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THERMODYNAMIC ENHANCEMENT OF OLIGOMERS IN DYNAMIC LIVING POLYMER SYSTEM INVOLVING END-GROUP INTERACTION

DISTRIBUTION OF LIVING OLIGOMERS IN EQUILIBRATED POLYDIMETHYLSILOXANES

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Abstract—The concentrations of living oligomers of structure $MtO[Si(Me)_2O]_nMt$ (n = 1 to 8, Mt = Na, K or Cs) are studied at equilibrium in the polymerization of permethylcyclopolysiloxanes initiated with alkali metal silanolates. The amounts of these oligomers are considerably higher than expected from the most probable distribution of molecular sizes, which is generally accepted as the distribution of linear chain size in equilibrated polydimethylsiloxane. This phenomenon is a consequence of interaction between living ends in connection with a dynamic character of a living polydimethylsiloxane system in which fast chain scrambling occurs. Other systems showing these features are expected to exhibit similar effects.

INTRODUCTION

Association phenomena involving living groups are important in living anionic polymerization. In particular, associations between living centres dominated the kinetic pattern in the anionic polymerizations of oxiranes [1, 2] and cyclosiloxanes [3–5]. Association phenomena also are important in the anionic polymerization of dienes and some vinyl monomers when Li [6] or a metal of Group II such as Ba or Sr [7, 8] is used as catalyst. Little attention, if any, has been paid so far to the fact that this interaction may also affect the thermodynamics of some living polymer systems; in particular the distribution of molecular weights may be seriously perturbed. The anionic polymerization of cyclosiloxanes is a good model for studying this problem as it constitutes a dynamic system in which fast making and breaking of all segment-to-segment bonds occurs in the equilibrium state [9–12]. Due to high reactivity of siloxane groups in monomer and oligomers as well as in polymers towards some silanolate active centres, the system can be fully equilibrated under various conditions. The living ends can be easily killed with trimethylchlorosilane, to form very stable trimethylsilyloxy end-groups which render the system easy for analysis.

Our approach was to study, by means of a gas–liquid chromatography, the concentration of linear oligomers in such equilibrated and subsequently killed polydimethylsiloxane (PDMS).

RESULTS AND DISCUSSION

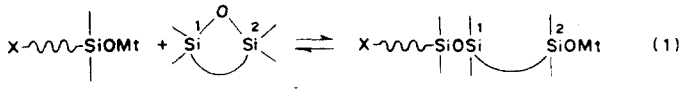
Equilibrated PDMS systems—enhancement of living oligomers in PDMS bearing both living and neutral end-groups

Two types of reversible, chemically analogous processes are important in anionic polymerization of siloxanes:

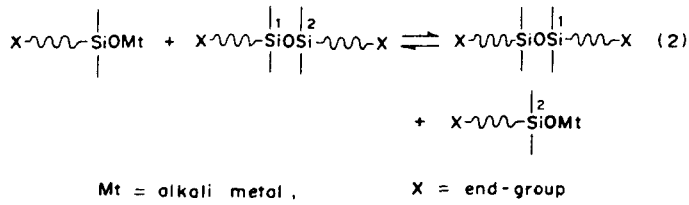
(1) Reactions of silanolate reactive groups with siloxane groups in cyclic species, leading to the growth of macromolecules (scheme 1) [9–11]. Reverse reactions constitute back-biting depolymerization giving rise to the series of cyclic oligomers in the system.

(2) Reactions of the silanolate groups with siloxane groups situated in the linear polymer molecule leading to chain transfer with redistribution of the linear polymer chains (scheme 2) [9–11].

These processes are fully reversible. Reaction (1) leads to well known ring-chain equilibria [13], extensively studied for the PDMS system as part verification of the Jacobson–Stockmayer theory of macrocyclization [13–15]. Reaction (2) in the absence of any extraordinary factors leads to the most probable distribution of sizes of linear polymeric species i.e. Flory distribution. The compliance of the system to the Flory theory of random reorganization [16] was proved earlier for the equilibrate of PDMS, the chains of which were mainly terminated with chemically inert trimethylsilyl groups and only a small amount of reactive end-groups was present to bring about the



(1)

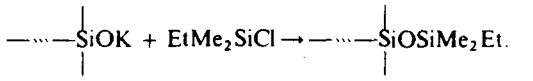


equilibration [17, 18]. Such a system may be obtained by polymerization of permethylcyclopolysiloxanes of formula $(Me_2SiO)_n$, (D_n), with a very small concentration of catalyst and introducing a considerable amount of trimethylsilyl ended permethylated linear siloxane oligomers $Me_3Si[OSi(Me)_2]_nOSiMe_3$, ($MD_nM$). These conditions are often applied in the technological polymerization of cyclosiloxane [19].

