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SELECTIVITY OF SILOXANE-SILOXANE COPOLYMER SYNTHESIS BY RING OPENING POLYMERIZATION

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Abstract: Anionic ring-opening polymerization of 1,1-diphenyl-2,2,3,3-tetramethylcyclotetrasiloxane was studied as a model polymerization of cyclic siloxane with mixed siloxane units. Sequencing of siloxane units was investigated by ^{29}Si NMR. Various initiator-promoter-solvent systems were used. In most cases reaction was highly chemoselective, as sequencing were not affected by back biting, chain transfer and terminal unit exchange processes. Reactions showed, however, low regioselectivity in monomer ring opening. The coordination of the metal counter-ion to monomer plays a considerable role in propagation and affects sequencing of the polymer.

INTRODUCTION

There has been a considerable interest in synthesis of siloxane-siloxane copolymers. Generation of macromolecules composed of two or more kinds of siloxane units often offers a better compromise between required properties of materials. Dimethylsiloxane copolymers draw particularly high attention in connection with growing interest in the side group modification of polydimethylsiloxane. Usually, only a part of dimethylsiloxane units is functionalized. The remaining part assures preservation of some important features of the copolymer inherent for polydimethylsiloxanes. Functional groups may be introduced to polysiloxane directly by reactions on the polymer. However, even in this case the polymer must have precursor functional groups such as Si-H, e.g. (Refs.1, 2), SiCH=CH_2 e.g. (Refs. 3, 4), $Si(CH_2)_nCl$, e.g.(Ref. 5) and others. These precursor copolymers also are synthesized from monomers. Polycondensation is seldom

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used as the route to siloxane-siloxane copolymers. Most of these copolymers are obtained by ring-opening polymerization (Ref. 6). Three methods are exploited in controlled synthesis of the siloxane copolymers via this route: 1) Equilibrium copolymerization, 2) kinetically controlled (non-equilibrium) copolymerization, 3) kinetically controlled homopolymerization of cyclic monomers with mixed siloxane units. The third method seems for us to be particularly interesting as it permits to obtain well defined copolymers with a narrow molecular weight distribution, which have uniform composition of macromolecules and uniform distribution of siloxane units along the chain (Ref. 6). Our purpose was to examine the chemoselectivity and regioselectivity of this process in the presence of various initiating systems using 1,1-diphenyl-3,3,5,5-tetramethylcyclotrisiloxane as a model monomer. The main approach to this problem is analysis of sequencing of the copolymer. Structural features of the copolymers are compared with those of copolymers obtained by other methods.

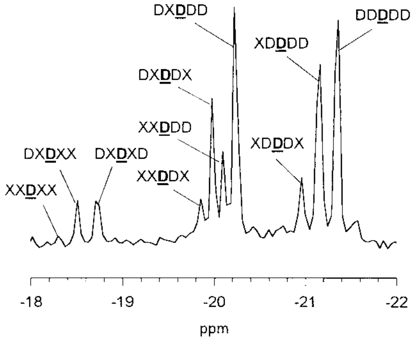
RESULTS AND DISCUSSIONS

Equilibrium and kinetically controlled copolymerizations

Equilibrium copolymerization is the most commonly used route to siloxane-siloxane copolymers because it is easy to control and does not impose any special requirements on initiator and monomers. Comonomers of various ring size as well as cyclics with mixed siloxane units may be used. Even mixture of linear polymers may be subjected to equilibration. Molecular weight is efficiently controlled by blockers.

It is strange that so little research has been made on this reaction. Careful studies were performed by Ziemielis and Saam for the equilibrium copolymerization of octamethylcyclotetrasiloxane, D_4, with 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (Ref. 7). Their conclusions were as follows: 1) contents of vinylmethylsiloxane units in chains and in cyclics are the same, 2) the sequencing in chains, at chain ends and in cyclics is completely random, 3) there is no enthalpic driving force in this copolymerization. In order to check whether these results can be generalized to other siloxane copolymerization systems we studied equilibrium copolymerization of hexaphenylcyclotrisiloxane with D_4. Two phenyl substituents have larger steric requirements and are more electronegative (Taft's $\Sigma\sigma^*=1.2$) as compared with vinyl and methyl substituents ($\Sigma\sigma^*=0.4$). Thus, someone could expect the influence of phenyl substituents on the chain-cyclic equilibria and their observable effects on the composition and sequencing of the copolymer at equilibrium. Fragment of the ^{29}Si NMR proton decoupled spectrum of the Ph_2SiO-Me_2SiO

copolymer isolated from the equilibrium mixture in the range of the Me_2SiO resonance is presented in Fig. 1. The assignment for the ^{29}Si NMR chemical shifts was based on earlier studies (Ref. 6, 8). A good resolution for pentads and a quantitative integration, as checked on model compounds, were achieved by addition of $[Cr(acac)_3]$ and using a gated decoupling technique.



