MAREK CYPRYK, BOGUMIŁA DELCZYK

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences
ul. Sienkiewicza 112, 90-363 Łódź
e-mail: mcypryk@cbmm.lodz.pl

New gradient siloxane copolymers

Summary — Anionic ring opening polymerisation of cyclotrisiloxanes allows to synthesise well-defined polysiloxanes. Experimental evidence for the selectivity of polymerisation and for the possibility of controlling the structure and functional group distribution in polysiloxanes obtaining by this method is provided. Siloxane copolymers of controlled gradient distribution of units along the chain may be obtained in this way. Kinetic studies of copolymerisation in combination with computer simulation make possible designing a copolymer structure. Thermal and dynamic mechanical studies confirm that properties of gradient copolysiloxanes are different from those of block copolymers of the same molecular weight and cumulative composition.

Key words: cyclotrisiloxanes, anionic ring opening polymerization, kinetics, gradient copolysiloxanes.

NOWE SILOKSANOWE KOPOLIMERY GRADIENTOWE

Streszczenie — Kopolimery gradientowe stanowią nową klasę polimerów o składzie zmieniającym się stopniowo wzdłuż łańcucha (rys. 1). W wyniku gradientowego rozkładu merów oddziaływania międzycząsteczkowe zmieniają się tu w sposób ciągły wzdłuż łańcucha, co odróżnia te kopolimery od innych kopolimerów, np. blokowych, lub bezładnych. Ta specyficzna cecha kopolimerów gradientowych powinna spowodować ich unikatowe własności termiczne i mechaniczne. Tego rodzaju siloksanowe kopolimery otrzymano w wyniku kontrolowanej anionowej kopolimeryzacji z otwarciem pierścienia heksametylocyklotrisiloksanu z cyklotrisiloksanami zawierającymi grupy funkcyjne przy atomach krzemu. Anionowa polimeryzacja cyklotrisiloksanów ma cechy polimeryzacji żyjącej i pozwala na kontrolę procesu oraz ciężarów cząsteczkowych i struktury otrzymanych polimerów (schemat A). Pokazano możliwości modyfikacji grup funkcyjnych w łańcuchu (schematy B i C) oraz możliwości kontroli ich rozkładu wzdłuż łańcucha. Przedstawiono wyniki własnych badań kinetycznych kopolimeryzacji mających na celu wyznaczenia współczynników reaktywności komonomerów (rys. 2 i 3), co stwarza możliwość projektowania i przewidywania struktur kopolimerów. Pokazano przykłady modyfikowania chwilowego składu kopolimerów siloksanowych otrzymanych metodą kopolimeryzacji równoczesnej oraz kopolimeryzacji z ciągłym dodawaniem jednego z monomerów do mieszaniny polimeryzacyjnej (rys. 3, 5 i 6). Przedstawiono również wstępne wyniki badań niektórych właściwości omawianych kopolimerów (rys. 7).

Słowa kluczowe: cyklotrisiloksany, anionowa polimeryzacja z otwarciem pierścienia, kinetyka, gradientowe kopolisiloksany.

The constant rapid development of technologies still demands new, higher performance and more specialized materials. This requires more precise control over the polymerisation process and over the structure of resulting polymers. It is particularly important when the more complex polymeric structures, such as graft, branched, star-shaped, dendritic polymers and polymer networks are needed. Since they are often built from linear polymeric building blocks, the precisely defined composition of these blocks is crucial. The factors, which are subject to control, are: molecular weight and polydispersity, structural topology of macromolecules, the type and distribution of functional groups.

The methods of control of the above factors in the synthesis of linear copolysiloxanes, in particular those having gradient unit distribution in the chain, are discussed.

TOPOLOGY OF LINEAR COPOLYMERS

Four classes of linear copolymers may be distinguished, depending on the distribution of the repeating units along the chain. They are symbolically illustrated in Figure 1 for the case of binary copolymers.

The normalized chain length represented on the x-axis can be related to monomer conversion [$F(M_1)$], according to equation (1) which is valid for the controlled/living polymerisation systems.