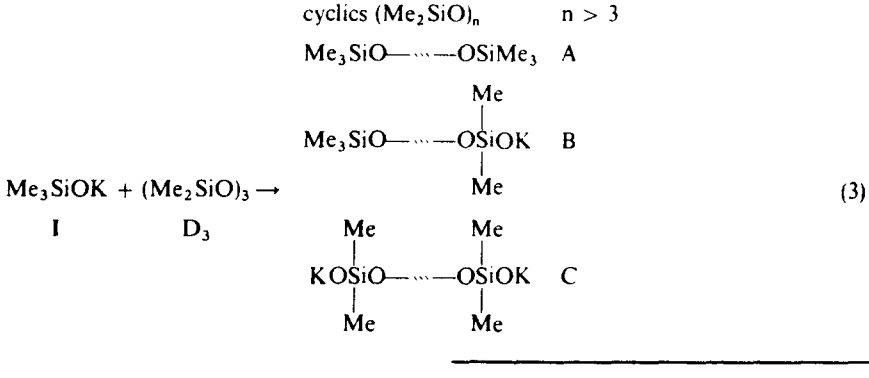
We were interested in equilibrated PDMS having exclusively silanolate end-groups or in which these groups eventually constitute an appreciable portion of the total amount of chain ends. In such systems we found that the equilibrium of reaction (2) shows remarkable deviation from that predicted by the theory of random reorganization. This can be well demonstrated by the polymerization of hexamethylcyclotrisiloxane (D_3) initiated with potassium trimethylsilanolate (scheme 3). This reaction finally leads to an equilibrium mixture which contains, besides a series of permethylpolycyclosiloxanes, three series of linear polymeric species differing with respect to the structure of their end-groups: (A) Chains terminated at both ends with a trimethylsilyl group; (B) Chains terminated with one trimethylsilyl group and one silanolate group; (C) Chains terminated at both ends with silanolate group (scheme 3).

matogram of the system (Fig. 1a) revealed considerable amounts of these MD_nM oligomers, which strongly exceeded (in some cases by more than one order of magnitude) the total amount of oligomers A, B and C anticipated from the most probable distribution. There is thus an enhancement in the equilibrium concentration of short chain oligomers.

In order to discriminate between species A, B and C, a second part of the living polymer was killed with dimethylethylchlorosilane. Thus, the silanolate ends were transformed into dimethylethylsilyl ends according to reaction (4).



The chromatogram of this system is shown in Fig. 1(b). Inspection indicates that there is a large excess of oligomers having silanolate groups at both ends. They appear at concentrations at least one order larger than corresponding oligomers with both ends terminated with trimethylsilyl groups.



If the breaking of siloxane bonds in process (2) occurred at random and if the process was not affected by any extraordinary factors, it should lead to random distribution of end-groups within polymeric species of different sizes. In this particular system, the number of silanolate groups equals the number of trimethylsilyl groups; thus the equilibrium mixture should show the molar ratio A:B:C for any particular polymerization degree equal to 1:2:1.

The polymerization of D_3 initiated with I was carried out in n-heptane solution (49.2% w/w) to equilibrium of processes (1) and (2). Then it was divided into three parts. The first part was treated with excess trimethylchlorosilane. In this system all linear oligomers were transformed into oligomers of type A. The chro-

Oligomers with mixed end-groups are not seen. Their peaks may however be hidden in the peaks of cyclic compounds. That is why the living polymer was also killed with diethylmethylchlorosilane. However, no definite peaks which could be attributed to oligomers with mixed end-groups were detected, so the concentration of oligomers B must be much lower than the concentration of corresponding oligomers C. Therefore most short chains are of type C while most long chains are of type A.

