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# Synthesis, structure and thermogravimetric analysis of α,ω-telechelic polydimethylsiloxanes of low molecular weight

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*Abstract*: A series of α,ω-telechelic polydimethylsiloxanes (PDMS), with pre-determined molecular weights of about 2500 g mol⁻¹, was synthesized by siloxane equilibration reaction. Syntheses were performed using octamethyl-cyclotetrasiloxane ($D_4$) and various disiloxanes: hexamethyldisiloxane (HMDS), 1,1,3,3-tetramethyldisiloxane (TMDS), 1,3-divinyltetramethyldisiloxane (DVTMDS), 1,3-bis(3-carboxypropyl)tetramethyldisiloxane (DCPTMDS) and 1,3-bis(3-aminopropyl)tetramethyldisiloxane (DAPTMDS). The role of the disiloxane was to introduce terminal functional groups at the end of the polymer chains and to control the molecular weight of the polymers. Polymers with trimethyl, hydrido, vinyl, carboxypropyl and aminopropyl end-groups were obtained in this way. The structure of the α,ω-telechelic PDMSs was confirmed by NMR and IR spectroscopy. The molecular weights of the polymers were determined by ¹H-NMR, gel permeation chromatography (GPC) and dilute solution viscometry. Thermogravimetric analysis (TGA) under nitrogen and air showed that the type of the terminal groups significantly influenced the thermal and thermo-oxidative stability, as well as the degradation mechanism of the α,ω-telechelic PDMSs.

*Keywords*: α,ω-telechelic PDMS; siloxane equilibration; thermal and thermo-oxidative degradation.

## INTRODUCTION

Linear polydimethylsiloxanes (PDMS) with potentially reactive functional groups at their chain ends, known as α,ω-telechelic PDMS, can be synthesized by the so-called equilibration reactions of functional disiloxanes and cyclic silox-

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anes in the presence of an appropriate reaction catalyst. The general synthetic procedure is presented in Fig. 1.
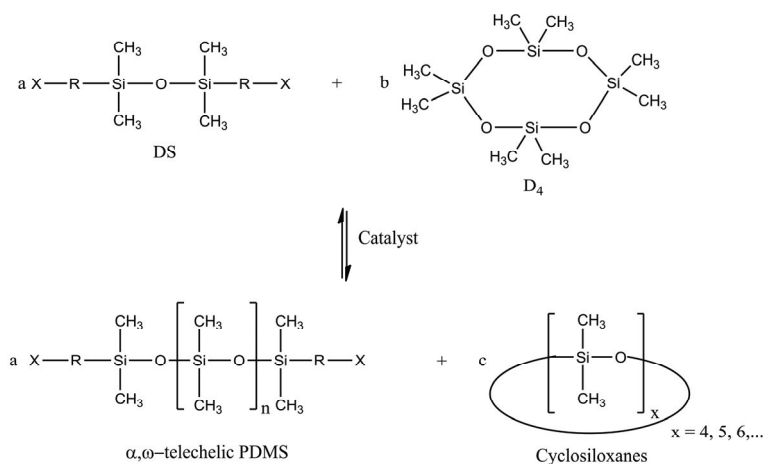


Fig. 1. Synthesis of $\alpha,\omega$-telechelic PDMS from disiloxane (DS) and $D_4$.

Functional disiloxanes (DS in Fig. 1) are the key starting reactants for the synthesis of $\alpha,\omega$-telechelic PDMS, since they not only determine the type of the end-groups, but also play the role of molecular weight regulator. The most commonly used cyclic siloxane is octamethylcyclotetrasiloxane ($D_4$ in Fig. 1). The catalyst can be an acid or base compound, which breaks siloxane bonds in linear and cyclic siloxanes, while the $Si–CH_3$, $Si–R$ and $R–X$ bonds remain intact. Group X in Fig. 1 is a reactive functional group while R is short organic moiety. $\alpha,\omega$-Telechelic PDMSs, that possess reactive X group bounded over moiety R, show several advantages in comparison with their Si–X analogs, where moiety R does not exist. First, the type and nature of the residue R has a significant effect on the chemical reactivity of the functional group X. Moreover, a suitable choice of the residue R may affect the solubility of Si–R–X terminated siloxanes, as well as their miscibility with appropriate organic monomers or polymers.[1] Strictly speaking, X does not include $CH_3$ groups, which are seen in "siloxane oil". However, polysiloxanes with terminal methyl groups are considered as telechelic PDMSs, since they often play the role of reference polymers.