$$\text{chain length} = \frac{\text{conversion}}{[\text{initiator}]_0} \tag{1}$$

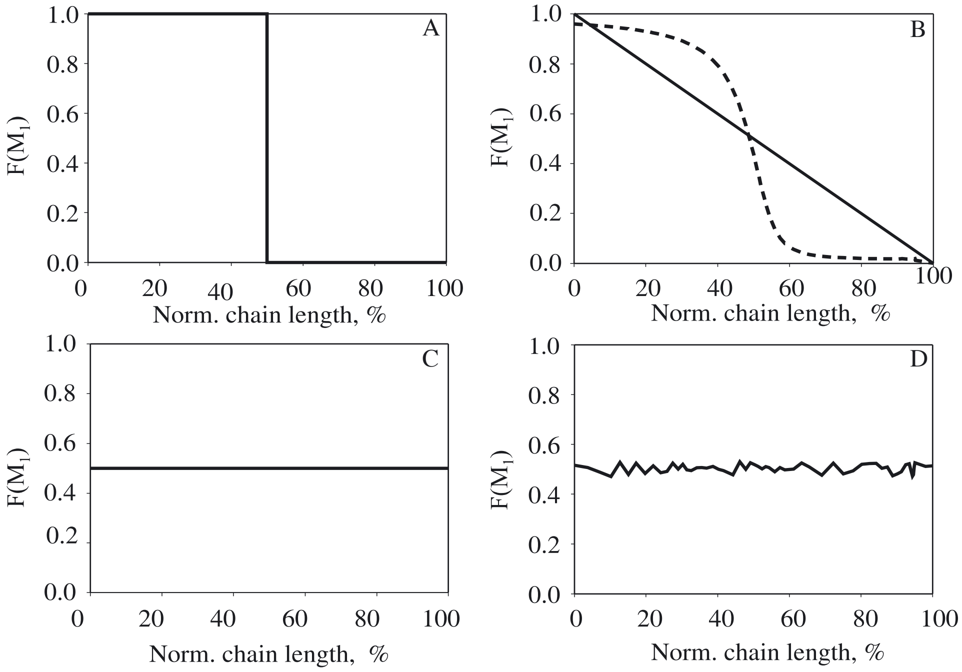


Fig. 1. Possible unit distributions in linear binary copolymers: A — block; B — gradient (continuous line — ideal distribution, dashed line — example of real distribution); C — alternate; D — random copolymer

The 'gradient' or 'tapered' copolymers (Fig. 1B) have been known for a long time. They are usually formed when two or more monomers are copolymerised together. However, uncontrolled polymerisation leads to copolymers having a non-uniform gradient, that is, the compositional drift may vary from one polymer chain to another (dotted line in Fig. 1). Constantly developing techniques of controlling the polymerisation processes and, consequently, of a chain composition stimulate a growing interest in gradient copolymers. Latest reports point to a significant difference of their physical properties compared to those of block and random copolymers [1, 2].

The DSC thermograms of gradient copolymers show that the phase transitions are broader and their temperatures are shifted compared to those of block copolymers of a similar cumulative composition and molecular weight. Moreover, the phase states of the gradient copolymer may strongly depend on the thermal history of the sample. Similar effects are observed for the temperature dependences of mechanical properties [1].

This behaviour is interpreted in terms of a specific morphology of gradient copolymers. Due to the presence of a segment of a variable composition, partially compatible with both homogenic phases, the microphase separation is disturbed and the interface is broader (more 'fuzzy'), compared to block copolymers. This affects segmental mobility and, consequently, thermal and mechanical properties of these polymers. Computer simulations predict that the microphase separation and related properties, such as interfacial activity, may be varied in a wide range by modifying the unit distribution along the chain [2—4].

Computer simulations show also that gradient polymers may have very interesting surface properties, which suggest their application as compatibilisers, surfactants and emulsifiers [1—4].

As it was already mentioned, gradient copolymers may be synthesised by simultaneous copolymerisation of two or more monomers, provided they are able to cross-polymerise. Assuming the Markov 1st order kinetic model, conversion of monomers in a binary copolymerisation (for the sake of clarity we restrict discussion only to the simplest two monomers copolymerisation system), is expressed by the following equations:

$$\sim M_1^* \xrightarrow{M_1\,(k_{11})} \sim M_1^* \qquad \sim M_2^* \xrightarrow{M_1\,(k_{21})} \sim M_1^* \qquad r_1 = \frac{k_{11}}{k_{12}} \tag{2a}$$

$$\sim M_1^* \xrightarrow{M_2\,(k_{12})} \sim M_2^* \qquad \sim M_2^* \xrightarrow{M_2\,(k_{22})} \sim M_2^* \qquad r_2 = \frac{k_{22}}{k_{21}} \tag{2b}$$

Therefore

$$\frac{d[M_1]}{dt} = -(k_{11}[M_1^*] + k_{21}[M_2^*])[M_1] \tag{3a}$$

$$\frac{d[M_2]}{dt} = -(k_{12}[M_1^*] + k_{22}[M_2^*])[M_2] \tag{3b}$$

Transformation of these equations leads to the well known copolymerisation equation [5]:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \tag{4}$$

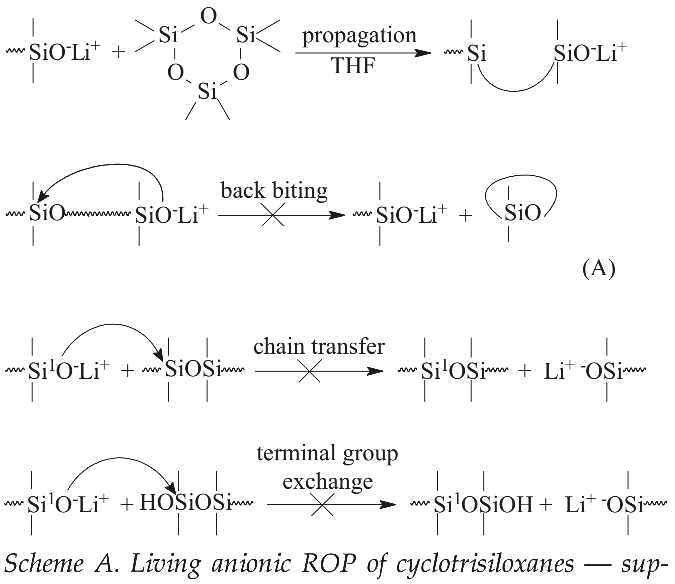
Thus, the composition of copolymer depends on the monomer concentrations in the feed and on parameters r_1 and r_2 which are termed the monomer reactivity ratios [5].