X = Ph_2SiO
D = Me_2SiO

Fig. 1. $^{29}Si\ \{^1H\}$ NMR spectrum of the linear fraction of poly($Me_2SiOcoPh_2SiO$), X=27 mol-%, at equilibrium, 30°C, in the range of the Me_2SiO resonance.

The peaks on the spectrum correspond to D-centred pentad. All 11 pentads are represented. Contributions from diads were determined which permitted to calculate the equilibrium constant of the formation of heterodiads from the homodiads, Eq. (1).

$$\sim DD \sim + \sim XX \sim \overset{K}{\rightleftharpoons} \sim DX \sim + \sim XD \sim \qquad (1)$$

Results are presented in Tab. 1. The equilibrium constant for the ideally random copolymer is equal to 1 while the value determined for the Ph_2SiO-Me_2SiO copolymer is 1.5-1.6, which points to the tendency to separation of units with more polar and more bulky substituents.

The content of the Ph_2SiO units is larger in cyclic fractions than in linear polymers. Thus, there is a natural tendency for the units bearing more bulky and polar side groups to escape to the ring fraction where steric requirements are lower (Ref. 9). A serious drawback of the equilibrium copolymerization as a synthetic route to copolymers with bulky or polar side groups is a low yield of linear copolymer particularly when the reaction is carried out in a solvent, see Tab. 1 (Ref. 9). The non-equilibrium copolymerization does not have this deficiency but it puts very strict confinements on comonomers and initiators. Thus, only copolymerization of ring-strained cyclotrisiloxanes leads to a high yield of copolymer having narrow molecular weight distribution and may be described by theories based on Markovian statistics (Ref. 6). The copolymers have two particular features. First, comonomers enter the chain undivided, thus on a "microscale" the copolymer has microsequential structure of a low value of run number related to siloxane units. Second, since comonomers usually differ in reactivity, the distribution of units is not uniform, but has a gradient character. On a "macroscale" the copolymer macromolecule may resemble a diblock copolymer.

Tab. 1. Equilibration of cyclic siloxanes having Me_2SiO units and Ph_2SiO units.

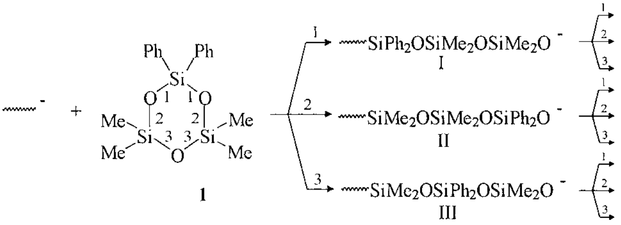
Solvent	Total siloxane w.-%	Yield of linear copolymer w.-%	Ph_2SiO in feed mol-%	Ph_2SiO at equilibrium mol-%		K	Total run number R_X+R_D
				in chains	in cyclics		
THF[a)]	50	27	33.3	27	36	1.6	44
bulk[a)]	100	62	50	44	59		
bulk[b)]	100	74	33.3	31	40	1.5	48
ideal random copolymer			27	27	27	1	39
			33.3	33.3	33.3	1	44

[a)] Equilibration of $(Ph_2SiO)_3$ with $(Me_2SiO)_4$.

[b)] Equilibration of $Ph_2SiO(Me_2SiO)_2$.

Polymerization of cyclotrisiloxanes with mixed siloxane units

Homopolymerization of cyclotrisiloxanes with mixed siloxane units leads to quite different sequencing than the non-equilibrium copolymerization. Siloxane units are dispersed in a uniform way along chains. The copolymer has a high run number showing a high degree of the alternate structure. The monomer studied by us was 1,1-diphenyl-3,3,5,5-tetrametylcyclotrisiloxane, **I**
The sequencing of the copolymer may be strongly affected by reactions of chain cleavage. Trivial processes taking place in almost all ring opening polymerization systems are back biting and chain transfer leading to randomization. Unusual reaction is the terminal unit exchange. The exchange between two silanolate ended chains postulated by Juliano et al. (Ref. 10) must be very slow. Much faster is the exchange between the silanolate and silanol end groups (Ref. 11). Thus, silanol end groups and water producing these groups must be carefully removed from the system, to avoid this reaction. If all processes leading to chain cleavage are excluded the polymerization is chemoselective and the microstructure of the polymer chain is fully controlled by the way in which monomer is added to the growing chain. There are three routes of opening of the monomer **I** ring involving cleavage of the Si-O bond marked by 1,2 and 3, respectively, Eq. (2).