$\alpha,\omega$-Telechelic PDMSs of low molecular weights are versatile starting materials for the preparation of a wide variety of linear siloxane-containing copolymers, such as siloxane–urethanes, siloxane–amides, siloxane–imides and siloxane–esters, which possess properties of thermoplastic elastomers. $\alpha,\omega$-Telechelic PDMSs are also used in the modification of network structures. Interest in PDMSs as reactive prepolymers is due to their unique combination of properties, which include extremely low glass transition temperature (–123 °C), excellent

thermal, oxidative and UV stability, very low surface energy, high gas permeability and biocompatibility (physiological inertness). Due to the mentioned properties, organic–siloxane copolymers have received special attention as elastomers, protective coatings, photoresists, biomaterials, gas separation membranes, emulsifiers, *etc*.[1–3]

In the hitherto published papers, homogeneous catalysts, such as sulfuric, trifluoromethanesulfonic and trifluoroacetic acid (acid type), or potassium and tetramethylammonium hydroxide (base type), were mostly used for the preparation of $\alpha,\omega$-telechelic PDMS,[4–6] with very few exceptions. On the other hand, it has long been known that siloxane equilibration polymerization can also be catalyzed by catalysts which are insoluble in the respective reaction mixture, such as, for example, ion-exchange resins.[7–12] The resulting heterogeneous catalysts exhibit many practical advantages over the homogeneous ones.[13,14] For example, a heterogeneously-catalyzed equilibration polymerization does not require time consuming and sometimes very tedious post-polymerization procedures, including catalyst deactivation, neutralization and isolation, which are necessary in homogeneous catalysis. Generally, these catalysts can be recuperated, permitting their multiple usages after simple separation, washing and drying. Among many different types of insoluble catalysts, particular attention has been devoted to cation-exchange resins (CER), since they are cheap, thermally stable, easy to handle and commercially available.[15]

Considering the importance of $\alpha,\omega$-telechelic PDMSs, a relatively small number of studies dealing with the impact of the terminal groups on polymer thermal and thermo-oxidative stability have been published to date.[16–21] It is well known that pronounced stability of polysiloxanes at elevated temperatures is a direct consequence of their fundamental properties, such as inherent strength of the Si–O bond, outstanding flexibility of the $-[\text{Si–O}]_x-$ chain segments and higher entropic stability of the low molecular weight cyclic siloxanes than of the linear siloxane polymers at degradation temperatures.[2,3,22–25] Polysiloxanes as a class are thermally more stable than their –C–C– counterparts. The temperature of the onset of irreversible thermal degradation of PDMS, the parent polymer of the polysiloxane family, may reach 300–400 °C[2,3] that is much higher than the degradation temperatures of most organic –C–C– polymers, the stability of which rarely exceeds 150–200 °C. The differences in degradation behavior of PDMSs result from three main factors: 1) the degradation atmosphere, 2) the type and the relative concentration of polymer end-groups[26] and 3) the purity of the examined sample, *i.e.*, the presence or absence of even catalytic amounts of ionic impurities, including additives or residual polymerization catalyst.[3,24] These factors can completely change the mechanism of the degradation process and hence the characteristic features of PDMS polymers. As a consequence, in inert atmosphere, PDMSs may degrade by three different reaction mechanisms, including:

1) the "unzipping" mechanism (proposed by Alexandrova and Rode in 1968––1969),[27,28] 2) the "random scission" mechanism (proposed by Thomas and Kendrick in 1969)[29] and 3) the "externally catalyzed" mechanism (proposed by Grassie and Macfarlane in 1978).[30] In dynamic thermal gravimetric analysis, in the absence of oxygen, PDMSs generally degrade in a single weight-loss step. On the other hand, thermo-oxidative degradation of the same PDMS is generally a more complex process, which usually shows two weight-loss steps, leading to pure silica at temperatures above 600 °C.