To prepare gradient copolymers in a controlled way, living (or quasi-living) polymerisation system is required. There are examples of copolymers of styrene derivatives with butadiene or isoprene [6, 7] and copolymers of ethylene oxide with butylenes oxide [8, 9] obtained in the anionic way. Synthesis of gradient copolymers by living cationic copolymerisation of some vinyl monomers was also reported [10, 11]. Recently developed controlled radical polymerisation techniques proved to be very useful for the synthesis of such copolymers [1, 12—20].

CONTROLLED SYNTHESIS OF SILOXANE COPOLYMERS

Unique surface properties of polysiloxanes open a wide range of potential applications for the siloxane gradient copolymers. Unusual flexibility of the backbone, low surface tension and amphiphilic character of polysiloxanes result in favourable surface properties of these polymers, making them very useful as surfactants, foam-controlling agents, adhesives, surface modifiers and so on [21, 22]. Polysiloxanes may be easily modified in side groups, which makes possible alteration of their properties in an extremely wide range. For example, typical alkylpolysiloxanes are strongly hydrophobic, but introduction of polar or ionic substituents makes them nucleophilic or even water soluble [21].

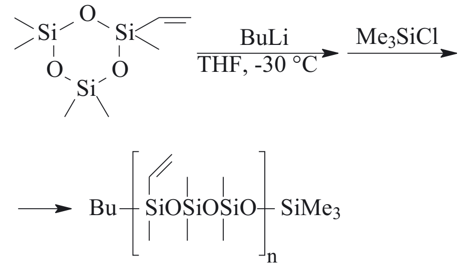
The process which offers the possibility of controlled synthesis of polysiloxanes is anionic ring opening polymerisation (AROP) of cyclotrisiloxanes. Cyclotrisiloxanes are the only class of available siloxane monomers, which possess a ring strain. This makes them much more reactive in the Si-O bond breaking reactions than the polymer chain itself and therefore high polymer yield (>90 %) can be achieved when the polymerisation is stopped before the side reactions become important (Scheme A). Anionic polymerisation of these monomers shows the features of the living process (fast and quantitative initiation, side reactions much slower than propagation, no termination) and is suitable for the synthesis of polysiloxanes of well defined structure [21—25].



Scheme A. Living anionic ROP of cyclotrisiloxanes — suppression of side reactions

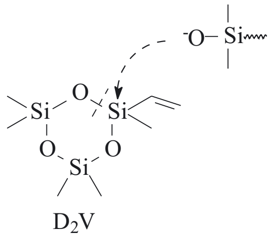
Chemo- and regioselectivity of AROP of cyclotrisiloxanes

The chemoselectivity of AROP of cyclotrisiloxanes was confirmed by MALDI TOF analysis of the polymers obtained in homopolymerisation of vinylpentamethylcyclotrisiloxane (D_2V, where D = Me_2SiO, V = ViMeSiO) initiated by BuLi in THF [equation (5)]. Besides the expected homologue series of linear chains, $Bu[(Me_2SiO)_2ViMeSiO]_nSiMe_3$, differing by n value corresponding to the molecular weight of the monomer, no other products were observed [23, 24].



(5)

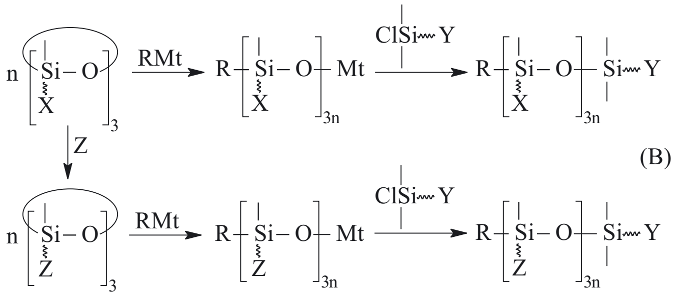
Sequence analysis based on the ^{29}Si NMR spectra of polymers obtained from D_2V revealed that the attack of lithium silanolate on the vinyl-substituted silicon atom dominates (Formula I) [23]. At room temperature this ring opening participates in 67 % in the propagation. At -30 °C it reaches 90 % of all monomer addition acts. Thus, using the monomers with mixed substituents, which contain siloxane units of different electrophilicity, the synthesis of regular copolymers by homopolymerisation is possible.



(I)

Control of functional groups structure

Anionic polymerisation may be used for a wide range of substituted cyclosiloxanes. In the case when the substituents are not stable under basic conditions, the monomers with precursor groups may be applied. The precursor groups are then converted to the desired functions by the reactions on polymer (Scheme B).