Enhancement of oligomers in equilibrated PDMS system containing exclusively silanolate end-groups. The effect of chain length

The polymerization of hexamethylcyclotrisiloxane

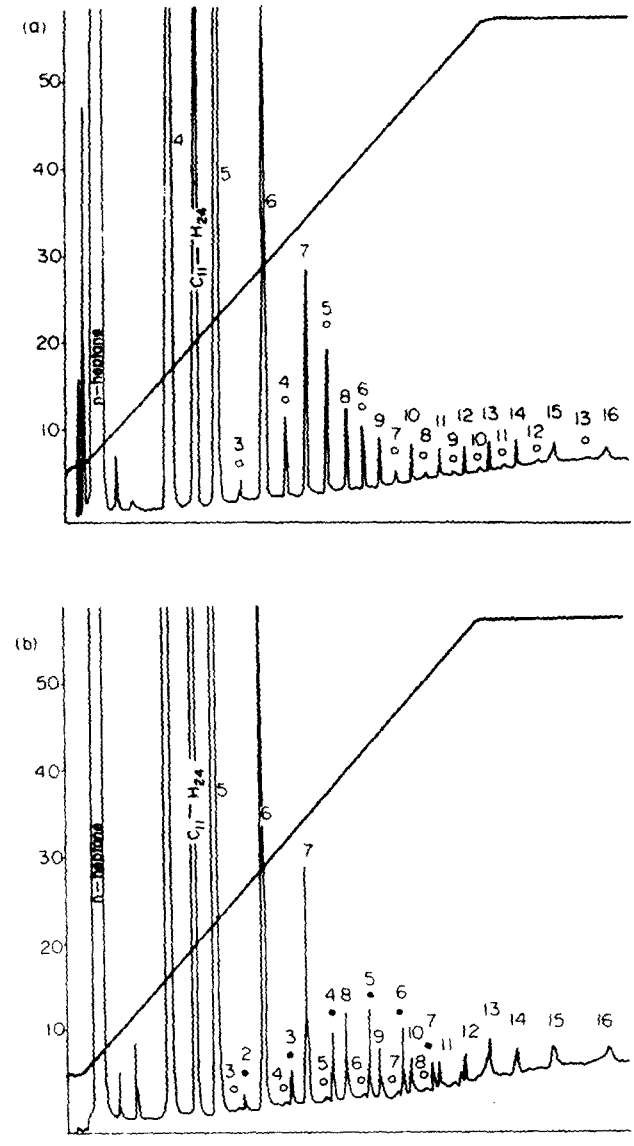


Fig. 1 Chromatograms of equilibrated system of living PDMS polymer (49.2 wt% solution in *n*-heptane) obtained by equilibration of D_3 with Me_3SiOK $4.7 \cdot 10^{-2}$ mol·kg^{-1} at 100°. (a) Polymer killed with Me_3SiCl, (b) polymer killed with $EtMe_2SiCl$. ○—oligomers $Me_3Si[OSiMe_2]_n OSiMe_3$, ●—oligomers $EtMe_2Si[OSiMe_2]_nOSiEtMe_2$, *n*—cyclic oligomers $[Me_2SiO]_n$. Yields of linear oligomers n = 4,5,6 in mol kg^{-1} were as follows: 2.4×10^{-3} (theor. 4.6×10^{-4}); 4.2×10^{-3}, (theor. 4.5×10^{-4}); 1.6×10^{-3}, (theor. 1.5×10^{-4}) respectively.

(D_3) or octamethylcyclotetrasiloxane (D_4), initiated with dipotassium polydimethylsiloxane ω,ω'-diolate, was carried out under conditions similar to those for the polymerization initiated by the trimethylsilanolate. In such a system apart from cyclics, only linear species C (scheme 3) having silanolate groups at both ends were present (Fig. 2). The polymerization system at equilibrium was quenched with trimethylchlorosilane and the concentration of oligomers obtained were evaluated and compared with that expected from the most probable distribution (see Fig. 3). Again there is a considerable excess of the equilibrium concentration of short chain species. About 50% of the total amount of potassium end-groups appear in oligomers having the number of siloxane units within the range 1–8.

As a consequence, there must be also an increase in the average size of the high molecular weight fraction of the polymer.