In this work, heterogeneous and homogeneous catalysis was combined for the preparation of $\alpha,\omega$-telechelic PDMSs, with targeted molecular weights of about 2500 g mol$^{-1}$. A cation-exchange resin based on macroporous sulfonated crosslinked polystyrene was used as the heterogeneous catalyst for the synthesis of trimethyl, hydrido, vinyl, and carboxypropyl terminated PDMS, while PDMS with aminopropyl end-groups was prepared using tetramethylammonium hydroxide as a homogeneous catalyst. Polymers of low molecular weight were obtained in all cases, in order to be later used for the synthesis of block copolymers. The syntheses were performed starting from D$_4$, while the disiloxane co-reactants for functional group incorporation were hexamethyldisiloxane (HMDS), 1,1,3,3-tetramethyldisiloxane (TMDS), 1,3-divinyltetramethyldisiloxane (DVTMDS), 1,3-bis(3-carboxypropyl)tetramethyldisiloxane (DCPTMDS) and 1,3-bis(3-aminopropyl)tetramethyldisiloxane (DAPTMDS). The structures of the $\alpha,\omega$-telechelic PDMSs were examined by NMR and IR spectroscopy. Molecular weights were obtained by $^1$H-NMR spectroscopy, gel-permeation chromatography (GPC) and dilute solution viscometry. Thermogravimetric analysis in nitrogen and air was used to examine the influence of the end-groups on thermal and thermo-oxidative stability of $\alpha,\omega$-telechelic PDMSs. Commercial PDMS samples with terminal methyl and silanol groups were also analyzed as reference polymers.

EXPERIMENTAL

*Materials*

D$_4$ (98.9 %), HMDS (100 %), TMDS (82.7 %), DVTMDS (98.7 %), DCPTMDS and DAPTMDS (61.8 %), are purchased from ABCR (Germany). In parentheses are shown the purities of the liquid chemicals, which were determined by gas chromatography, while the molecular structure was confirmed by NMR spectroscopy. DAPTMDS was also analyzed by IR spectroscopy.

A commercial grade macroporous cation-exchange resin Duolite C26 (CER), strong acid type, from Diamond Shamrock (USA), having a total ion-exchange acid capacity of 1.85 eq L$^{-1}$, was used as the reaction catalyst after overnight drying by warming at 50 °C in a vacuum dryer. An aqueous solution of tetramethylammonium hydroxide, TMAH, concentration of 25 %, purchased from Fisher Scientific (England), was used as received. Chloroform from Lachema (Czech Republic), was distilled at atmospheric pressure, and the fraction boiling at 61 °C was collected. Toluene, from Alkaloid-Skopje, was distilled at atmospheric pressure, and the fraction boiling at 110 °C was collected.

Constant viscosity PDMS standards (B1–B7, Brookfield Laboratories, USA), terminated entirely with methyl groups were used for calibration of the GPC system. Cyclosiloxanes, $D_4$, and decamethylcyclopentasiloxane, $D_5$ (ABCR, Germany) were also used for the construction of a calibration curve. The average molecular weights of the Brookfield standards were calculated from their zero shear viscosities.[31] The zero shear viscosities and the molecular weights of the Brookfield standards are given in Table S-I of the Supplementary material. The standard sample B3, with $\eta_0$ of 50.5 mPa s and molecular weight of 3270 g mol$^{-1}$ (Table S-I of the Supplementary material to this paper), was used for thermogravimetric analysis, as well as a commercial $\alpha,\omega$-disilanol-polydimethylsiloxane, PDMS-OH (ABCR, Germany). The molecular mass of the sample PDMS-OH, according to the producer specification, was 2000–3500 g mol$^{-1}$, with $\eta_0$ of 45–85 mPa s.

*Synthesis of α,ω-telechelic PDMSs*

All siloxane equilibration reactions were performed in a 100 cm$^3$, four-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, gas inlet and a thermometer. The compositions of the reaction mixtures are given in Table I.

In syntheses No. 1, 3 and 4, the appropriate amount of $D_4$, disiloxane (DS) and the catalyst (CER) were charged into the reactor flask, and the flask was placed in a constant temperature oil bath at 50 °C. The amount of CER catalyst was in all cases 22 meq per 100 g of reaction mixture. The reaction mixture was stirred for 2 h at 50 °C, and then 22 h at 95 °C. After stirring the reaction mixture for 24 h, at a speed of 500 rpm, it was filtered through a stainless steel net filter to remove the catalyst. The filtrate was fractionated by distillation under a reduced pressure of 0.5 mm Hg (66.7 Pa) to remove the volatiles. The equilibrate was gradually heated to a temperature of 200 °C and then this temperature held constant for 30 min. From the weight of the separated fractions of cyclics and linear polymers, the quantitative composition of equilibrates was calculated. The catalyst was washed with three portions of dichloromethane and then dried 24 h at 50 °C before the next use.

Synthesis No. 2 (sample PDMS-H) was performed with a different temperature regime. Due to the relatively low boiling temperature of TMDS (70 °C), the reaction mixture was first thermostated at 50 °C for 22 h, then 1 h at 65 °C and finally 1 h at 95 °C. The remaining procedure was completely the same as previously described.