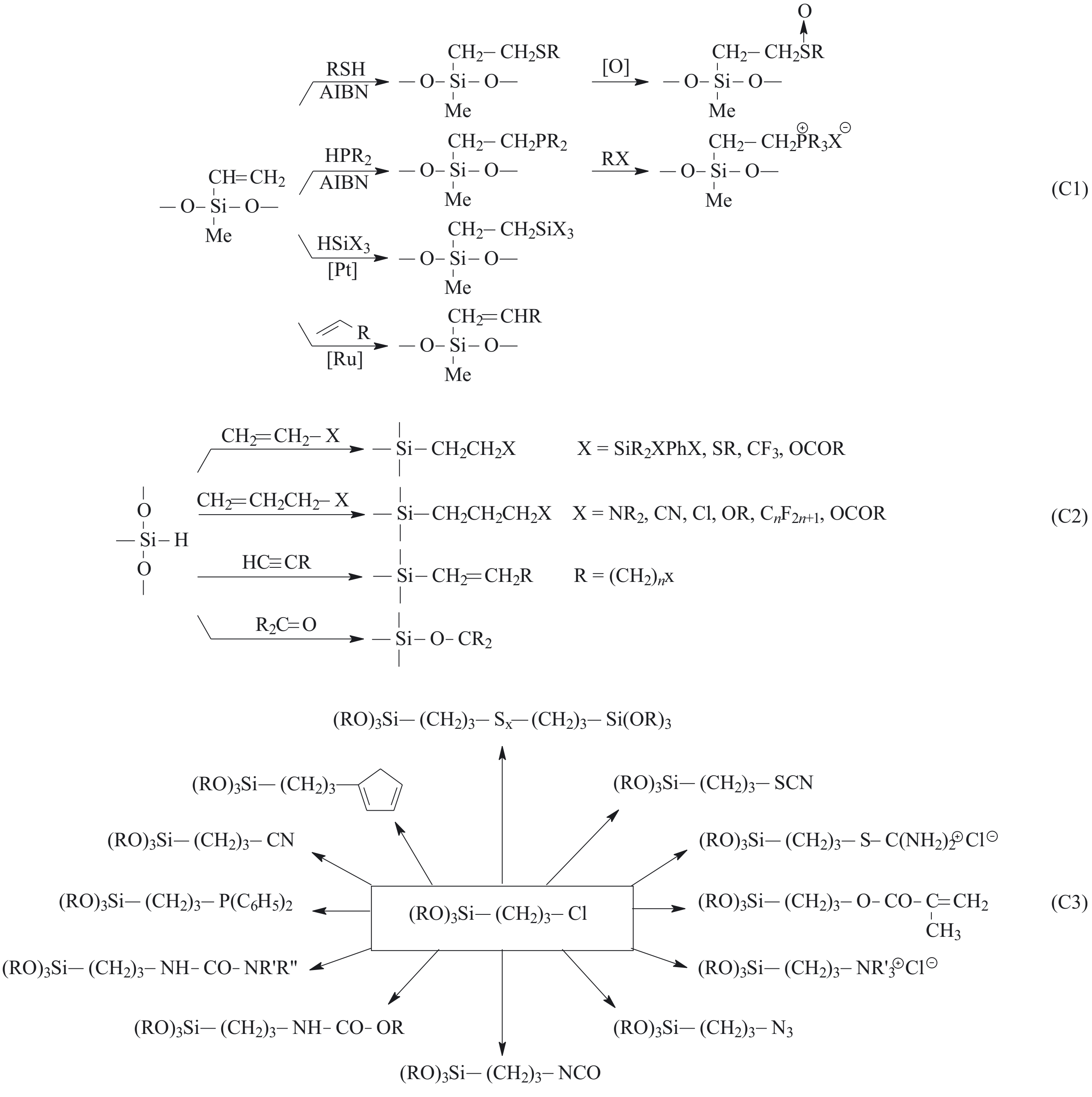
Scheme B. Modification of functional groups in AROP of cyclotrisiloxanes

Widely used precursor groups are the vinyl group Si-Vi [21, 26, 27], Si-H [28, 29] and the chloropropyl group Si-C_3H_6Cl [30]. They are relatively stable under anionic conditions (selective polymerisation of hydrogensiloxanes requires low temperatures [31]) and can be easily modified. Some examples of modification reactions are presented in schemes C1—C3.

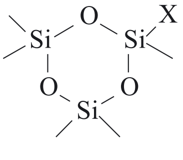
Among the presented reactions, hydrosilylation which involves addition of Si-H to various kinds of multiple bonds, is particularly important as it offers a vast possibility of introducing a great variety of functional groups to silicon [28, 29].

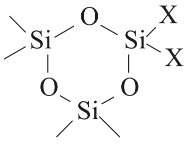
Control of the functional group distribution

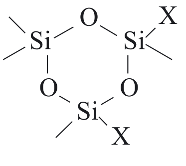
Reactivity ratios determine the polymer composition in the simultaneous copolymerisation, according to

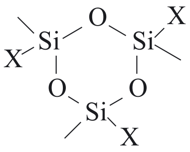


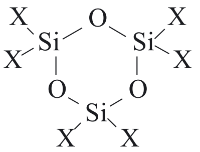
Scheme C. Common modification reactions of vinyl (C1), hydride (C2) and chloropropyl (C3) pendant groups in polysiloxanes equations (2) and (3) (assuming the Markov 1st order model). Reactivity ratios may be altered to some extent by changing a solvent and initiator, what modifies the structure of active centre [22]. The density of functional group distribution may be varied using monomers with different content of these groups. The content of functional groups X in cyclotrisiloxanes may vary from 1 to 6 [Formula (II)—(VI)]:


(II)


(III)


(IV)


(V)


(VI)

To control the functional group distribution in a copolymer, the knowledge of the kinetics of polymerisation and, in particular, of the reactivity ratios, is necessary. The example runs of simultaneous copolymerisations of D_3 + V_3 and D_3 + D_2V are shown in Fig. 2A [24] and Fig. 2B [23], respectively.