(2)

Rates of the addition also depend on the structure of the chain end which may be I, II and III. Thus, there are nine combinations which should be taken into account in the first order analysis of sequences. If the process occurs regioselectively, only one route of the addition is possible and alternate copolymer is formed. On the other hand, if all nine combinations are equally probable, the polymerization proceeds chemoselectively as statistical random addition process. The random addition copolymer has only four Ph_2SiO-centred pentads compared with ten pentads in the equilibrated copolymer. Remaining six pentads are forbidden for the chemoselective polymerization of **1**. Their absence proves that processes leading to chain cleavage do not occur in the copolymerization system. There are also seven Me_2SiO-centred pentads allowed and three forbidden for the chemoselective polymerization. Regioselective polymerization, irrespective of the place of the monomer ring cleavage leads to copolymer with one X centered pentad (DD**X**DD) and one D centred pentad (DX**D**DX + XD**D**XD).

We have studied the polymerization of **1** using various types of initiator and solvent. Results are presented in Table 2. The ^{29}Si NMR spectrum of the copolymer synthesized using the common initiator-solvent system, lithium silanolate in THF, is shown as an example in Fig. 2. The spectrum does not contain any pentad forbidden for the chemoselective process which exclude the occurrence of any polymer cleavage reactions. However, apart from pentads DD**X**DD and DX**D**DX characteristic for the alternate structure of the copolymer, there are considerable amounts of XD**X**DD and four D centred pentads forbidden for the regioselective reaction. It is worth to notice that both observed X-centred pentads belong to the same triad DXD - characteristic for the alternate copolymer. Thus, on the bases of the observation of X-cent]red triads alone this process could be erroneously assumed to be regioselective.

Inspection of results in Tab. 2 permits to conclude that the reaction for all initiators used, with the exception of potassium silanolate in toluene and in THF, is chemoselective. This result confirms our earlier observations according to which multidentate interactions of polydimethylsiloxane chain with counter-ion of the silanolate propagation centre are responsible for considerable acceleration of back biting and chain scrambling (Ref. 12). This observation allows to classify chemoselective anionic polymerization systems of cyclotrisiloxanes according to the way in which these undesired siloxane-counter ion interactions are suppressed (Ref. 13).

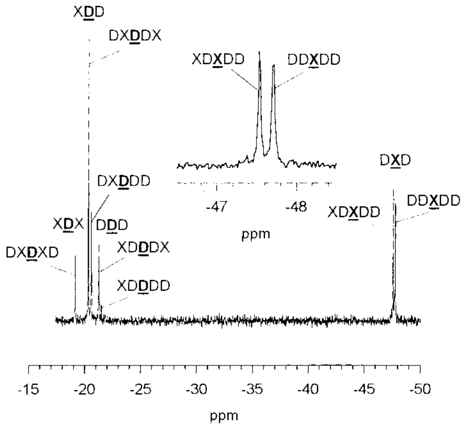


Fig. 2. $^{29}Si\{^1H\}$ NMR spectrum of the poly(Me_2SiO co Ph_2SiO) synthesized by polymerization of 1 in 50 w.-% solution in THF initiated with $BuMe_2SiOLi$ $5.0 \cdot 10^{-3}$ mol dm^{-3} at 50°C.

Tab. 2. Chemo- and regioselectivity of the anionic polymerization[a] of $\lfloor\overline{Ph_2SiO(Me_2SiO)_2}\rfloor$.

No	Initiator[b]	Promoter (I:P)	Solvent[c] (temp. °C)	Chemoselectivity % of allowed pentad	Regioselectivity % of allowed triad (pentad)	Run number R_D+R_X
1.	$BuMe_2SiO^-Li^+$	none	THF (50)	100	82 (48)	66
2.	$BuMe_2SiO^-Li^+$	HMPT (1:100)	THF (50)	100	82 (49)	66
3.	$BuMe_2SiO^-Li^+$	HMPT (1:100)	Toluene (50)	100	80 (50)	64
4.	$(Me_4N^{+-}OSi)_2\sim$	none	Toluene (30)	100	75 (39)	60
5.	$[(Me_2N)_3$-P=N$]_3$-P=N-tBu	H_2O (1:1)	Toluene (30)	99	81 (49)	62
6.	$K^{+-}OSi \sim SiO^-K^+$	crown 18/6 (1:1)	Toluene (50)	99	85 (64)	63
7.	$K^{+-}OSi \sim SiO^-K^+$	none	THF ( )	96	63 (25)	53
8.	$Me_3SiO^-K^+$	none	Toluene (50)	94	50 (~25)	51
9.	Fully random addition			100	70 (32)	59.3
10.	Alternate copolymer			100	100 (100)	66.7