Synthesis No. 5 was performed using tetramethylammonium hydroxide as a homogeneous catalyst, in the following way: appropriate amounts of $D_4$, DAPTMDS and TMAH (0.5 g of TMAH per 100 g of reaction mixture) were charged into the reaction flask and the mixture was stirred 2 h at 50 °C, then 22 h at 95 °C and finally 1 h at 150 °C. Heating at 150 °C provokes thermal degradation of TMAH catalyst. The remaining procedure was completely the same as previously described for the polymers obtained with CER catalyst.

*Measurements*

*NMR spectroscopy*. $^1$H- (200 MHz), $^{13}$C- (50 MHz) and DEPT-NMR spectra were obtained on a Varian Gemini-200 instrument. The samples were solutions in CDCl$_3$, with tetramethylsilane (TMS) as the internal standard.

*Gas chromatography, GC*. Gas chromatography was realized on a Hewlett Packard, model HP 5890S instrument, with a 4 m long DB-wax column and a flame ionization detector. The injector temperature was 250 °C, the column was held 3 min at 50 °C and then heated at 10 °C min$^{-1}$ to 270 °C, and the detector temperature was 300 °C.

*Infrared spectroscopy, IR*. A Perkin–Elmer Model 1725X spectrophotometer was used to record the IR spectra of the DAPTMDS and PDMS-NH$_2$ samples as films on KBr pellets.

*Intrinsic viscosometry*. The intrinsic viscosities, $[\eta]$, of the PDMS samples were calculated based on the flow time, $t$, in toluene at 25 °C, using an Ubbelohde viscosimeter ($l = 86.05$ mm, $R = 1$ mm). The concentrations of the samples were 0.2–2.0 g dL$^{-1}$. The mean value of two measurements of $t$ was taken to calculate the relative viscosity, $\eta_r = t/t_0$, where $t_0$ is the flow time of the solvent. Based on the relative viscosity, the specific viscosity ($\eta_{sp}$) was calculated as $\eta_{sp} = \eta_r - 1$.

The reduced, $\eta_{red}$, and inherent, $\eta_{inh}$, viscosities were calculated by Eq. (1) and (2):

$$\eta_{red} = \eta_{sp}/c \tag{1}$$

$$\eta_{inh} = \ln \eta_r/c \tag{2}$$

where $c$ is concentration, in g dL$^{-1}$.

Extrapolation of the straight-lines of $\eta_{red}$ and $\eta_{inh}$, as functions of solution concentration to zero concentration gave $[\eta]$. The mean viscometric molecular weight ($\overline{M}_\eta$) was calculated using the Mark–Houwink equation:

$$[\eta] = K\overline{M}_\eta{}^a \tag{3}$$

where the values of $K = 2.15 \times 10^{-4}$ dL g$^{-1}$ and $a = 0.65$ are constants for the system PDMS/toluene at 25 °C.[32]

*Gel permeation chromatography, GPC*. Gel permeation chromatography (GPC) was performed on a Waters 600E instrument equipped with a refractive index detector, on three Supelco Pl-Gel columns connected in line (cross-linked polystyrene with pore sizes of 10$^{-5}$, 10$^{-6}$ and 10$^{-7}$ m, respectively) at 30 °C. Twenty microliters of a 10 wt.% sample in chloroform solution was injected in all cases. The flow-rate of the chloroform was 1.5 cm$^3$ min$^{-1}$. The system was calibrated with Brookfield PDMS standards (Table S-I), D$_4$ and D$_5$. Elution volumes ($V_e$) were determined and the calibration curve $V_e = f(\log \overline{M})$ was constructed, where $\overline{M}$ is the average molecular weight calculated based on the Barry's equation.[31] The calibration curve is depicted in Fig. S-1 of the Supplementary material.

*Thermogravimetric analysis, TGA*. The thermal and thermo-oxidative stability of the PDMS samples were determined using a TA Instruments SDT Q600 analyzer in the temperature range from 30 to 700 °C. The heating rate was 10 °C min$^{-1}$. The TGA scans were recorded under a dynamic nitrogen or air atmosphere with gas flow rates of 100 cm$^3$ min$^{-1}$. The sample mass was around 10 mg.

RESULTS AND DISCUSSION

*Synthesis and structure of α,ω-telechelic PDMSs*

Four heterogeneously and one homogeneously catalyzed siloxane equilibration reaction are performed to obtain *α,ω*-telechelic PDMSs with targeted molecular weight of 2500 g mol$^{-1}$. The syntheses were performed starting from D$_4$ and the required disiloxane. The reaction scheme is shown in Fig. 1.