Reactivity ratios for both monomer pairs were determined by computer simulation program which numerically solved the kinetic equations of polymerisation assuming Markov 1st order model [equations (2)—(4)] and fitted all propagation rate constants to the monomer conversion curves [23, 24]. This method has a universal applicability, provided the kinetic law of copolymerisation is correctly defined. For comparison, the reactivity ratios were also estimated using the Kelen-Tüdös method [32]. Both methods give very similar results, confirming that the Markov 1st order statistics is an appropriate model for cyclotrisiloxane polymerisation. Good agreement between simulation and Kelen-Tüdös method was also obtained for other copolymerisation systems studied, for example, D_3 + $[CF_3(CH_2)_2(Me)SiO]_3$ (F_3) and D_3 + $[Cl(CH_2)_3(Me)SiO]_3$ (D^{PrCl}_3) [33]. The calculated values

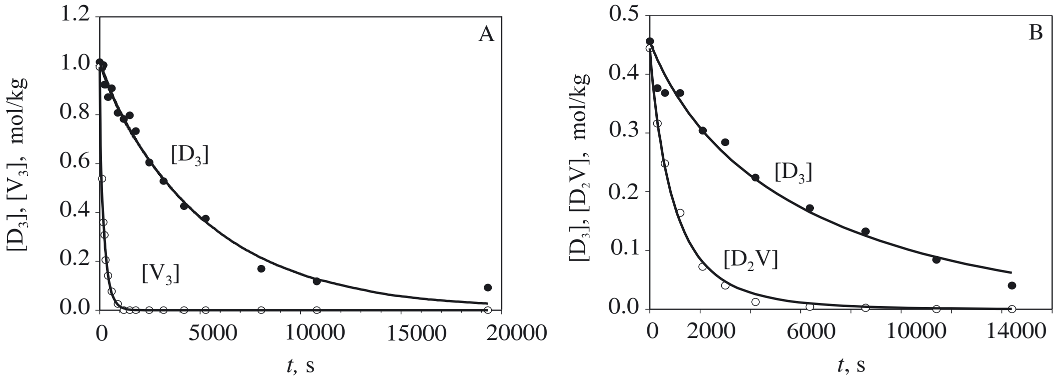


Fig. 2. Kinetics of conversion of comonomers for the anionic (initiated by BuLi) copolymerisations D_3 + V_3 (1:1) (A) and D_3 + D_2V (1:1) (B) in THF. Initial concentrations: (A) $[D_3]_0 = [V_3]_0 = 1.0$ mol/kg, $[BuLi]_0 = 0.0021$ mol/kg [24]; (B) $[D_3]_0 = [D_2V]_0 = 0.45$ mol/kg, $[BuLi]_0 = 0.0256$ mol/kg [23]

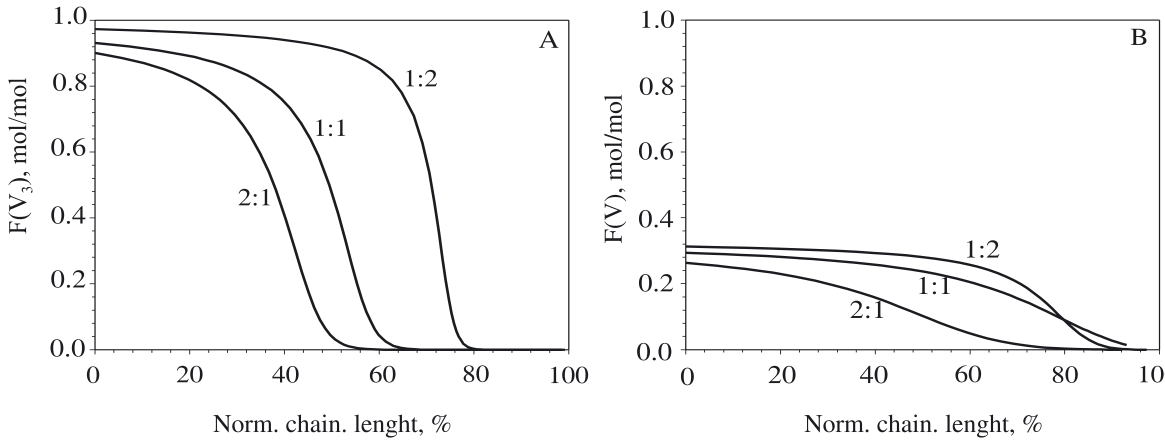


Fig. 3. Instantaneous composition of copolymers for the copolymerisations: (A) D_3 + V_3 (2:1, 1:1, 1:2 mol/mol) and (B) D_3 + D_2V (2:1, 1:1, 1:2 mol/mol). Reactivity coefficients (determined by computer simulation using the procedure described in [23]): (A) $r_{D3} = 0.036$, $r_{V3} = 17.83$; (B) $r_{D3} = 0.21$, $r_{D2V} = 7.7$

of reactivity ratios for these copolymerisation systems are collected in Table 1.

