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Controlled synthesis of vinylmethylsiloxane–dimethylsiloxane gradient, block and alternate copolymers by anionic ROP of cyclotrisiloxanes

J. Chojnowski*, M. Cypryk, W. Fortuniak, K. Rózga-Wijas, M. Ścibiorek

[a]Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland

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Abstract

Three methods for the controlled synthesis of vinylmethylsiloxane–dimethylsiloxane copolymers have been explored. These methods were based on the anionic ring-opening polymerisation of 2-vinyl-2,4,4,6,6-pentamethylcyclotrisiloxane (VD_2) and on the copolymerisation of this monomer with hexamethylcyclotrisiloxane (D_3). All of them permit control of the molecular weight of the copolymer, the structure of the chain ends and the distribution of vinyl groups along the chain.

Polymerisation of VD_2 was performed using *n*-butyllithium as an initiator in THF. Studies on the sequencing of the siloxane units in the polymer were performed using ^{29}Si NMR spectroscopy and first order Markov chain statistics. These methods were complemented by determination of the sequencing at the chain end bearing a fragment of initiator. The structure of the copolymer obtained at −30 °C is highly regular. Almost 90% of the monomer is added to the chain as a result of the attack of the silanolate centre on the vinyl-substituted silicon in the monomer.

The copolymerisation of VD_2 with D_3 leads to copolymer with gradient distribution of the vinyl groups along the chain. The conversion of both monomers was followed by gas chromatography and the results were analysed by a simulation method and by the classical methods of Mayo–Lewis and of Kelen–Tüdös. These methods gave similar values for the reactivity ratio $r_{D_3} = 0.22$, 0.21 and 0.22, $r_{VD_2} = 7.8$, 7.7 and 8.3 from the M–L, K–T and simulation methods, respectively.

The sequential copolymerisation of D_3 with VD_2 gave the diblock AB copolymers. The block formed in the second step may be contaminated with mers coming from the comonomer.

Keywords: Cyclosiloxanes; Copolymerisation; Chain microstructure

1. Introduction

There has been considerable interest in the functionalisation of polysiloxanes with organic side groups to give special properties to the polymer. Various types of functional groups have been introduced to organic radicals bound to silicon atoms in polysiloxanes [1]. For example, these groups make the polymer hydrophilic [1–4], nucleophilic [5–7], cause it to become a polyelectrolyte [8,9], increase its hydrophobicity [10,11], give it biocidal [12], or special optical properties [13,14], specific reactivity or catalytic properties [15–17]. Certain functional groups may induce mesomorphism [18,19], ferroelectric properties [20] and others.

Synthesis of functionalised polysiloxanes of well-defined structure is particularly important. Such polymers should have a defined molecular weight and low polydispersity, and should also exhibit uniform structure of the macromolecules and a well-defined arrangement of functional groups along the chain. Also important is the precise functionalisation of the polymer chain ends so as to make the controlled building of more complex structures possible. Anionic ring-opening polymerisation and copolymerisation of cyclotrisiloxanes seems to be the unique method, permitting the synthesis of functional polysiloxanes with control of all above-mentioned structural features of the polymer. The silanolate active propagation centre may be stable under vacuum or an inert gas atmosphere and its side reactions with polymer chain, such as back-biting and chain to chain transfer may be avoided or strongly reduced, which makes the polymerisation system close to a living one [21].

Direct synthesis of side-functionalised polysiloxanes by anionic ring-opening polymerisation or copolymerisation is often inconvenient or even impossible. Some functional groups, if they are acidic or electrophilic, do not tolerate the anionic propagation centres. Monomers bearing certain functional groups are often difficult to isolate and purify

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* Corresponding author. Tel.: +48-42-684-4014; fax: +48-42-684-7126.
E-mail address: jchojnow@bilbo.cbmm.lodz.pl (J. Chojnowski).

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[22]. Polymerisation may be too fast to control and interaction of functional groups with active propagation centres may lead to enhanced back-biting or chain scrambling. In such cases, a preferential synthetic strategy may be that involving a precursor group. Cyclotrisiloxanes bearing suitable precursors can be polymerised and the precursor groups in the polymer are then transformed to the target functional groups [1,3,23].

The vinyl group at silicon is a versatile precursor, very often being used in the synthesis of side functionalised polysiloxanes. It can be easily converted into many useful functional groups by various types of addition reactions, such as hydrosilylation [1,24,25], hydrophosphination [26], thiol-ene addition [2–4,7,27] and others. Thus, knowledge of the controlled synthesis of polysiloxanes having vinyl groups pendant to a polymer chain is important for generation of many side functionalised polysiloxanes.

The purpose of this research is to study the synthesis of copolymers composed of vinylmethylsiloxane and dimethylsiloxane units of controlled structures using various approaches based on the anionic ring-opening polymerisation and copolymerisation of cyclotrisiloxanes having vinylmethylsiloxane and dimethylsiloxane units. These routes lead to different well-defined distributions of the vinyl groups along the polymer chain. The first method is the homopolymerisation of the monomer having mixed siloxane units, 2-vinyl-2,4,4,6,6-pentamethylcyclotrisiloxane (VD_2). Such a polymerisation, if it occurred regioselectively, would lead to the regular alternate distribution of vinyl-substituted units [24]. Otherwise, it would lead to a disordered siloxane unit arrangement. However, the single vinyl group should occur in every three siloxane units (in each of monomer units) in the polymer chain as the monomer enters the polymer chain unfragmented and side reactions of chain cleavage are eliminated [28]. The second method is the classical copolymerisation of VD_2 with hexamethylcyclotrisiloxane (D_3). Since all the macromolecules grow simultaneously and chain transfer and back-biting are eliminated in this process, macromolecules should have a uniform structure. A gradient distribution of vinyl groups should be observed if the monomers significantly differed in their reactivity. The third method is sequential copolymerisations of D_3 with VD_2 and VD_2 with D_3 which should lead to diblock copolymers when a monofunctional initiator is used. Thus, all three approaches give copolymers with a different controlled arrangement of functional groups along the polymer chain.