The structural formulas of disiloxanes, the role of which was the introduction of functional groups and molecular weight regulation, as well as the formulas of *α,ω*-telechelic PDMSs, are shown in Fig. 2. The more correct titles of the end--groups of the polymers would be (trimethylsilyl)oxy (PDMS-CH$_3$), (dimethyl-silyl)oxy (PDMS-H), (dimethylvinylsilyl)oxy (PDMS-CH=CH$_2$), [(3-carboxy-propyl)dimethylsilyl]oxy (PDMS-COOH) and [(3-aminopropyl) dimethylsilyl-

oxy (PDMS-NH$_2$). As the siloxy residue exists in all structures shown, simplified titles were assigned to the polymers and are used in Fig. 2.
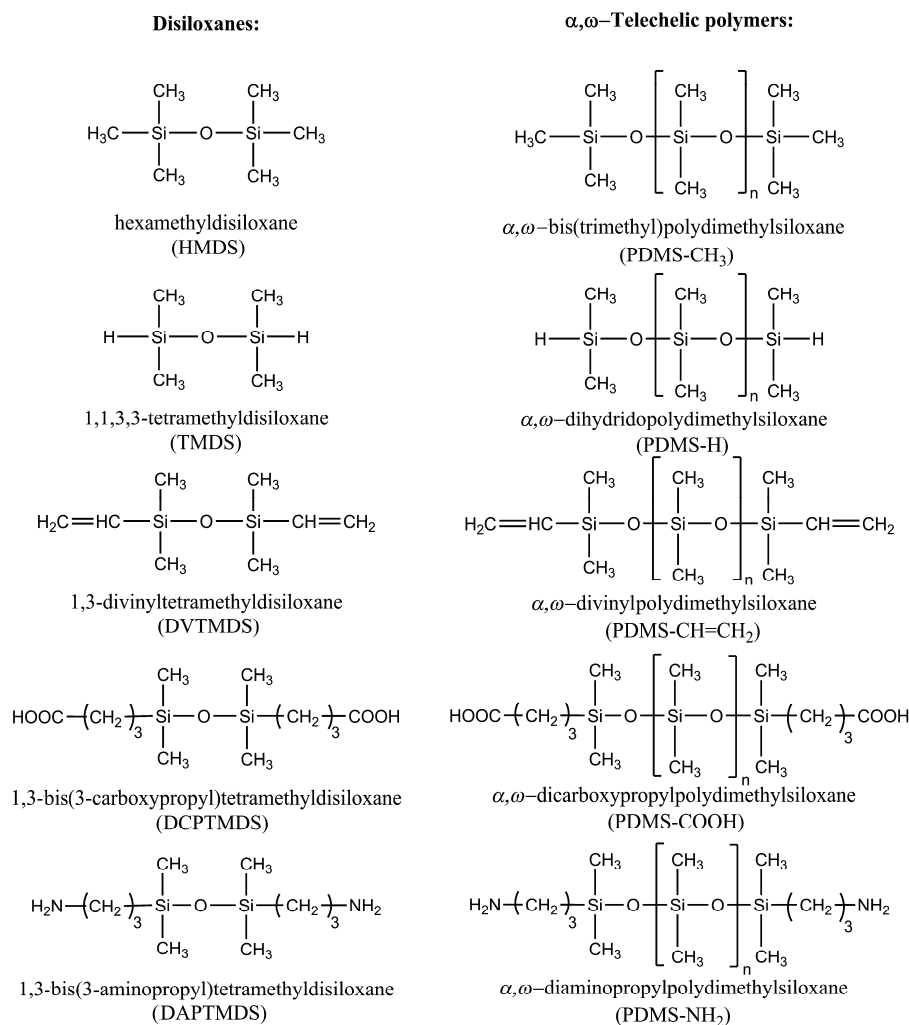
**Disiloxanes:**  $\alpha,\omega-$**Telechelic polymers:**

hexamethyldisiloxane
(HMDS)

$\alpha,\omega-$bis(trimethyl)polydimethylsiloxane
(PDMS-CH$_3$)

1,1,3,3-tetramethyldisiloxane
(TMDS)

$\alpha,\omega-$dihydridopolydimethylsiloxane
(PDMS-H)

1,3-divinyltetramethyldisiloxane
(DVTMDS)

$\alpha,\omega-$divinylpolydimethylsiloxane
(PDMS-CH=CH$_2$)

1,3-bis(3-carboxypropyl)tetramethyldisiloxane
(DCPTMDS)

$\alpha,\omega-$dicarboxypropylpolydimethylsiloxane
(PDMS-COOH)

1,3-bis(3-aminopropyl)tetramethyldisiloxane
(DAPTMDS)

$\alpha,\omega-$diaminopropylpolydimethylsiloxane
(PDMS-NH$_2$)

Fig. 2. The structure of disiloxanes and $\alpha,\omega$-telechelic PDMSs.