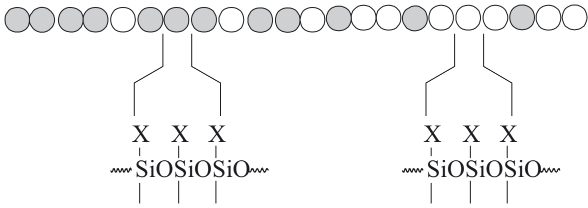
T a b l e 1. Reactivity ratios for the cyclotrisiloxane copolymerisation systems initiated by BuLi in THF

Copolymerisation system	Kelen-Tüdös		Simulation	
	r_{D3}	r_{X3}	r_{D3}	r_{X3}
D_3+V_3	0.036[a)]	17.8[a)]	0.054	17.3
D_3+D_2V	0.21[b)]	7.7[b)]	0.19	8.07
D_3+F_3[c)]	0.12	38.0	0.12	31.7
D_3+$(D^{PrCl})_3$[c)]	0.18	1.09	0.24	1.36

[a)] ref. [24], [b)] ref. [23], [c)] ref. [33].

Both vinyl-substituted cyclosiloxanes, V_3 and D_2V, are more reactive than D_3. However, the difference in reactivity between V_3 and D_3 is significantly greater than for the D_2V-D_3 system. This is reflected in a chain structure. Knowing the reactivity ratios it is possible to predict and design the chain microstructure of a gradient copolymer. Fig. 3 shows the simulated compositions of V_3-D_3 and D_2V-D_3 copolymers produced by simultaneous copolymerisations of mixtures of comonomers with different starting proportions [33]. Previously determined reactivity ratios were assumed [23, 24]. Copolymer D_3-V_3 consists of the two almost homogeneous blocks joined by the short intermediate segment of a 'steep' composition gradient (Fig. 3A). In the case of D_2V-D_3 system, the composition gradient is broad and extends from the beginning to the end of a chain (Fig. 3B). It should be noticed that the density of the V units in the latter copolymer cannot exceed 1/3, as there is only one V unit in the monomer.

It is worth mentioning that each addition of a monomer molecule to the growing chain is equivalent to adding a sequence of three siloxane units [Formula (VII)]. Thus, the simulated instantaneous composition and the density of functional groups are only a statistically justified approximation.



(VII)

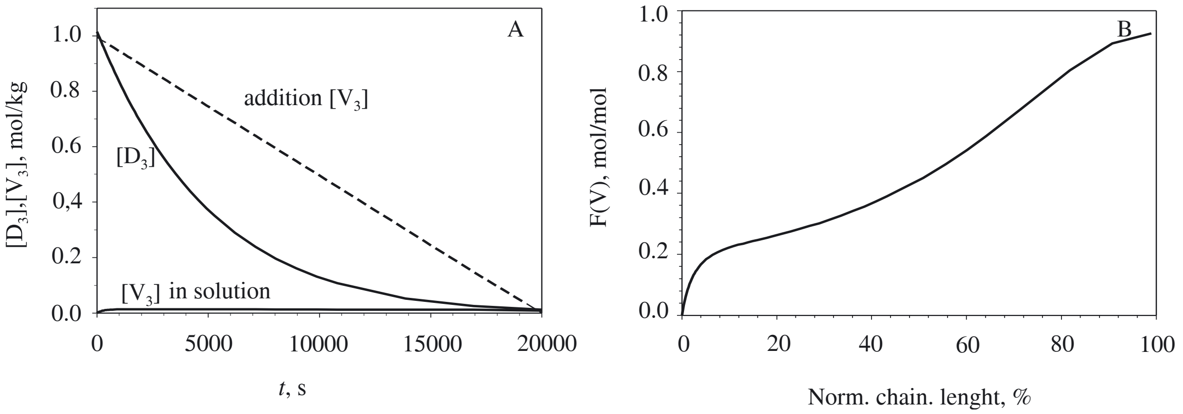


Fig. 4. Simulated monomer conversion (A) and instantaneous composition of D_3-V_3 copolymer (B) obtained in a semi-batch process; rate of V_3 addition: $3 \cdot 10^{-3}$ mol/min

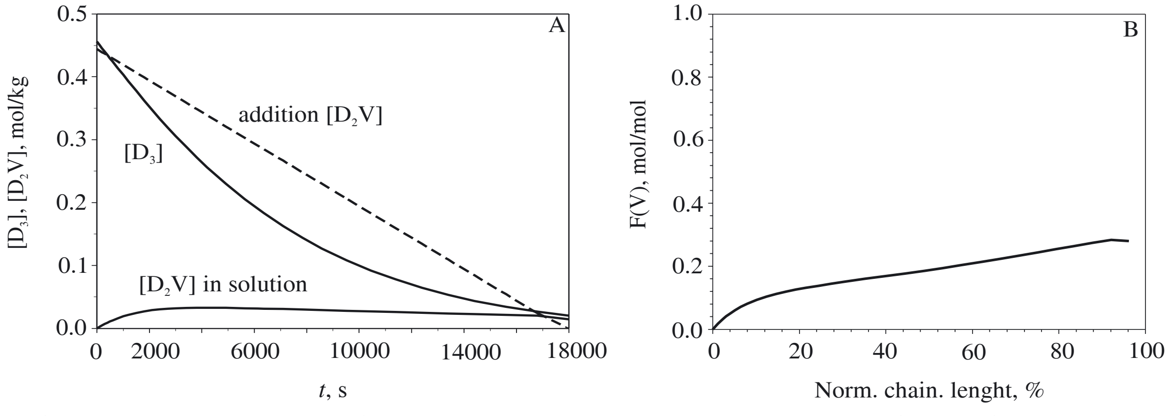


Fig. 5. Simulated monomer conversion (A) and instantaneous composition of D_3-D_2V copolymer (B) obtained in a semi-batch process; rate of D_2V addition: $1.5 \cdot 10^{-3}$ mol/min