2. Experimental

2.1. Chemicals

Solvent. THF (Polskie Odczynniki Chemiczne, POCH) was purified according to the method described in Ref. [29]. It was stored under vacuum over Na/K alloy in an ampoule fitted with a teflon stopcock.

Initiators. *n*-Butyllithium, 2.5 M solution in *n*-heptane (Aldrich) was analysed by the method described in Ref. [30]. Lithium trimethylsilanolate was prepared by the Frye method [30]. Octamethylcyclotetrasiloxane (ABCR-Gelest), prepurified by drying for several days over CaH_2, (1.11 g, 3.75×10^{-3} mol) was placed in the reactor purged with argon, fitted with a teflon stopcock, a dropping funnel with a double stopcock connected to a dry argon reservoir and a magnetic stirrer. During vigorous stirring, 10 ml of dried diethyl ether solution containing 1.5×10^{-2} mol of methyllithium (Fluka) was slowly added from the dropping funnel. After the addition was completed, the sample was withdrawn, quenched by triethylchlorosilane and analysed by gas chromatography. 1,1,1-Triethyl-3,3,3-trimethyldisiloxane was the only species observed in the chromatogram, confirming that Me_3SiOLi is the only product of the reaction. A solution containing 1.34×10^{-2} mol of Me_3SiOLi was obtained.

Monomers. Hexamethylcyclotrisiloxane (D_3) (Dow Corning) was kept melted over CaH_2 in an ampoule equipped with a teflon stopcock for several days and distilled under vacuum. 2-Vinyl-2,4,4,6,6-pentamethylcyclotrisiloxane (VD_2) was synthesized as described in Ref. [7]. The method of its purification was analogous to that of D_3.

2.2. Polymerisation of VD_2

A standard high vacuum line was used in all polymerisation experiments. Monomer, 2.36 g (1.01×10^{-2} mol), was sublimed under vacuum into the glass reactor equipped with two teflon stopcocks and a magnetic stirrer. Then, THF (2.65 ml) was distilled under vacuum into the reactor to obtain a solution. The vacuum line and the reactor were then filed with argon. While maintaining a positive pressure of argon, 0.094 ml of 2.5 M butyllithium solution in *n*-hexane (2.34×10^{-4} mol) and a known amount of *n*-decane (used as standard for gas chromatography analysis) were added using a precision Hamilton syringe. The polymerisation was carried out at 25 °C for 45 min. It was quenched by introducing 0.05 ml of Me_3SiCl. The polymer was precipitated by addition of 3 ml methanol. It was then separated and purified by repeated dissolution in methylene chloride and precipitation from methanol. Then the polymer was heated at 60 °C under vacuum (10^{-3} Torr) for several hours. The yield of polymer was 2.22 g (94%), $\bar{M}_n = 1 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.2$ (size-exclusion chromatography, SEC). The polymer was characterised by ^{29}Si NMR spectroscopy.

The polymerisation of VD_2 at −30 °C was performed in a similar way. A catalyst solution, 0.056 ml (1.39×10^{-4} mol) was introduced to the solution of 1.40 g (5.98×10^{-3} mol) of VD_2 in 4.0 ml of THF at −78 °C. Then the reactor was sealed and placed in the Neslab CC-80 immersion cooler at −30 °C for 80 h. After that time, the reaction was quenched.

The monomer conversion was about 99%. Polymer, after threefold precipitation from CH_2Cl_2 solution by addition of methanol and heating in vacuum, was analysed by ^{29}Si NMR and MALDI TOF spectroscopy.

2.3. Simultaneous copolymerisation

The solution of D_3, 5.96 g (2.7×10^{-2} mol) and VD_2 3.38 g (1.4×10^{-2} mol) in 10.8 ml of THF was prepared by sequential vacuum distillation of monomers and solvent to the thermostated reactor installed on a vacuum line fitted with two stopcocks and a magnetic stirrer. After purging the reactor with argon, 0.46 ml (1.16×10^{-3} mol *n*-BuLi) of *n*-BuLi solution in *n*-hexane and a known amount of *n*-decane were added. The reaction, carried out at 25 °C, was monitored by sampling and gas chromatography analyses. Samples were withdrawn under pressure through the stopcock to an analytical vessel under vacuum. The reaction was quenched after 220 min at 95% conversion of the less reactive monomer, D_3, by addition of an excess of Me_3SiCl. After threefold precipitation in methanol from CH_2Cl_2 solution and heating at 60 °C/10^{-3} Torr for several hours, 8.61 g of the copolymer was obtained $\bar{M}_n = 1 \times 10^4$, $\bar{M}_n/\bar{M}_w = 1.2$, yield 92% not allowing for the samples withdrawn during the reaction. Copolymerisations at initial D_3 to VD_2 molar ratios of 4:1, 1:1 and 1:2 were performed in an analogous way.

2.4. Sequential copolymerisation

Sequential copolymerisations were performed using a similar technique, but comonomers were polymerised subsequently in a one pot experiment, similarly to that described in Ref. [3].