In heterogeneously catalyzed reactions, where HMDS, TMDS, DVTMDS and DCPTMDS were used as the disiloxane, the catalyst was CER, while in homogeneously catalyzed reaction, where DAPTMDS was used as the disiloxane, the catalyst was TMAH. The synthesis of $\alpha,\omega$-diaminopropyl PDMS could not be realized with an acid catalyst such as CER, because the amino groups of DAPTMDS are strong proton-acceptors. The protons, which catalyze siloxane redistribution reaction, are "caught" by the free electron pairs of the nitrogen of

amino groups. As shown in Fig. 3, salt formation occurs in the presence of DAPTMDS, which leads to inactivation of the CER catalyst.[33] Therefore, for the synthesis of $\alpha,\omega$-diaminopropyl PDMS, a base-type catalyst, such as for example an anion-exchange resin, should be used.[9] As a suitable anion exchange resin is not available at the moment, it was decided to use TMAH, a homogeneous catalyst, but very easy to handle, which is not usual for this type. TMAH is unstable at higher temperatures, and simple heating at 150 °C provokes its complete thermal degradation, which means there was no need for further neutralization and purification of the reaction mixture. The only drawback of TMAH in comparison with heterogeneous catalysts is the impossibility of its recycling and reuse.
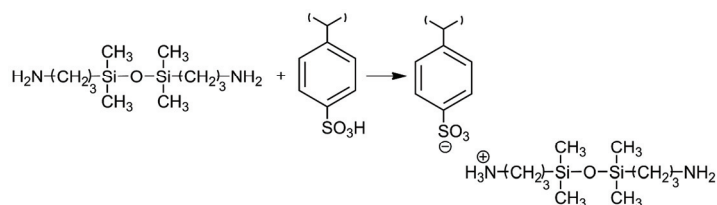


Fig. 3. Inactivation of CER in the presence of DAPTMDS.

The mole ratio of $D_4$ and disiloxane determines the degree of polymerization, *i.e.*, the molecular weight of linear telechelic PDMSs. The ratio of $D_4$ and disiloxane was selected to obtain molecular weights of 2500 g mol$^{-1}$ in all syntheses (*i.e.*, degree of polymerization $\cong$ 30). In the calculation of the initial reaction mixture compositions, it was assumed that 90 wt. % of the starting siloxane units, $[Si(CH_3)_2O]$, originating from $D_4$, would be incorporated in the linear polymer, considering that the usual proportion of cyclics in equilibrates is about 10 wt. %.[1,2]

After completion of the equilibration reaction, the cyclics were separated from the linear polymer by distillation under the reduced pressure, as described in Experimental. The weight of the cyclics was calculated from the weight of equilibrate before distillation and the weight of linear polymer after distillation. The composition of the initial reaction mixtures and the compositions with respect to linear polymers and cyclics ($D_4$ and higher) after completion of the reactions, *i.e.*, at assumed equilibrium, are given in Table I. It could be seen that the found fractions of cyclics at assumed equilibrium varied from 8.2 wt. % for the sample PDMS-COOH to 10.6 wt. % for the sample PDMS-NH$_2$. The content of cyclosiloxanes in the equilibrates was in agreement with literature data.[1–3] Simultaneously, the calculated degrees of polymerization, $\overline{X}_{n(calc)}$, which are given in Table I, varied from 29.6 (PDMS-COOH) to 30.4 (PDMS-NH$_2$).

The calculated degrees of polymerization and the molecular weights of the polymers were obtained by a procedure shown for the sample PDMS-CH$_3$. From the difference in the weight of $D_4$ and of the cyclics after distillation (2.8 g), the

weight of the siloxane units, $[(CH_3)_2SiO]$ incorporated into the linear chains were calculated: 28.05 g – 2.80 g = 25.25 g.