The increase in average molecular weight of macromolecules of the linear fraction, equivalent to the decrease of the living end concentration, leads only to minor changes of mutual proportions of living oligomers of different sizes (Table 1). A distinct maximum on the oligomer size distribution curves, which appears for potassium centres at n = 4 or 5, is always observed. Within the range of $\overline{M}_n$ of the linear fraction studied (2000–60,000), the ratio of the amount of

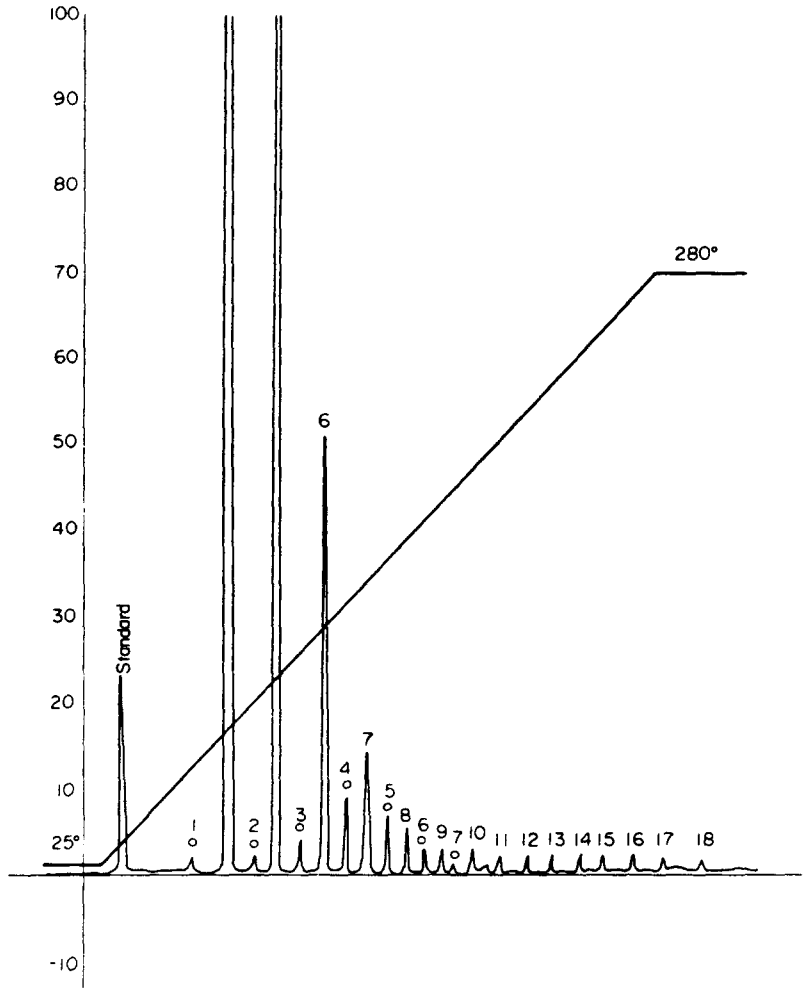


Fig. 2. Gas–liquid chromatogram of PDMS equilibrate containing exclusively potassium silanolate end-groups killed with trimethylchlorosilane. 72 wt% PDMS in toluene $\bar{M}_n = 10^4$ (excluding cyclosiloxane), 100°, $\overset{n}{\circ}$—oligomers $Me_3Si[OSiMe_2]_nOSiMe_3$, *n*-cyclic oligomers $[Me_2SiO]_n$.

living ends in an oligomer *n* to the amount of living ends

$$\frac{[LE]_n}{[LE]_{total}}$$

seems to undergo only minor variation with change in average molecular size of living polymer (Table 2). Consequently the enhancement, taken as ratio of the concentration of oligomers found to that calculated from the Flory distribution function, is to a reasonable approximation proportional to $\bar{M}_n$, or inversely proportional to silanolate living end concentration $[LE]_{total}$ (Table 1).

The effect of counter-ion, medium and temperature

Since the fraction of silanolate groups in oligomers is almost independent of the average size of the polymer, it was used to compare results obtained in different media and in the presence of different counter-ions (Table 2).

The data indicate that there is no drastic change in the oligomer enhancement effect caused by these factors. The maximum in the size distribution curve shifts from $n = 4$ for sodium silanolate towards $n = 5$ for caesium counter-ion. Rather similar proportions of living oligomers are formed in THF as in hydrocarbon solvents or in bulk siloxane. The temperature also had only minor effects (see Table 3).