2.5. Initiation experiment

The polymerisation of VD_2 initiated with Me_3SiOLi was performed in an analogous way to that initiated by *n*-BuLi. Thus, to 3.75 g (1.6×10^{-2} mol) of VD_2 in 4.5 ml of THF, 0.94 ml of 1.34 M solution of Me_2SiOLi in Et_2O was introduced. After 20 min of stirring at room temperature, the polymerisation was quenched at 56% of monomer conversion by introducing 0.5 ml of water. After 15 min of stirring with water the polymer was extracted with CH_2Cl_2, precipitated repeatedly in methanol, dried by heating in a vacuum and subjected to ^{29}Si NMR analysis.

2.6. Analyses

A MALDI TOF spectrogram of the product of the polymerisation of VD_2 was recorded with a Voyager Elite (Per Septive Biosystem) using a DT/Ag/TFA matrix.

Gas chromatography analyses were performed with a Hewlett Packard 6890 chromatograph equipped with a TCD detector and HP-1 column $l = 30$, $d = 0.53$ mm.

^{29}Si NMR analyses were performed with a Bruker MSL 300 spectrometer, using deuterated chloroform as the solvent. Quantitative integration and high resolution spectra were achieved using the gated decoupling technique in the presence of $Cr(acac)_3$. A pulse delay of 15 s was usually used and a typical pulse length was 15 μs.

Molecular weights and molecular weight distribution of polymers were determined by SEC in toluene, using the LDC Analytical chromatograph equipped with refracto-Monitor IV.

2.7. Simulation procedure

Kinetics of copolymerisation were simulated by numerical solving of the approximate differential kinetic equations. In the first approximation, the aggregation of silanolate [31–33] was neglected and first order of reaction was assumed both in the monomers and in silanolate. The initial concentrations of silanolate formed on D_3 and VD_2 end units, D_3^* and VD_2^*, respectively, were calculated according to Eq. (1). This procedure may lead only to determination of apparent values of propagation constants which are concentration dependent and themselves have no real meaning. However, it is assumed that the ratio of these parameters is independent of concentration, thus the reactivity coefficients obtained by this procedure should be close to the real values.

$$\begin{aligned}
[\sim VD_2^*] &= [\mathrm{BuLi}]\frac{k_{12}[VD_2]_0}{k_{21}[D_3]_0 + k_{12}[VD_2]_0} \\
[\sim D_3^*] &= [\mathrm{BuLi}] - [\sim VD_2^*] \\
-\frac{d[D_3]}{dt} &= k_{11}[\sim D_3^*][D_3] + k_{21}[\sim VD_2^*][D_3] \\
-\frac{d[VD_2]}{dt} &= k_{12}[\sim D_3^*][VD_2] + k_{22}[\sim VD_2^*][VD_2]
\end{aligned} \tag{1}$$

Differential equations (1) were solved using the Runge–Kutta–Fehlberg procedure [34]. Apparent propagation constants were found using the non-gradient Rosenbrock optimization procedure, in which the least squares sum of deviations of the calculated concentrations of both monomers from those found experimentally was minimized [35]. Reactivity coefficients r_{D_3} and r_{VD_2} were estimated from the apparent propagation constants found by the simulation of the polymerisation kinetics (using monomer conversion data); r_{D_3} and r_{VD_2} were separately determined by the routine Mayo–Lewis [36] and Kelen–Tüdös methods [37].

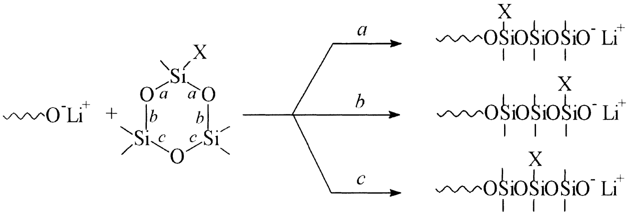
2.8. Sequential analysis

Statistical analysis of the copolymer sequencing (microstructure) at the pentad level was performed using the Markov first order model. The mathematical procedure was described in detail in Ref. [28].

3. Results and discussion

3.1. Polymerisation of 2-vinyl-2,4,4,6,6-pentamethylcyclotrisiloxane

Anionic ring-opening polymerisation of cyclotrisiloxanes may occur without side reactions involving chain cleavage. In this case, the microstructure of the polymer chain arises solely from propagation. The sequencing of siloxane units in the polymer formed by polymerisation of a cyclotrisiloxane with mixed units, such as presented in Eq. (2), depends on the site, at which the ring is opened by the active propagation centre. Opening at any of the three non-equivalent places, marked by *a*, *b*, *c* in scheme (2), leads to different arrangements of units in the triad resulting from the monomer addition.



(2)

Regioselective polymerisation takes place if the opening occurs exclusively at one site. Independently of whether this site is *a*, *b* or *c*, the sequencing of units is the same with X appearing regularly at every third silicon atom in the chain. An example of the fully regioselective reaction of this type of monomer is the polymerisation of 2-hydrido-2,4,4,6,6-pentamethylcyclotrisiloxane in THF at −78 °C initiated by a lithium silanolate as shown by Paulasaari and Weber [23].

Anionic ring-opening polymerisation of VD_2 has been studied earlier [7,25]. Two systems were used: Me_3SiCH_2Li (initiator)/DMSO (activator)/toluene (solvent) [7] and *n*-BuLi (initiator)/THF (activator and solvent) [25]. In both cases, the regioselectivity, determined by ^{29}Si NMR spectroscopy, was poor. A sequential analysis was performed only for the Li/DMSO/toluene system according to simple Bernoulli statistics, which did not permit the determination of the site of the ring-opening.

In this study the polymerisation in the Li/THF system is reinvestigated. The sequencing is analysed at the pentad level using more precise method based on first order Markov chain statistics. The sequential analysis is complemented by studies of initiation by lithium trimethylsilanolate modelling the lithium silanolate propagation centre. It has recently been shown by us that this approach gives the possibility of determining the contribution from the ring-openings at various sites, i.e. at *a*, *b*, *c* [28].