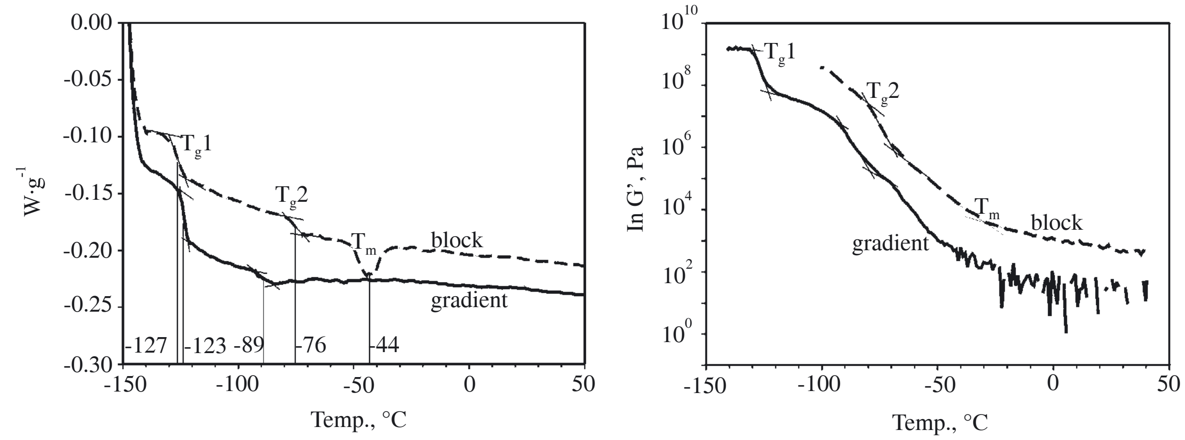


Fig. 6. (A) Comparison of DSC thermograms for block and gradient copolysiloxanes obtained by simultaneous copolymerisation of D_3 + F_3; (B) Temperature dependences of shear modulus G' for block and gradient copolysiloxanes obtained by simultaneous copolymerisation of D_3 + F_3 (both copolymers D_3:F_3 = 2:1 mol/mol, M_n ca. 15 000, M_w/M_n = 1.1) [34]

Continuous addition of one, more reactive monomer to a polymerisation mixture containing the other monomer is another method of controlling the compositional gradient along the chain. This technique is referred to as semi-batch copolymerisation [1]. Using this method, one can obtain gradient copolymers from any pair of monomers which are able to cross-polymerise.

Examples simulation curves for the V_3-D_3 and D_2V-D_3 semi-batch polymerisation systems are shown in Fig. 4 and 5, respectively [33]. The simulations were performed using the modified computer procedure and the reactivity ratios reported previously [23, 24]. Fig. 4 shows the kinetics of monomer conversion when V_3 is added at a constant rate of $3 \cdot 10^{-3}$ mol/min to the D_3 polymerisation. Fig. 5 shows the analogous monomer conversion when D_2V is added at a constant rate of $1.5 \cdot 10^{-3}$ mol/min to the D_3 polymerisation. In both cases, rate constants values for simulation were assumed as calculated from kinetic studies (Fig. 2).

Simulations suggest that the quasi-stationary concentration of the added monomer is quickly established in the polymerisation mixture. Its concentration is the lower, the more reactive is the monomer, because it is preferentially consumed.

DSC measurements for the D_3 + F_3 copolymers (D_3:F_3 = 1:1 and 2:1 mol/mol, M_n = 15 000, M_w/M_n = 1.1) show distinct differences between block and gradient copolymers. Glass transitions of both chain fragments in the gradient copolymer are moved toward each other (that is, T_g for the PDMS segment raises, while T_g for the PFMS segment decreases) and the melting of PDMS segment disappears, which indicates that gradient chain microstructure prevents crystallisation of polydimethylsiloxane segments (Fig. 6A) [33]. These changes are also reflected in plots of shear modulus-temperature dependences showing that the modulus *G'* for the gradient copolymer is by one order of magnitude lower than that for the block copolymer (Fig. 6B) [34].

CONCLUSIONS

Anionic ring-opening polymerisation of functionalised cyclotrisiloxanes is a useful method for synthesis of functionalised polysiloxanes with precise control of molecular weight and of distribution of the functional groups pendant to the polymer chain.

The functional group distribution along the chain may be regular, random, gradient or block. Polysiloxanes may be functionalised in various ways to give them specific reactivity, catalytic activity, and/or specific physical property. Precursor groups, such as Si-CH=CH_2, Si-H, Si-$(CH_2)_3$Cl, may be used if a target function is not tolerated by the anionic centre.