General explanation of the phenomenon

It is well known that triorganosilanolates form strong complexes, which may be considered as ion aggregates bound by dipole-dipole interaction [20]. Some of these aggregates were isolated and identified [20a]. Kinetic results for the anionic polymerization of cyclic siloxanes so far obtained were rationalized in terms of the formation of analogous complexes by the terminal silanolate groups of polysiloxane chains [3–5]. The aggregated silanolates constitute dormant

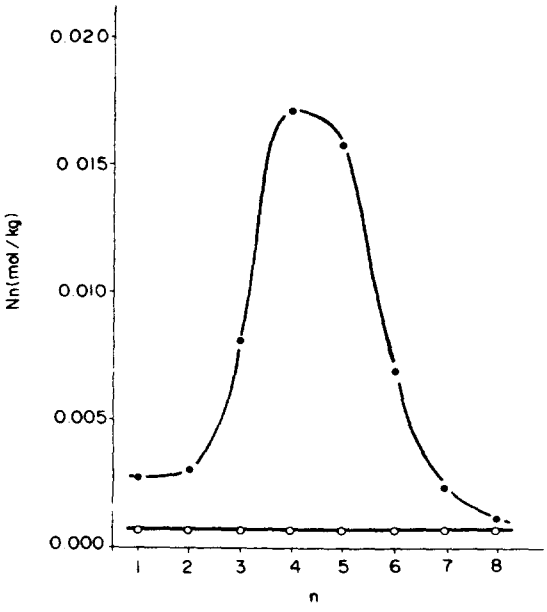
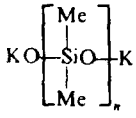
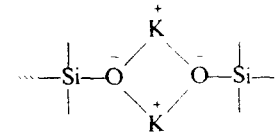


Fig. 3. Concentrations of living oligomers



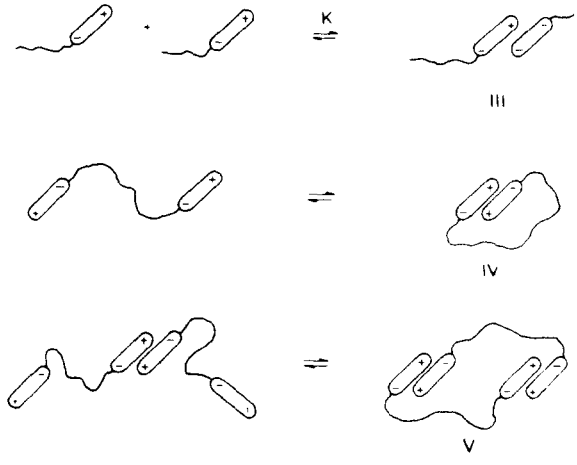
in equilibrated PDMS living polymers having exclusively potassium siloxanolate end-groups. ●—observed; ○—anticipated from the most probable distribution. Conditions: 72 wt% solution in toluene, 100°, $\bar{M}_n$ of linear polymer fraction.

centres*, which are in equilibrium with a small amount of free silanolate groups able to undergo propagation, depropagation and chain transfer. The polymerization with Na, K and Cs silanolates have order 0.5 with respect to the catalyst [9, 21, 22] and so indicate that silanolate groups in polymeric species form binary complexes. Structure **II** of these polymer end-group complexes is analogous to the structure of other known dipole-dipole complexes [23].



II

These aggregates may be produced as a result of an intermolecular complex **III** between two end-groups belonging to two different chains or as a result of an intramolecular complex between two end-groups of the same chain, which adopts a ring conformation **IV**†. The formation of ring structures **V** containing two or more aggregates is also feasible.

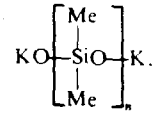


The formation of these cyclic structures is strongly preferred for short chains, because end-groups of these chains always operate at a short mean distance from each other. Incidentally, theoretical calculations of the probability of the meeting of ends of short siloxane chains has been recently performed [24] and results suit reasonably well the experimental data on ring chain equilibria. The effective equilibrium constant K_{eff}, taking into account structures **IV** and **V**, is

*All silanolate groups will be called living groups, whether they are free or complexed.

† All chains having living groups will be here called linear chains regardless whether they form rings or linear chains.

Table 1. Oligomer enhancement effect $N_{n(obs)}/N_{n(theor)}$ and fractions of silanolate groups $\frac{[LF]_n}{[LE]_{total}}$ in oligomers



n = 3, 4, 5, 6 for various number-average polymerization degree $\bar{n}$ (number of siloxane units) in equilibrated, two living group ended PDMS (excluding cyclosiloxanes), 72 wt% of total siloxane in toluene, 100°