The polymerisation experiments were performed at room temperature and at −30 °C. It has recently been shown by Hadjichristidis et al. [38] that the anionic polymerisation of D_3 by lithium silanolate, when it is carried out at a low temperature shows very high chemoselectivity. This was confirmed by us for the polymerisation of VD_2. The reaction performed at −30 °C was quenched by Me_3SiCl at almost full monomer conversion (about 99%). The absence of any side reactions involving chain cleavage, such as chain transfer and back-biting, was confirmed by the MALDI TOF analysis of the polymer shown in Fig. 1. The MALDI TOF spectrum exhibits only the population of peaks corresponding to macromolecules of general formula $Bu[(SiMe_2O)_2SiViMeO]_nSiMe_3$. Thus, the polymer contains solely macromolecules (polymerohomologues) having an integral number of monomer units with the fragment of initiator at one chain end and the fragment of terminator at the other chain end. This result provides evidence of high precision in the synthesis of the copolymer and supports the view that precise functionalisation of the polymer at a single terminus of the chain is possible. The comparison of the MALDI TOF spectrogram with the size-exclusion chromatogram of the same polymer sample, both presented in Fig. 1, puts in doubt the reliability of the MALDI TOF method for the determination of average molecular weights and polydispersity indices of polymers.

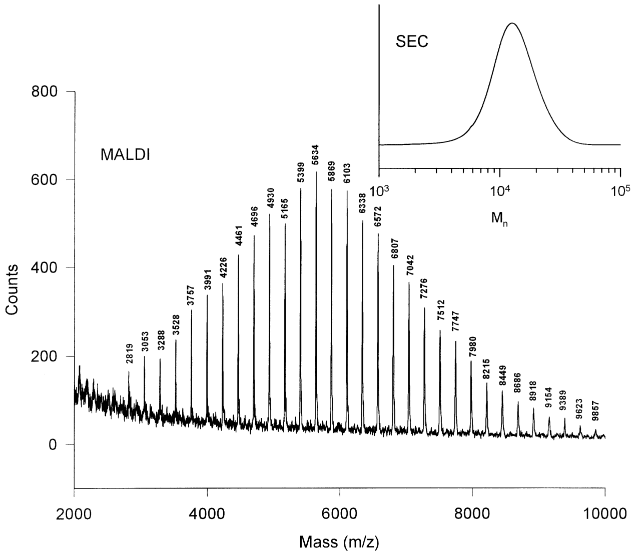


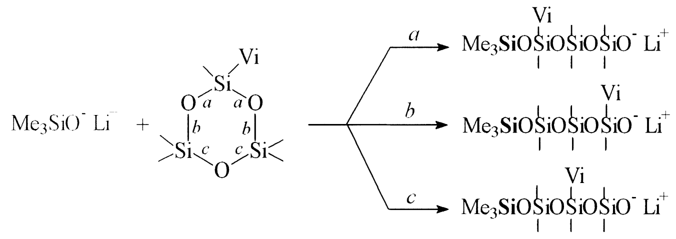
Fig. 1. MALDI TOFF spectrum of the polymer obtained by the polymerisation of VD_2 initiated by BuLi in THF at −30 °C, quenched by Me_3SiCl. The SEC chromatogram of the polymer is shown in the upper right corner; $\bar{M}_n = 11\,500$, PDI = 1.2.

^{29}Si NMR spectra of the polymer obtained at two temperatures are compared in Fig. 2. Signals of Me_2SiO (D) and MeViSiO (V) units are split into pentads reflecting sequencing of D and V units. No splitting is observed due to the existence of different stereoisomers, in accord with earlier results [7]. The assignment of pentads was made on the basis of earlier studies [39]. The fully regioselective polymerisation would lead to only one signal for the

Me_2SiO resonance, corresponding to the DV**D**DV + VD**D**VD pentad and one signal due to the ViMeSiO resonance for the DD**V**DD pentad. Pentads forbidden for the regioselective polymerisation appear in significant amounts in the spectra of polymers obtained at room temperature. However, considerable improvement in the regioselectivity is observed for the polymerisation carried out at low temperature. The intensity of the forbidden signals is significantly lower compared with the signals of polymers formed at room temperature.

The contributions of pentads (Table 1) were determined from the quantitative integration of signals of the respective pentads. Statistical analysis according to first order Markov chain statistics, performed as described in Ref. [28], gave probabilities (relative rates) or ring-opening at various sites (Table 2). The analysis confirms much higher regioselectivity for the polymerisation at low temperature. At −30 °C almost 90% of ring-opening occurs at one place, compared to 67% at ambient temperature.

The statistical method gives two solutions as it does not discriminate between the two unsymmetrical openings, *a* and *b*. An additional experiment of the initiation of polymerisation of VD_2 by lithium trimethylsilanolate in THF was performed in order to select the true solution and hence determine the mechanism by which the polymerisation occurs. It was assumed that trimethylsilanolate opened the monomer ring in a similar way as the propagation centre. The intensity ratio of signals of the $Me_3\mathit{Si}O$ terminal group, formed according to Eq. (3), corresponds to the ratio of the rates of the opening at *a*, *b* and *c*.



δ $Me_3\underline{Si}$ in ppm	
from ref. [37]	found
8.26	8.18
7.22	7.20
7.34	7.30

(3)

The positions of the ^{29}Si NMR signals of terminal Me_3Si groups for the three possible arrangements of siloxane units of monomer attached to the initiator (pathways *a*, *b* and *c* in scheme (3)) were identified based on the chemical shifts of model compounds reported by Ziemelis and Saam [39].