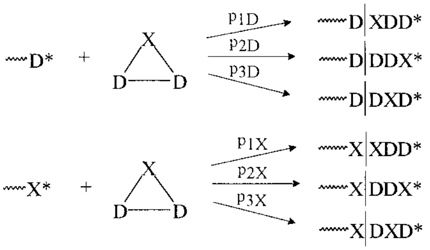
[a] Polymerization was quenched at 60-90% of the monomer conversion.

[b] Concentrations of initiators were $1\text{-}5 \cdot 10^{-3}$ mol·dm^{-3}.

[c] Concentration of 1 was 50 w %.

These systems include: 1) Strongly interacting cation-solvent systems, such as often used hard acid Li^+-hard base THF. In contrast, the interaction of THF with K^+, which is a softer acid, is not efficient enough to compete with the potassium-soft base siloxane multidentate interaction. 2) Systems containing alkali metal and nucleophilic promoter, such as HMPT. 3) Supramolecular complexes of cations, such as complexes with crown ethers (Ref. 14) or cryptates (Ref. 15). 4) Very weakly interacting cations such as tetraalkylammonium or tetraalkylphosphonium, including conjugated acid of the Schwesinger-Schlemper phosphazene base (Ref. 16). Representatives of these four groups are presented in Tab. 2 and all of them are chemoselective.

All copolymers presented in Tab. 2, apart from triads (XDD+DDX) and DXD, contain considerable amounts of non-allowed triads for the regioselective monomer addition, which shows clearly that the process exhibits very poor selectivity in the choice of place of the monomer ring opening. To compare this selectivity on a more quantitative basis we have analysed triad and pentad composition according to first order Markovian statistics. We used simplifying assumption that the rate of monomer addition to the active propagation centre is dependent on the structure of the ultimate siloxane unit only. This assumption reduced the number of possible combinations of monomer addition to six, Eq. (3). On the basis of determined mol% contributions of triads we calculated numerically the conditional probabilities p_{1D}, p_{2D}, p_{3D} and p_{1X}, p_{2X}, p_{3X} of addition of monomer by routes 1, 2 and 3, respectively, to chain ends D and X, respectively, as well as probabilities P_1, P_2 and P_3 of ring opening at 1, 2 and 3, respectively, using set of equations 4.



(3)

$$
\begin{aligned}
P_1 &= (P_1 + P_3)\cdot p_{1D} + P_2\cdot p_{1X} \qquad & p_{1X} + p_{2X} + p_{3X} = 1\\
P_2 &= (P_1 + P_3)\cdot p_{2D} + P_2\cdot p_{2X} & p_{1D} + p_{2D} + p_{3D} = 1\\
P_3 &= (P_1 + P_3)\cdot p_{3D} + P_2\cdot p_{3X} & \\
&P_1 + P_2 + P_3 = 1 &
\end{aligned}
$$

$$
\begin{aligned}
0.03\,[D\underline{D}D] &= P_1(p_{2D}+p_{3D}) + (P_1+P_3)\,p_{2D}\\
0.03\,\{[X\underline{D}D]+[D\underline{D}X]\} &= P_1(1+p_{1D})+P_2(1+p_{2X})+P_3(p_{2D}+p_{3D})+(P_1+P_3)p_{3D}\\
0.03\,[X\underline{D}X] &= P_3\,p_{1D} + P_2\,p_{3X}\\
0.03\,[D\underline{X}D] &= (P_1+P_3)p_{1D} + P_2(p_{2X}+p_{3X}) + P_3\\
0.03\,\{[D\underline{X}X] + [X\underline{X}D]\} &= 2\,P_2\;p_{1X}
\end{aligned}
\tag{4}
$$

Calculated probability parameters, which correspond to relative rates, were checked by Monte

Carlo simulation of the triad contents. However, the analysis at the level of triads proved to be useless as calculations gave many solutions for the same set of triads. Analysis was thus made at the pentad level according to the same general scheme, Eq. (3), using set of 15 equations. In this case solutions were often univocal, see Tab. 3, although, in some cases two equivalent sets of the probability parameters were obtained, Tab. 3, entries 1, 6.