	$N_{n(obs)}/N_{n(theor)}$				$100 \cdot [LE]_n/[LE]_{total}$			
n	$\bar{n}$ = 31	$\bar{n}$ = 140	$\bar{n}$ = 470	$\bar{n}$ = 820	$\bar{n}$ = 31	$\bar{n}$ = 140	$\bar{n}$ = 470	$\bar{n}$ = 820
3	1.9	10.5	28	95	5.7	7.5	6.1	11.5
4	5.0	22.2	61	128	14.6	15.8	13.0	15.5
5	5.1	20.6	45	91	14.6	14.6	9.5	11.0
6	2.0	9.2	14	50	5.6	6.5	3.0	6.1

Table 2. The effect of counter-ion and medium on enhancement of oligomers $KO[Si(Me)_2O]_nK$ $n = 3, 4, 6, 5$. Comparison of fraction of silanolate groups in oligomers

$$100 \times \frac{[LE]_n}{[LE]_{total}}$$

in various systems

No.	Medium	Catalyst	Characteristics of living polymer: Temp. (°C)	$\bar{n}$	$n = 3$	$n = 4$	$n = 5$	$n = 6$
1	Bulk (92% in tol.)	$KO[(Me)_2SiO]_mK$	100	390	4.1	10.2	8.9	3.7
2	71 w % in THF	$KO[(Me)_2SiO]_mK$	100	290	4.8	8.1	4.7	1.1
3	52 w % in *n*-hept.	$KOSiMe_3$	50	60	6.9	12.1	14.0	7.8
4	52 w % in *n*-hept.	$CsOSiMe_3$	50	60	6.7	9.5	11.1	5.7
5	64 w % in *n*-hept.	$NaOSiMe_3$	100	220	7.3	11.6	5.2	1.4

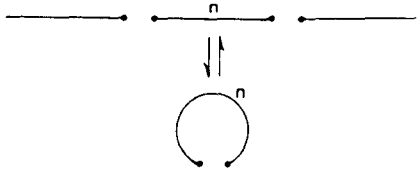
larger than the equilibrium constant K under conditions in which only the intermolecular interaction leading to open chain structure **III** occurs. Therefore, this intramolecular interaction effect leads to a decrease of the thermodynamic potential.

$$-\Delta\Delta G = RT \ln K_{eff}/K. \tag{5}$$

The formation of shorter chains is connected with a large drop in potential. Thus the fundamental assumption in the Flory–Scott statistical treatment [16, 17], viz. that the standard free energy change in process 2 is independent of the length of chains which appear at both sides of the scheme (2), is not valid for systems in which there is strong interaction between end groups. Under conditions of random reorganization [2] in which chains are constantly broken and coupled, there is a tendency for enhanced formation of living short chain species.

Though a more quantitative treatment does not seem feasible, we hope that the following discussion will shed light on the dependence of the enhancement on certain factors, particularly $\bar{M}_n$ of living polymer.

Both forms of living *n*-segment oligomer (ring and linear) are in equilibrium (scheme 6) determined by the competition between intermolecular and intramolecular association.



(6)

This competition is characterized by the ratio $B_{n\,eff}/[LE]_{total}$ where $[LE]_{total}$ is the total concentration of silanolate groups, and $B_{n\,eff}$ is the local effective concentration of one end-group in the neighbourhood of the other end-group of the same chain having n segments (e.g. [25]). It corresponds to the concentration of end-groups for which the probability that there will be intermolecular reaction for the living end (being a part of an n segment chain) is the same as the probability that it will react intramolecularly. The ratio of equilibrium amounts of both ring $(N_n)_{ring}$ and linear forms $(N_n)_{linear}$ should be proportional to $B_{n\,eff}/[LE]_{total}$. Since $B_{n\,eff}$ is independent of the end-group concentration, this ratio should be proportional to $\bar{n}$ the number average degree of polymerization of living polymer (excluding cyclosiloxanes).

$$\frac{(N_n)_{ring}}{(N_n)_{linear}} \propto \frac{B_{n\,eff}}{[LE]_{total}} \propto \bar{n}. \tag{7}$$

The factor $(N_n)_{ring}/(N_n)_{linear}$ determines the extent to which silanolate groups in the oligomer n lose their reactivity due to intermolecular complexation (scheme 2). This is the effect responsible for the overall enhancement in oligomer n, therefore to a first approximation the amount of n-segment oligomer in equilibrium (N_n) may be obtained from the Flory Eqn (8) modified for the factor $(N_n)_{ring}/(N_n)_{linear}$

$$\frac{N_n}{(N_{total})_{linear}} \approx \frac{(N_n)_{ring}}{(N_n)_{linear}} \cdot \left(1 - \frac{1}{\bar{n}}\right)^{n-1} \cdot \frac{1}{\bar{n}}. \tag{8}$$