The comparison of results of this initiation experiment with those of the Markov chains analysis presented in Table 2 points to the dominant opening at *a* in the propagation. The fractions of openings *a*, *b* and *c* in the initiation compare well with those in propagation with the dominant opening at *a*, despite some differences in structure between the initiator and the propagation centre.

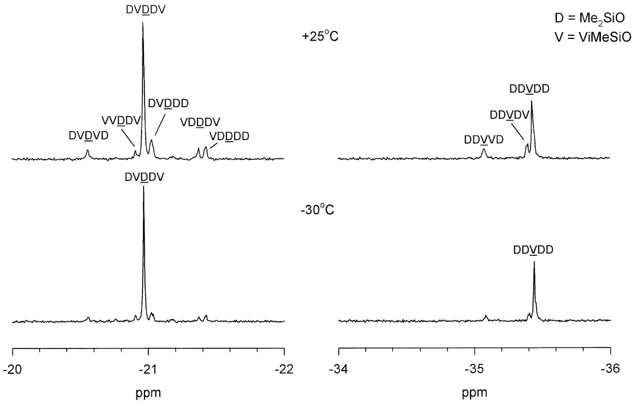


Fig. 2. ^{29}Si NMR spectra of the polymer obtained by the polymerisation of VD_2 initiated by BuLi in THF at 25 and −30 °C.

Thus, the nucleophilic attack on the monomer ring is mostly directed towards the most electrophilic centre, which is the vinyl-substituted silicon atom. The vinyl-substitutent is more electron-attracting (Taft constant $\sigma^* = 0.4$ [40]) than the methyl substituent ($\sigma^* = 0$). Two other factors, i.e. the stabilisation of the formed silanolate (opening at *b*) and the activation of monomer by complexation with counter-ion (opening at *c*), discussed in Ref. [28], here play a minor role. A similar effect of the Si–H substituent ($\sigma^* = 0.49$ [40]) was suggested to be responsible for the very selective ring-opening of 2-hydrido-2,4,4,6,6-pentamethylcyclotrisiloxane by lithium silanolate in THF at −78 °C [23]. These results are different from those observed for opening of 2,2-diphenyl-4,4,6,6-tetramethylcyclotrisiloxane by potassium–silanolate crown ether complex [28] and for 2-naphthyl-2-phenyl-5,5-dimethyl-2,5-disilacyclopentane opened by lithium silanolate [41]. In both these cases, stabilisation of the silanolate centre was the factor controlling ring-opening. On the other hand, monomer activation by the counter-ion was the most

Table 1
Contribution of pentads in the copolymer obtained by anionic polymerisation of VD_2. Values simulated by Monte Carlo method, using parameters from sequential analysis according to Markov first order statistics, are given in parentheses

Polymerisation system, propagation centre/ solvent/temperature	Contribution from allowed pentads[a]										
	VD$\underline{D}$DD	VD$\underline{D}$DV	DV$\underline{D}$DD	VV$\underline{D}$DD	DV$\underline{D}$DV	VV$\underline{D}$DV	DV$\underline{D}$VD	DD$\underline{V}$DD	VD$\underline{V}$DD	VD$\underline{V}$DV	DD$\underline{V}$VD
~ Me_2SiOLi/THF/ −30 °C	4.7 (4.2)	2.7 (1.2)	1.7 (3.8)	2.8 (2.8)	50.8 (51.9)	1.9 (2.3)	2.8 (0.3)	29.1 (27.6)	0 (0.6)	0 (0)	4.7 (5.2)
~ Me_2SiOLi/THF/ 25 °C	5.2 (5.1)	4.0 (3.3)	9.9 (10.3)	1.1 (1.4)	39.6 (39.6)	3.9 (3.6)	4.3 (3.4)	21.7 (22.0)	5.4 (5.9)	0 (0.5)	5.0 (5.0)

[a] Underlined are the central units in pentads.

important factor in the polymerisation of 2,2-diphenyl-4,4,6,6-tetramethylcyclotrisiloxane in THF initiated with BuLi [28].

3.2. Simultaneous copolymerisation of VD_2 with D_3

The anionic ring-opening copolymerisation of cyclotrisiloxane monomers should show similar features to the classic free-radical copolymerisation of vinyl monomers. It should conform to Markov statistics and to the copolymerisation equation. On the other hand, the structure of the copolymer should be different. Since there is no chain cleavage and no termination as the copolymerisation proceeds, all chains are growing in parallel. Under such conditions, macromolecules should be uniform with regard to the composition of units, as well as to the arrangement of units along the chain. Unless the reactivity in copolymerisation of monomers is similar, a gradual change in the density of the functionalised units along the copolymer chain is observed. Since the more reactive monomer enters preferentially the polymer chain, the density of the units derived from this monomer in the copolymer is enhanced at the beginning of the reaction. It drops as the reaction proceeds because the feed becomes poorer in the more reactive monomer. The structure of such a copolymer is between those of statistical and block copolymers.

In the copolymerisation of VD_2 with D_3 some complications occur which may be the reason for deviation of the process from the first order chains Markov statistics, to which the free radical copolymerisation of vinyl monomers conforms. First, the opening of the VD_2 ring at different places leads to the formation of various structures for the active propagation centres which may differ in reactivity. Second, the silanolate propagation centres reversibly form aggregates, in which they are dormant centres [31–33]. In the copolymerisation system various mixed aggregates are formed [32], which may have different dissociation constants. Thus, the aggregation may influence the effective concentration ratio of the silanolate centres of various structures.