Tab. 3. Probabilities of various ways of monomer addition to active propagation centres in the polymerization of $\lfloor \overline{Ph_2SiO(Me_2SiO)_2} \rfloor$.

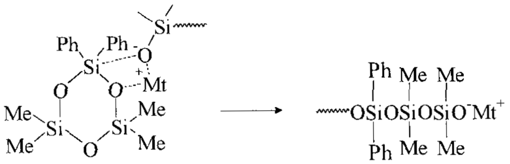
Exp. No[a)]	Probability of addition to end D			Probability of addition to end X			Probability of ring-opening		
	p_{1D}	p_{2D}	p_{3D}	p_{1X}	p_{2X}	p_{3X}	P_1	P_2	P_3
1.	0.47	0.04	0.49	0.12	0.35	0.53	0.45	0.06	0.49
	(0.02)	(0.38)	(0.60)	(0.03)	(0.22)	(0.71)	(0.02)	(0.33)	(0.65)
2.	0.49	0.07	0.44	0.06	0.63	0.31	0.43	0.15	0.42
3.	0.18	0.23	0.59	0.14	0.53	0.33	0.17	0.33	0.50
4.	0.35	0.43	0.22	0.22	0.56	0.22	0.29	0.50	0.21
5.	0.56	0.26	0.18	0.11	0.76	0.13	0.33	0.52	0.15
6.	0.16	0.73	0.11	0.12	0.73	0.15	0.13	0.73	0.14
	(0.73)	(0.13)	(0.14)	(0.64)	(0.15)	(0.21)	(0.72)	(0.13)	(0.15)

[a)] Numbers correspond to numbers of experiments in Tab. 2.

Data in Tab. 3 show that the monomer ring is opened in all three places with a significant probability. This result was unexpected. The anionic polymerization of some partially phenyl substituted cyclotrisiloxanes was reported to proceed regioselectively (Refs. 17, 18). Moreover, 1,1-diphenyltetramethylcyclotrisiloxane was found to be more reactive monomer in the anionic copolymerization than its fully substituted analogue (Ref. 19), which pointed to the preferential attack at the Ph_2SiO unit giving rise to the addition according to route 1.

This unexpected lack of regioselectivity requires comment. Monomer **1** has a complex structure and several factors may affect its reactivity. If the decisive factor in the monomer addition to the polymer end is the formation of the new bond, then the nucleophilic attack should indeed be directed to the most electrophilic center which is silicon bonded to phenyl groups Eq. (5). It may, however, happen that the cleavage of the bond in cyclotrisiloxane is more important and the ring will be ruptured in such a place where the best leaving group from silicon is formed. This factor gives preference to route 2 where the most stable silanolate is formed, Eq. 6.

Finally, we should remember that the propagation centre is an ion pair. Thus, a coordination of the counter-ion to monomer may be important (Ref. 13).



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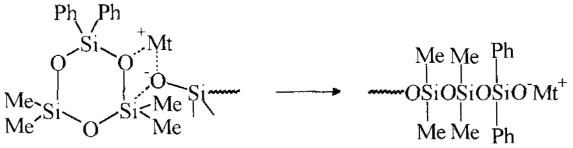
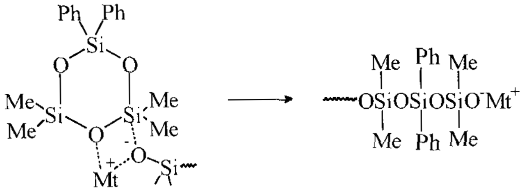


(6)

In contrast to larger siloxane rings which interact with counter-ion multidentally (Ref. 12), the interaction with cyclotrisiloxanes is localized (Refs. 19, 20). The most probable place of the coordination is oxygen linking two methyl substituted silicon atoms as this oxygen is the centre of the highest electron density. Such coordination would facilitate the cleavage of the ring according to route 3, Eq. (7), although, a possible interaction of the cation with the phenyl ring may complicate the situation, giving some preference to route 2.



(7)

Inspection of the data in Table 3 seems to confirm the above conclusions. Route 3 is the most important for systems containing lithium cations which is known of a high ability to coordinate to electron-rich centres. In contrast, for systems containing weakly interacting cations, (Tab. 3, entries 4, 5, 6) the contribution from route 3 is low. Instead, route 2 is preferred by these systems, because it leads to the silanolate anion stabilized by phenyl groups. This stabilization is important as the anion cannot be efficiently stabilized by the counter-ion.

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