If n is small and the polymer is of relatively high average molecular weight and taking into account that $N_n \approx (N_n)_{ring}$, we can write

$$\frac{(N_n)_{linear}}{(N_{total})_{linear}} \propto \frac{1}{\bar{n}}. \tag{9}$$

It may be deduced from (7) and (9) that

$$\frac{(N_n)_{ring}}{(N_{total})_{linear}}$$

is independent of $\bar{n}$. Thus the fraction of silanolate groups included in the oligomer n, $[LE]_n/[LE]_{total}$, should be independent of average size of the living macromolecule. Consequently, the enhancement effect should increase with the increase of $\bar{M}_n$.

Table 3. The effect of temperature on equilibrium concentration of living oligomers $KO[Si(Me)_2O]_nK$, $n = 3,4,5,6$. Polymerization system D_3, 39 wt% in *n*-heptane, equilibrated with Me_3SiOK at four temperatures. Contents of oligomers in 10^3 mol·kg^{-1}

n	Temperature: 20	60	90	120
3	2.8	2.1	2.9	3.0
4	5.1	5.8	6.0	5.5
5	5.9	6.8	7.3	5.2
6	2.8	2.3	2.0	2.3

The enhancement effect is approximately proportional to $B_{n\,eff}$. Generally, $B_{n\,eff}$ is supposed to decrease with increase of n, however for very short chains ($n = 1, 2$) it may be small or even zero if the formation of unstrained cyclic structure IV is impossible. Thus a maximum of the enhancement for some size of oligomer is anticipated. It is also worth noting that short chain oligomers ($n = 1,2$) may appear in considerable quantity if they form cyclic structure V and so complicate the situation.

$B_{n\,eff}$ for a given n is supposed to vary to some extent with the nature of the alkali counter-ion, particularly for smaller n; however if complexes for all these cations are strong enough, the effect should not be large because, in the series Na^+, K^+, Cs^+, ionic sizes are not greatly different and structures of the bonding parts of complexes are expected to be analogous.

The driving force for the enhancement lies in the entropy factor; therefore the phenomenon should be independent of temperature.

Any drastic variation of the enhancement effect with change of medium is expected only when the character of interaction of end-groups is altered. The data included in Tables 1–3 with the above discussion lead to the conclusion that the experimental observations are, in general, consistent with all the above consequences of the end-to-end interaction model, which is also consistent with our earlier work [4, 5]. A more precise discussion based on more quantitative theoretical grounds will be feasible after obtaining more precise data; work is continuing with this aim.

Some consequences of the phenomenon

Interaction between end-groups may strongly perturb the molecular weight distribution of the polymer in a dynamic living system, e.g. PDMS obtained by the anionic polymerization of cyclosiloxanes. The general direction of the effect is an enlargement of the polydispersity of molecular sizes. Since $\bar{M}_n$ for the polymer is not affected, the oligomer enhancement phenomenon is manifested in an increase of $\bar{M}_v$, $\bar{M}_w$ and $\bar{M}_z$ of the polymer; therefore all properties related to $\bar{M}_v$, $\bar{M}_w$, and $\bar{M}_z$ are affected. If there are also neutral groups at the ends of macromolecules, then there is a tendency of these groups to occupy the position in longer chains.

The kinetics of anionic polymerization of cyclosiloxane are affected by the formation of the ring shape complexes of living groups because this phenomenon leads to decrease of the reactivity in the propagation step. Silanolate groups being at the end of longer chains react faster and contribute most to the conversion of the monomer. Deviation from first internal order in monomer may also be expected.

The enhancement of oligomers in equilibrated living polymer systems can also serve as evidence for the role of the interaction between living ends. For example the enhancement effect in equilibrated PDMS having potassium silanolate living ends is also observed when a considerable amount of hexamethylphosphoroamide (HMPT) is present in the system, indicating that HMPT does not prevent aggregation of the end-groups.

It seems also important to mention that the oligomer enhancement phenomenon renders dynamic living polymer systems unsuitable for studying end-to-end association phenomena by methods based on comparison of viscosity before and after neutralization of living ends.

EXPERIMENTAL

Monomers

Hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4), and decamethylcyclopentasiloxane (D_5) were obtained and purified as described earlier [26].