The above-mentioned complications were the reason for which we studied the copolymerisation by following the conversion of both comonomers and analysed the kinetic data using two approaches. The classical one was based on the Mayo–Lewis [36] and Kelen–Tüdös [37] methods and the other one was the computer simulation to the best fit with experimental conversion–time dependencies for both monomers using a set of approximate kinetic equations (see Section 2).

The conversion time curves simulation to the best fit to the experimental points, are shown in Figs. 3 and 4. The simulated curves for both monomers fit almost ideally to the experimental points which permits belief that the assumption made in the simulation procedure is a reasonable approximation.

The reactivity factors determined by Mayo–Lewis,

Table 2
Results of sequential analysis of the copolymer obtained by anionic ROP of VD_2. Fractions of monomer openings (%) at sites *a*, *b*, and *c* (schemes (2) and (3)) obtained by statistical analysis of pentads of siloxane units (selected solutions are underlined) and by analysis of initial triads formed by reaction of monomer with initiator

No.	Polymerisation system, propagation centre/solvent/ temperature	% of the monomer ring-opening					
		From analysis of pentads according to Markov first order statistics (%)			From analysis of initial triads observed in initiation experiment		
		a	*b*	*c*	*a*	*b*	*c*
1	~ Me_2SiOLi/THF/−30 °C	$\underline{89}$ 8	$\underline{8}$ 89	$\underline{3}$ 3			
2	~ Me_2SiOLi/THF/25 °C	$\underline{67}$ 21	$\underline{21}$ 67	$\underline{12}$ 12	78	11	11

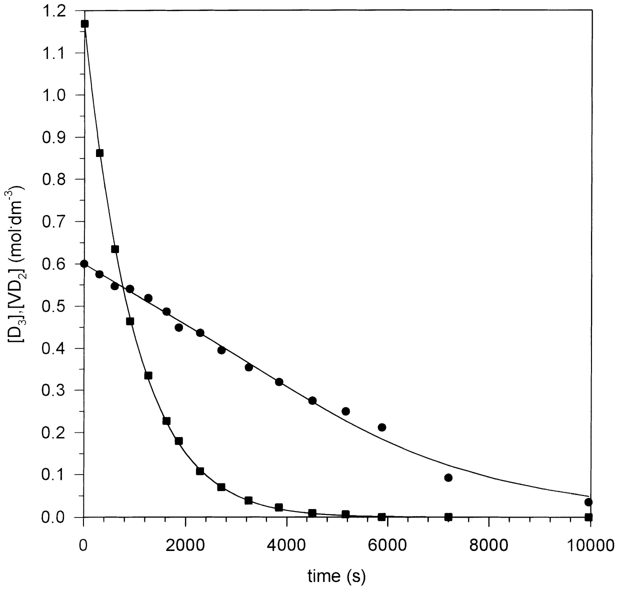


Fig. 3. Conversion–time curves for the simultaneous copolymerisation of VD_2 (■), and D_3, (●), initiated by BuLi in THF, 25 °C, $[VD_2]_0/[D_3]_0 = 2$. Points are obtained from experiments while curves are simulated; $[BuLi]_0 = 5.62 \times 10^{-2}$ mol dm^{-3}.

Kelen–Tüdös and simulation methods are presented in Table 3. In spite of a crude approximation of the simulation method, it gives results very close to those obtained by routine methods based on the copolymerisation equation. The linear plot of Kelen–Tüdös function (Fig. 5) gives confidence for the validity of the assumption that the copolymerisation of VD_2 with D_3 approximately obeys the Markov first order chain statistics.

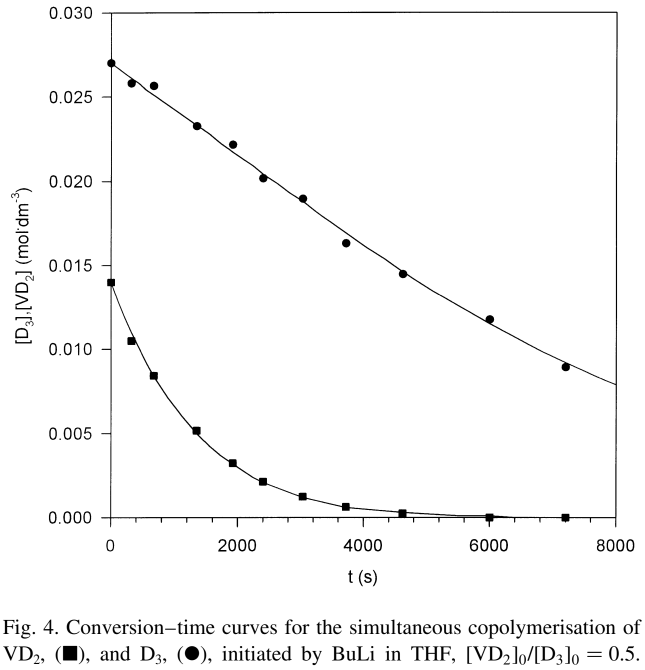


Fig. 4. Conversion–time curves for the simultaneous copolymerisation of VD_2, (■), and D_3, (●), initiated by BuLi in THF, $[VD_2]_0/[D_3]_0 = 0.5$. Points are obtained from experiments while curves are simulated; $[BuLi]_0 = 4.6 \times 10^{-2}$ mol dm^{-3}, 25 °C.