The number of moles of siloxane units was calculated from the proportion:

$$1 \text{ mol}:74 \text{ g} = x:25.25 \text{ g}, x = 0.3412 \text{ mol}$$

where the molecular weight of siloxane unit is 74 g mol$^{-1}$.

TABLE I. Composition of the initial and equilibrium mixtures and the calculated average number degree of polymerization, $\overline{X}_{n(calc)}$ of $\alpha,\omega$-telechelic PDMSs

| Synthesis No. | Type of polymer | Initial mixtures | | Equilibrium mixtures | | Polymer $\overline{X}_{n(calc)}$ |
| | | $m_{DS}$ / g[a] | $m_{D4}$ / g[b] | Weight fraction, % | | |
| | | | | Polymer | Cyclics | |
| 1 | PDMS-CH$_3$ | 1.85 | 28.05 | 90.6 | 9.4 | 29.9 |
| 2 | PDMS-H | 1.44 | 28.50 | 90.2 | 9.8 | 29.8 |
| 3 | PDMS-CH=CH$_2$ | 2.10 | 27.76 | 91.6 | 8.4 | 30.1 |
| 4 | PDMS-COOH | 2.49 | 20.05 | 91.8 | 8.2 | 30.4 |
| 5 | PDMS-NH$_2$ | 2.72 | 27.00 | 89.4 | 10.6 | 29.6 |

[a]Mole fraction of DS was in all cases 0.11; [b]mole fraction of D$_4$ was in all cases 0.89

From the mole ratio of siloxane units that are incorporated in the linear polymer chains and the number of moles of HMDS (1.85 g $\Rightarrow$ 0.0114 mol), the number average degree of polymerization, $\overline{X}_{n(calc)}$ was calculated:

$$\overline{X}_{n(calc)} = \frac{0.3412 \text{ mol}}{0.0114 \text{ mol}} = 29.9$$

The number average molecular weight, $\overline{M}_{n(calc)}$, was calculated based on $\overline{X}_{n(calc)}$:

$$\overline{M}_{n(calc)} = 74\,\overline{X}_{n(calc)} + 162 = 2380 \text{ g mol}^{-1}$$

where 162 g mol$^{-1}$ is the molecular weight of disiloxane HMDS.

The calculated molecular weights of the polymers, $\overline{M}_{n(calc)}$, are given in Table II. It could be seen that the values of $\overline{M}_{n(calc)}$ were in the range from 2340 to 2560 g mol$^{-1}$.

TABLE II. Molecular weights of $\alpha,\omega$-telechelic PDMSs

| Polymer | $\overline{M}_{n(calc)}$ g mol$^{-1}$ | $\overline{M}_{nNMR}$ g mol$^{-1}$ | $\overline{M}_{nGPC}$ g mol$^{-1}$ | $\overline{M}_{wGPC}$ g mol$^{-1}$ | $I$ | $M_{peak}$ g mol$^{-1}$ | $[\eta]$ dL g$^{-1}$ | $\overline{M}_\eta$ g mol$^{-1}$ |
| PDMS-OH | 2500–3000[a] | – | 3420 | 5600 | 1.64 | 4000 | – | – |
| PDMS-CH$_3$ | 2380 | – | 2890 | 5420 | 1.88 | 4750 | 0.051 | 4510 |
| PDMS-H | 2340 | 8170 | 5240 | 9790 | 1.87 | 8460 | 0.062 | 6090 |
| PDMS-CH=CH$_2$ | 2410 | 5170 | 4430 | 7760 | 1.75 | 6630 | 0.055 | 5070 |
| PDMS-COOH | 2560 | 3100 | 3160 | 6280 | 1.99 | 4750 | 0.044 | 3590 |
| PDMS-NH$_2$ | 2440 | 3720 | 2820 | 7010 | 2.49 | 9920 | 0.061 | 5930 |

[a]Given in the producer's specifications

The structures of the disiloxanes and $D_4$, and of the assumed structures of the polymers, given in Fig. 2, were confirmed by ^{1}H-, ^{13}C- and 2D-NMR spectroscopy. The spectra are depicted in Figs. S-2 (^{1}H-NMR), S-3 (^{13}C-NMR) and S-4 (two-dimensional DEPT spectrum) of the Supplementary material.