Solvents

The purifications of *n*-heptane and THF were as described in the literature [4, 26, 27]. Toluene, analytical grade, was refluxed over Na and distilled with an efficient column, before distilling into the ampoule with Na–K alloy where it was kept for several days.

Catalysts

Sodium, potassium and caesium trimethylsilanolates were synthesized by reaction of trimethylsilanol with alkali metal mirror under high vacuum by a procedure similar to that used in preparing phenyldimethylsilanolates [2]. Sodium and potassium silanolates were additionally purified by resublimation on high vacuum line.

Mixtures of ω,ω'-dipotassium polydimethylsiloxanediolate in *n*-heptane or toluene, used in the preparation of living polymer terminated at both ends with siloxanolate groups, were obtained by Hyde's method [28]. These diolates were either kept on K mirror or were subjected to repeated operations of addition and distilling off prepurified toluene in order to remove traces of silanol groups and water. The concentration of silanolate groups was determined by acidimetric titration and the concentration of the siloxane unit D was evaluated by ^{1}H-NMR.

Equilibration procedure

Polymerization of the cyclosiloxanes with trimethylsilanolate catalyst was carried out in fused ampoules under high vacuum. In most experiments with siloxanodiolate catalysts, equilibration was achieved under prepurified N_2. The catalyst was added with Hamilton gas-tight syringe through a side-arm with a rubber membrane, which was subsequently fused out. The reaction was carried out for a period sufficient to guarantee attainment of equilibrium as shown by the cyclic oligomer populations being consistent with known equilibrium concentration of these compounds [11–13]. For the polymerization with K catalyst at 100°, the sample was heated for 5–10 days. The sample was treated with an excess of a conc solution of trimethylchlorisilane in THF.

Gas–liquid chromatographic analysis

GLC analyses of equilibrates were carried out using a JEOL 1100 gas–liquid chromatograph with a thermal conductivity detector and a Takeda Riken 2215 A integrator. Undecane, *n*-octane or toluene was used as internal standard, although in some cases the contents of linear oligomers were calculated with respect to peaks of cyclic oligomers D_4–D_7 the equilibrium concentrations of which in mol·dm^{-3} for $n > 100$ were assumed to be independent of silanolate group concentration, solvent and dilution [13]. Response factors were determined in separate experiments with standard mixture of oligomers of cyclic D_n and linear MD_nM series, including standards. In principle the GLC analysis was performed as described earlier [29–31]. Conditions of analysis were usually as follows: 2 m × 3 mm steel column, 10% OV-101 on Varaport 30, 80/100 mesh. Column temp was programmed from 30° to 280° at 10°/min. First 5 min isothermic in 25°. Injector and detector temperatures were 250 and 310° respectively. Carrier gas – hydrogen with flow 40 ml/min. TCD current 90 mA.

Calculation of concentrations of living oligomers

Since killing of living groups with Me_3SiCl is complete and fast in comparison with processes (1) and (2), concentrations of MD_nM oligomers in the derivatized system correspond quantitatively to appropriate $KO[Si(Me)_2O]_nK$ oligomers in the living system if chains had exclusively silanolate end-groups. Concentrations of these oligomers observed $N_{n(obs)}$ in $mol \cdot kg^{-1}$ were calculated directly from the GLC results. Theoretical concentrations of living oligomers $N_{n(theor)}$ were calculated from the Flory Eqn (10) for the most probable distribution.

$$N_{n(theor)} = N \cdot \frac{1}{\bar{n}}\left(1 - \frac{1}{\bar{n}}\right)^{n-1}. \quad (10)$$

N is the concentration of all living molecules in the system, which for two living ended polymer is equal to $\frac{1}{2}[LE]_{total}$ $\frac{1}{2}$ (total concentration of silanolate groups in $mol \cdot kg^{-1}$); $\bar{n}$ is the number-average degree of polymerization of linear fraction of PDMS calculated from Eqn. (11).

$$\bar{n} = \frac{2[Si(Me)_2O]_{total} - [Si(Me)_2O]_{cyclosiloxane}}{[LE]_{total}}. \quad (11)$$

The concentration of cyclic polysiloxanes in $mol \cdot kg^{-1}$ were found from a known variation of the fraction of cyclics with dilution of PDMS equilibrate [13].

For experiments with trimethylsilanolates, $N_{n(obs)}$ was calculated with the assumption that linear oligomers of types other than $KO[Si(Me)_2O]_nK$ $3 \leqslant n \leqslant 6$ appear in negligible amount. The error in this assumption was usually less than 5%.

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