Table 3
Reactivity coefficients, r_{D_3} and r_{VD_2}, estimated by Mayo–Lewis and Kelen–Tüdös methods and by kinetic simulation

	M–L method	K–T method	Simulation[a]
$r_{D_3} = k_{D_3^*/D_3}/k_{D_3^*/VD_2}$	0.22	0.21	0.22
$r_{VD_2} = k_{VD_2^*/VD_2}/k_{VD_2^*/D_3}$	7.8	7.7	8.1

[a] Average parameters used in the simulation, i.e. average apparent propagation constants in dm^3 mol^{-1}s^{-1} were: $k_{D_3^*/D_3} = 0.0058$, $k_{D_3^*/VD_2} = 0.0026$, $k_{VD_2^*/D_3} = 0.0021$, $k_{VD_2^*/VD_2} = 0.017$. Since the aggregation of silanolates [31–33] is neglected here, the true specific rates of propagation are much higher. Nevertheless, they remain in a similar mutual quantitative relationship as the above-mentioned parameters. D_3^* and VD_2^* denote the active propagation centres resulting from the addition of D_3 and VD_2, respectively, to the growing chain.

The comparison of the experimental dependencies of the conversion–time for both comonomers also permits the direct determination of the density distribution of the vinyl group along the polymer chain (Fig. 6). The considerable difference in reactivity of both monomers in the copolymerisation is reflected in a gradient structure of the copolymer macromolecule shown in Fig. 6.

3.3. Sequential copolymerisation of VD_2 with D_3

The anionic ROP of cyclotrisiloxanes can be used for the controlled synthesis of siloxane–siloxane block copolymers. Such copolymers were synthesized by sequential copolymerisation of two cyclotrisiloxane monomers initiated by butyllithium [3]. The second monomer was added when the conversion of the first one attained not more than about 90–95%. Further conversion of the monomer in the first step of the sequential copolymerisation could

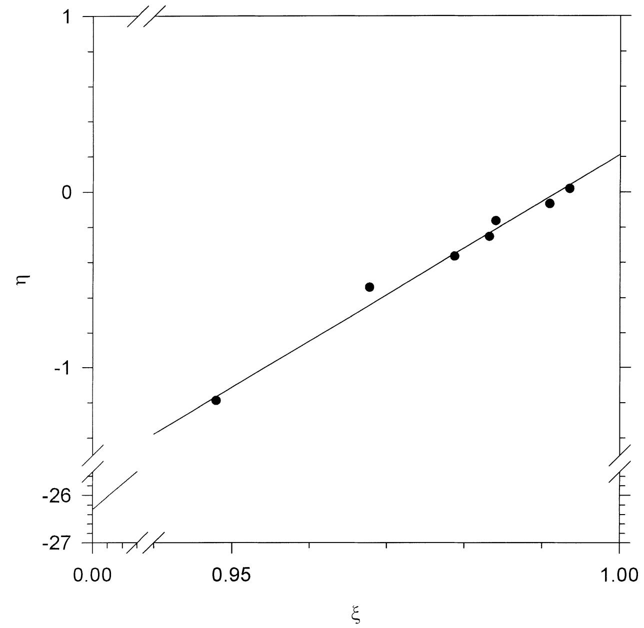


Fig. 5. Kelen–Tüdös plot for the simultaneous copolymerisation of D_3 and VD_2 in THF.

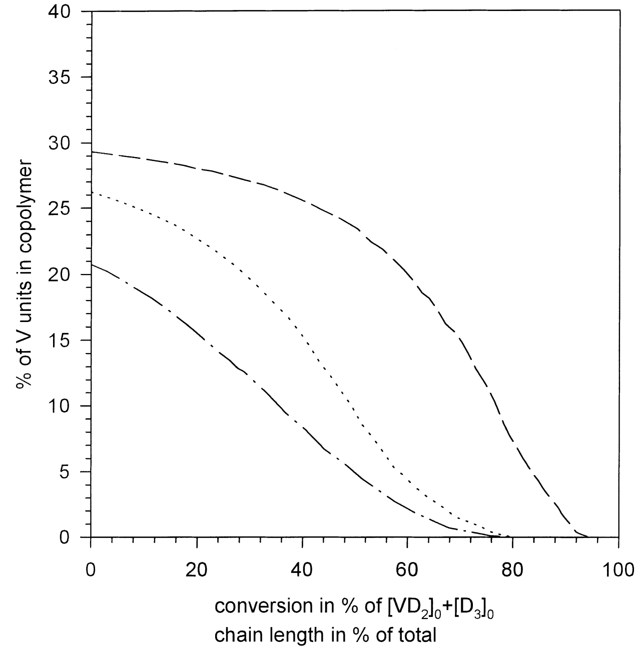


Fig. 6. Simulated density distribution of vinyl group along the chain, i.e. instant contribution of V units in copolymer versus chain length as it grows, in the copolymer obtained by the simultaneous copolymerisation of VD_2 and D_3 initiated by BuLi in THF; $[VD_2]_0/[D_3]_0 = 1 : 4$, -·-, 1:2, ···, 1:1, - - -.