Gradient functionalised polysiloxanes may be useful as surface active agents such as polymer blend compatibilisers, surfactants, emulsifiers. They may also serve as reactive blocks for the formation of various complex macromolecular architectures, such as star-branched, comb-branched and dendritic structures as well as polysiloxane-inorganic solid hybrids [25, 35].

ACKNOWLEDGMENT

This work was partially supported by the Polish Ministry of Education and Science (grant no 3 T09A 07326).

REFERENCES

1. Matyjaszewski K., Ziegler M. J., Arehart S. V., Greszta D., Pakula T.: *J. Phys. Org. Chem.* 2000, **13**, 775.
2. Pakula T., Matyjaszewski K.: *Macromol. Theory Simul.* 1996, **5**, 987.
3. Aksimentiev A., Holyst R.: *J. Chem. Phys.* 1999, **111**, 2329.
4. Shull K. R.: *Macromolecules* 2002, **35**, 8631.
5. Odian G.: "Principles of polymerization", 3rd Ed., J. Wiley & Sons, New York 1991, p. 454.
6. Ishizu K., Sunahara K., Asai S.: *Polymer* 1998, **39**, 953.

7. Sardelis K., Michels H. J., Allen G.: *Polymer* 1987, **28**, 244.
8. Yu G-E., Mistry D., Ludhera S., Heatley F., Attwood D., Booth C.: *J. Chem. Soc. Faraday Trans. 1* 1997, **93**, 3383.
9. Knopf R. J., Hoy K. L.: *Pat. USA* 4 195 167 (1980).
10. Lu J., Kamigaito M., Sawamoto M., Higashimura T., Deng Y. X.: *Macromolecules* 1997, **30**, 27.
11. Bailey E. F., Dohlen W. C., Matzner M., Young R. H., Robeson L. M.: *Pat. USA* 4 065 520 (1977).
12. Matyjaszewski K., Xia J.: *Chem. Rev.* 2001, **101**, 2921.
13. Dettmer C. M., Gray M. K., Torkelson J. M., Nguyen S. T.: *Macromolecules* 2004, **37**, 5504.
14. Gray M. K., Zhou H., Nguyen S. T., Torkelson J. M.: *Macromolecules* 2004, **37**, 5586.
15. Matyjaszewski K., Davis K. A.: *Adv. Polym. Sci.* 2002, **159**, 1.
16. Mignard E., Leblanc T., Bertin D., Guerret O., Reed W. F.: *Macromolecules* 2004, **37**, 966.
17. Lee H., Matyjaszewski K., Yu S., Sheiko S. S.: *Macromolecules* 2005, **38**, 8264.
18. Charleux B., Nicolas J., Guerret O.: *Macromolecules* 2005, **38**, 5485.
19. Min K., Li M., Matyjaszewski K.: *J. Polym. Sci. A* 2005, **43**, 3616.
20. Scherer M., Bollinger J. M., Souchik J.: *Pat. USA* 6 403 745 (2002).
21. "Silicon-Containing Polymers" (eds. Jones R. G., Ando W., Chojnowski J.), Kluwer Academic Publ., Dordrecht 2000.
22. Kennan J. J.: "Siloxane Copolymers", in "Siloxane Polymers" (eds. Clarson S. J., Semlyen A. S.), PTR Prentice Hall, Englewood Cliffs 1993, p. 81.
23. Chojnowski J., Cypryk M., Fortuniak W., Rózga-Wijas K., Ścibiorek M.: *Polymer* 2002, **43**, 1993.
24. Chojnowski J., Cypryk M., Fortuniak W., Ścibiorek M., Rózga-Wijas K.: *Macromolecules* 2003, **36**, 3890.
25. Chojnowski J., Cypryk M., Fortuniak W., Kaźmierski K., Rózga-Wijas K., Ścibiorek M.: "Controlled Synthesis of All-Siloxane Functionalized Architectures by Ring-Opening Polymerization", *ACS Symp. Ser.* 2003, **838**, 12.
26. Rózga-Wijas K., Chojnowski J., Zundel T., Boileau S.: *Macromolecules* 1996, **29**, 2711.
27. Rózga-Wijas K., Chojnowski J., Boileau S.: *J. Polym. Sci A* 1997, **35**, 879.
28. Marciniec B., Guliński J., Urbaniak W., Kornetka Z. W.: "Comprehensive Handbook on Hydrosilylation" (ed. Marciniec B.) Pergamon Press, Oxford 1992.
29. Ojima I.: "The hydrosilylation reaction" in "The Chemistry of Organic Silicon Compounds" (eds Patai S., Rappaport Z.), Wiley, New York 1989, p. 1479.
30. Deschler U., Kleinschmit P., Panster P.: *Angew. Chem. Int. Ed. Engl.* 1986, **25**, 236.
31. Paulasaari J. K., Weber W. P.: *Macromolecules* 1999, **32**, 6574.
32. Kelen T., Tüdös F.: *J. Macromol. Sci.-Chem.* 1975, **A9**, 1.
33. Cypryk M., Delczyk B.: in preparation.
34. Dynamic mechanical measurements for D_3-F_3 copolymers were carried out by the late prof. Tadeusz Pakuła at Max-Planck Institute, Mainz, Germany.
35. Rózga-Wijas K., Chojnowski J., Fortuniak W., Ścibiorek M., Michalska Z., Rogalski Ł.: *J. Mater. Chem.* 2003, **13**, 2301.