxanolate group at the end of polysiloxane chain should in general have the same structure as binding parts of aggregates composed of low molecular weight silanolate (like I). Consequently ideal cross-aggregation could be expected in a system involving both types of ≡SiOMt groups so more than the reactions of I with MM and MDM keep well to the pseudo-first-internal-order kinetics. However, rather considerable deviation toward strong cross-aggregation from the ideal system is found when $\xi_1 = 7 \times 10^{-2}$

$$\xi_1 = \frac{4[(PhMe_2SiOK)_2][(\sim Me_2SiOK)_2]}{[(\sim Me_2SiOK \cdot PhMe_2SiOK)]^2} \qquad (31)$$

indicating enhanced tendency to the formation of the cross complexes of the initiator (I) and the active center of polymer. Recently we have found some evidence of the role of an internal interaction of an unaggregated siloxanolate group with the chain of the polymer during the anionic polymerization of siloxanes.[18] Similar interactions may appear between chain and aggregated siloxanolates (eq 32) and it is highly probable that they cause a perturbation of the structure and are therefore responsible for the deviation of the cross-aggregation system from ideality.

These interactions are more effective in stabilization of the structure of uncomplexed species because the positive charge on the counterion is not additionaly stabilized by the aggregation. Consequently the interaction shifts the equilibria 32b and 32c toward free species making aggregates of polymeric species less stable. This effect is not additive because two chains in the complex of two polymer species may interfere somehow with each other in their interaction with the aggregating center and consequently neither of them is as effective in stabilization of the structure of aggregate as is the chain in the cross complex of the polymer and initiator. The conformational freedom of both chains is also reduced. The situation may be such as illustrated in Figure 16 (which has only demonstrative character).

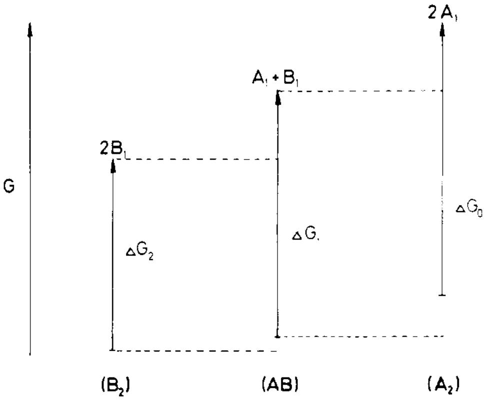
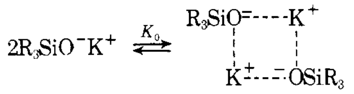
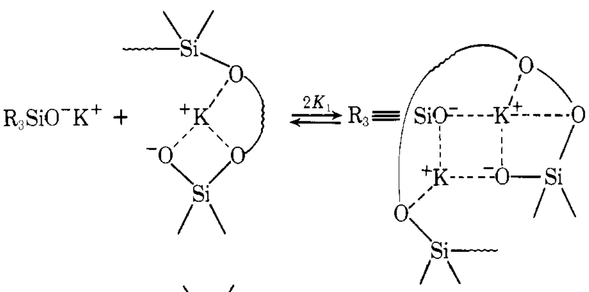


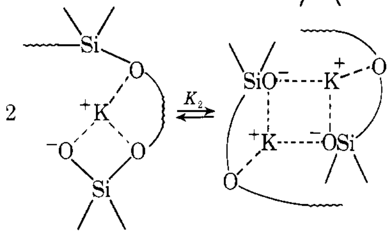
Figure 16. Diagram of free enthalpies of free and aggregated silanolate groups; A denotes ≡SiOK group in low molecular weight compound for example initiator; B denotes ≡SiOK group at the end of polysiloxane chain.



$$2R_3SiO^-K^+ \underset{}{\overset{K_0}{\rightleftharpoons}} \begin{array}{c} R_3SiO^- \cdots K^+ \\ \vdots \qquad \vdots \\ K^+ \cdots {}^-OSiR_3 \end{array} \qquad (32a)$$



(32b)



(32c)

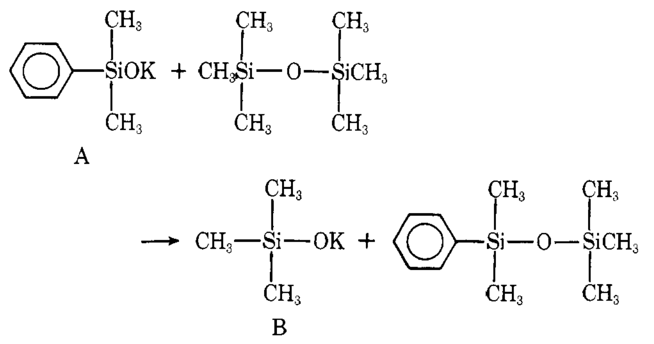
Cross complex being weaker than simple complex of initiator $\Delta G_1 < \Delta G_0$ is sufficiently stronger than simple complex of polymer $\Delta G_1 > \Delta G_2$ that eq 33 is satisfied.

$$K_1 > (K_0 \cdot K_2)^{1/2} \qquad -\Delta G_1 > \frac{(-\Delta G_0) + (-\Delta G_2)}{2} \qquad (33)$$

The interaction between the chain and counterion permits the understanding of why polymeric silanolate does not form aggregates of multiples higher than two.

The above interpretation seems to be in agreement with the observation of the first-order kinetics of the reactions of I with MM and MDM as the reaction leads to the formation of low molecular weight products which do not exhibit the interaction of the counterion with the siloxane oxygen.