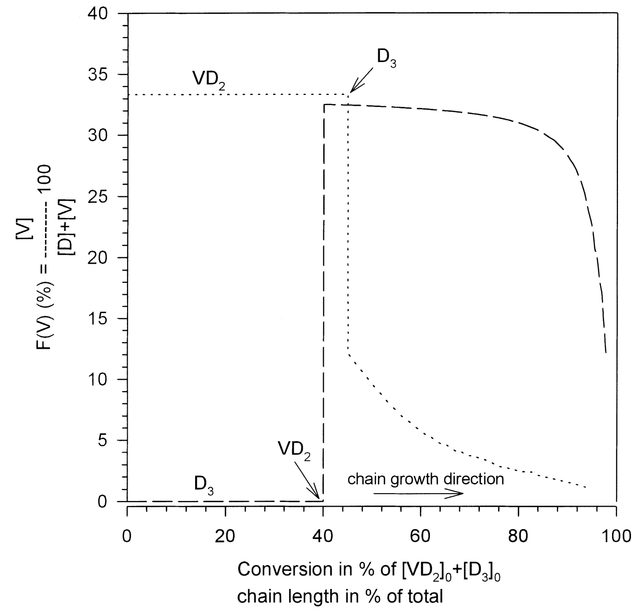


Fig. 7. Simulated density distribution of vinyl groups along the chain, i.e. instant contribution of V units in copolymer versus chain length as it grows, in the block copolymers of VD_2 and D_3 obtained in sequential copolymerisation of VD_2 with D_3 as the second comonomer introduced at 90% conversion of VD_2, ···, D_3 with VD_2 as the second comonomer introduced at 90% conversion of D_3, - - -, (simulated dependencies for the copolymerisation in THF, 25 °C on SiOLi centres; initial concentrations of comonomers are the same in both cases).

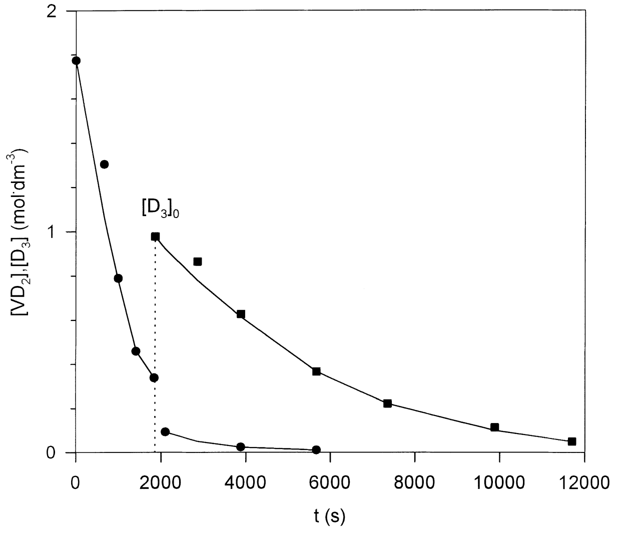


Fig. 8. Conversion–time curves for the sequential copolymerisation of VD_2, (■), and D_3, (●), on SiOLi centres in THF, 25 °C; $[Me_3SiOLi]_0 = 3.55 \times 10^{-2}$ mol dm^{-3}. Discontinuity of the concentration curve for VD_2 corresponds to dilution resulted from addition of the D_3 solution.

lead to a significant role of the chain cleavage processes. Thus up to about 10% of the initial monomer concentration used in the first step remained unreacted when the second monomer was introduced, which inevitably led to the contamination of the second block with the comonomer units. A knowledge of the kinetic parameters of the copolymerisation of VD_2 with D_3 permits us to predict the distribution of vinyl groups in both diblock copolymers, one obtained by the polymerisation of VD_2 in the second step and the other with the VD_2 polymerised in the first step (Fig. 7). Since the vinyl-substituted monomer shows a higher reactivity, it was advantageous to polymerise D_3 in the first step. Remaining D_3 entered only very reluctantly to the block built by the VD_2 units. The simulated conversion–time curves are shown in Fig. 7. The contamination of the poly-VD_2 block with D_3 may be avoided by quenching the polymerisation of VD_2 well before the full consumption of this comonomer. On the other hand, when the vinyl-substituted monomer was polymerised first, its remaining part entered the second poly-D_3 block relatively fast. This block therefore became seriously contaminated with the vinylmethylsiloxane units. An example of the kinetics of the sequential copolymerisation of VD_2 with D_3 confirming this conclusion is shown in Fig. 8.

It is worth adding that the ratio of specific rates of the homopropagation of both monomers evaluated from the kinetics of their sequential copolymerisation is $k_{VD_2^*/VD_2}/k_{D_3^*/D_3} = 2.65–3.15$.[1] These values compare well

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[1] These values were obtained allowing for the dilution of the propagation centre as a result of introducing the comonomer solution in the second step of the sequential copolymerisation. The correction was calculated, assuming that polymerisation order in the propagation centre is in the range of 0–0.25, on the basis of Ref. [33].

with that of 2.93 evaluated for the reactivity ratio from the simulation procedure.

4. Conclusions

Vinylmethylsiloxane–dimethylsiloxane copolymers of a low polydispersity with various controlled arrangements of siloxane units may be obtained by anionic ring-opening polymerisation of 2-vinyl-2,4,4,6,6-pentamethylcyclotrisiloxane (VD_2) and by its copolymerisation with hexamethylcyclotrisiloxane (D_3).

Polymerisation of VD_2 in THF initiated by BuLi leads to polysiloxane containing one vinyl group in each of the monomer units. The order within the monomer units achieves a high degree of regularity when the monomer is polymerised at a very low temperature. This makes possible synthesis of the copolymer having an almost perfectly alternative $-V-D_2-$ chain structure. At −30 °C the regioselectivity in the ring-opening is high, as about 90% of the monomer is opened at the silicon bearing the vinyl group.

Copolymerisation of VD_2 with D_3 in THF initiated by BuLi gives a gradient arrangement of vinyl groups. VD_2 being more reactive, respective apparent reactivity ratios, $r_{VD_2} = 7.9$ and $r_{D_3} = 0.22$, adds to the chain more readily. Therefore, the density of vinyl groups in the polymer chain decreases with the growth of the copolymer chain.

A block arrangement of the VD_2 and D_3 in the copolymer is achieved using sequential copolymerisation of both monomers. VD_2 may be polymerised in the second or in the first step. In the latter case, the purity of the second block is lower.

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