The ideal cross-aggregation observed by us in the initiation of the anionic polymerization of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane[4] (eq 7) may result from the stiff structure of the silethylene–siloxane chain, in comparison with


A

B

the pure siloxane chain, which hinders the interaction of siloxane oxygen with the active center.

The conformational elasticity of the chain is consider to be an important factor in deciding the possibility of the polydentate interaction between active center and polymer chain.[12,25]

The cross-aggregation which appears in the propagation step of the anionic polymerization of siloxane, when both sodium and potassium active centers are present, shows also a distinct deviation from the ideal system ($\xi_1 = 0.05$). The interaction of the sodium cation with the siloxane oxygen seems to be stronger than a similar interaction involving the potassium cation and a preferential interaction with sodium in cross-aggregate may lead to the observed deviation from the ideal system. However, deviation may be here somehow related to the fact that in this case the structures of binding parts in the series of aggregates and cross-aggregates are no longer the same.

It is assumed in our approach that the first-order kinetics takes place only if the state of aggregation includes only one ideal series of cross-aggregates. It should, however, be noted that similar kinetics may be obtained if the system contains aggregates of different multiples. The state of aggregation in the reaction of MM with I may serve as a good example. In this case binary and ternary aggregates exist in comparable amounts. The average multiples of one-component complexes of A and B are equal. It is easy to show that such a situation is possible only if both series of binary and of ternary aggregates are ideal and in both these series $\Delta\Delta G_{A\rightarrow B}$ is close to zero. Otherwise the average multiple of one-component aggregates of A and B would change in a different way with concentration and this would lead to a complicated system of cross-aggregates. The exchange of components in these aggregates must affect to a very small extent the binding forces in aggregates.

Experimental Section

The high-vacuum technique was employed in all kinetic experiments. The methods of kinetic studies of the reaction of silanolate with siloxanes as well as synthesis and purification of reagents have been described previously.[4,18]

A modified cryometer allowing the measurements of melting points under inner gas was used in the studies of molecular weights of aggregates of alkali metal silanolates.

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(26) A large excess of the second substrate (siloxane) is used and it does not have to be considered in the kinetic analysis developed here.

(27) All aggregates of given n and m are considered here as the same species, however the entropy concerned with the statistical factor $\binom{n}{m}$ is not taken into account.

(28) Equation 9 was derived from eq 9.1 making use of eq 9.2–9.5: $R = k[A_1][M]$ (9.1); $K_0 = [AA]/[A_1]^2$ (9.2); $[A] = 2[(A_2)] + [(AB)]$ (9.3); $[B] = 2[(B_2)] + [(AB)]$ (9.4); $\xi_1/4 = K_0 \cdot K_2/4K_1{}^2 = \{[(A_2)][(B_2]\}/[(AB)]^2$ (9.5).

(29) An attempt to solve eq 9 led us to Euler integrals.

(30) On the basis of a simple electrostatic model one could expect a weaker tendency to the formation of cross-aggregates, e.g., $\xi_1 > 1$. Assuming parallel orientation of dipoles, free enthalpy of dipole–dipole interaction in an (AB) complex would be a geometrical mean of the analogous interaction in (A_2) and (B_2),[17] which was less or equal to the arithmetical mean characteristic for the ideal cross-aggregation series (eq 4). No documented case of the weak tendency to cross-aggregation of ion pairs is known to our knowledge. Instead many systems with a strong tendency to cross-aggregation, e.g., $\xi_1 < 1$, have been described,[14–16] from which it may be concluded that the electrostatic model does not adequately describe the nature of forces binding ion pair in aggregates.

(31) In the case of a series of aggregates $(A_{n-m}B_m)$ where the change of free enthalpy $\Delta\Delta G_{A\rightarrow B}$ corresponding to the substitution of A by B is variable with m according to

$$\Delta\Delta G_{A\rightarrow B} = \Delta\Delta G_{(A(n))\rightarrow(A(n-1)B)} + m \cdot \text{constant}$$

then $\xi_1 = \xi_2 = \ldots = \xi_{n-1}$ and there is only one parameter determining the shape of the curve (see for example Figure 3). We call such a case symmetrical cross-aggregation because of the symmetry of the plot illustrating the variation of relative concentration of aggregates with f (see for example Figure 4). Simple binary aggregates system, like all ideal systems, involve the symmetrical cross-aggregation.

(32) D and M denote the dimethylsiloxy unit $-(CH_3)_2SiO-$ and the trimethylsiloxy unit $(CH_3)_3SiO_{1/2}$, respectively.

(33) We suggested previously that the complication might result from the contribution of processes which we called specific redistribution.[4] These are processes, generally proceeding according to reaction 1, which involve a siloxane bond situated in the vicinity of a silanolate group. They manifested themselves in immediate disappearance of sodium and potassium phenyldimethylsilanolates in hydrocarbons after addition of a living siloxane polymer.[4] However, we have found recently that the small amount of dioxane was sufficient to restrain this specific redistribution, which must play only a minor role in the system studied and should not affect the shape of the kineitc curve.

(34) For the system involving (ABB) as the only cross complex the rate would be inversely proportional to $[A]_0$ and if (AAB) determined the kinetics, the final portion of the first-order kinetics plot would not be linear.

(35) Kučera and Jelinek[21] noticed that the presence of the sodium counterion slows down markedly the propagation of anionic polymerization of cyclosiloxanes on the silanolate group with the potassium counterion. In general they interpreted correctly the phenomenon in terms of the formation of unreactive complexes; however, the detail structure of complexes and the quantitative relationships they proposed require some reinterpretation.

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