The ^{1}H-NMR spectrum of PDMS-CH$_3$ (Fig. S-2 of the Supplementary material) showed a signal at 0.06 ppm of the protons of the methyl groups bound to silicon. The ^{1}H-NMR spectrum of PDMS-H (Fig. S-2) showed a signal at 0.14 ppm of the Si–CH$_3$ protons and a signal at 4.71 ppm of the protons connected directly to silicon, Si–H. The signal at 0.07 ppm indicates the presence of mono-functional polymer, *i.e.*, arises from the methyl groups of 1,1,1-trimethyl-substituted silicon atoms. GC of TMDS also confirmed the presence of two disiloxane compounds. The contribution of TMDS in gas chromatogram was 82.7 % while the contribution of 1,1,1,3,3-pentamethyl-disiloxane was 12.9 %. There was also found a small fraction of other compounds (4.4 %).

The ^{1}H-NMR spectrum of PDMS-CH=CH$_2$ (Fig. S-2) showed a signal at 0.15 ppm of the protons from the methyl groups bound to silicon, as well as a multiplet at 5.95 ppm of the vinyl-group protons, CH=CH$_2$. The ^{13}C-NMR spectrum of PDMS-CH=CH$_2$ (Fig. S-3) showed signals at 131.66 and 139.40 ppm of the CH and CH$_2$ carbons of the vinyl groups respectively, while the signal at 1.00 ppm arises from the carbons of the methyl groups connected to silicon.

The ^{1}H-NMR spectrum of PDMS-COOH (Fig. S-2) showed signals at 0.59, 1.69 and 2.38 ppm of the protons from the propane-1,3-diyl CH$_2$ groups (closer to the carboxyl group have higher $\delta$ shift), while at 0.05 ppm, the signal of Si–CH$_3$ protons is observed. In the spectrum of DCPTMDS disiloxane, the signal of the protons from the carboxyl-groups, COOH was found at 11.42 ppm. This signal was not found in the spectrum of PDMS-COOH because of the low concentration of terminal COOH groups. The ^{13}C-NMR spectrum of PDMS-COOH (Fig. S-3) showed signals at 17.84, 18.85 and 37.38 ppm of the carbon atoms from CH$_2$ groups. The signal at 1.00 ppm is of the carbon atoms from the methyl groups bound to silicon, while the signal at 179.72 ppm comes from the carbon atoms of the carboxyl groups, COOH.

The ^{1}H-NMR spectrum of PDMS-NH$_2$ (Fig. S-2) showed a signal at 0.07 ppm of the protons of the methyl groups bound to silicon. The signals at 0.52, 1.50 and 2.66 ppm are from the CH$_2$ protons from the propane-1,3-diyl groups, while the signal at 1.38 ppm arises from NH$_2$ protons. The signal at 0.96 ppm is from the protons of methyl groups bound to the methyne (CH) groups. Analysis of the ^{1}H-NMR spectrum showed that the commercial DAPTMDS product is a mixture of structural isomers (Fig. 4). As all three compounds participate in the equilibration reactions, the resulting PDMS-NH$_2$ polymers may contain both propane-1,3-diyl (–CH$_2$–CH$_2$–CH$_2$–, Fig. 4-I) or both propylene (–CH(CH$_3$)CH$_2$–, Fig. 4-II) moieties, as well as one propane-1,3-diyl and one propylene group (Fig. 4-III).
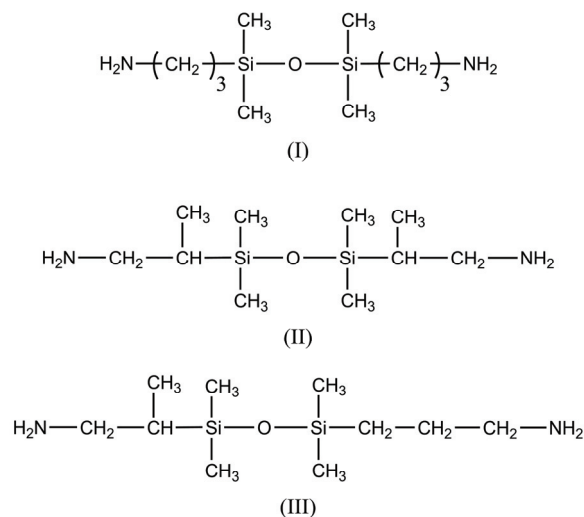
Fig. 4. Structural isomers of DAPTMDS.

The $^{13}$C-NMR spectrum of PDMS-NH$_2$ (Fig. S-3 of the Supplementary material) showed a signal at 0.09 ppm of carbons from the methyl groups bound to silicon. The signals at 15.14, 27.44 and 45.21 ppm arise from CH$_2$ carbons of the propane-1,3-diyl groups. The signal of carbon from the methyl groups bound to a methyne group appears at 11.36 ppm. The signal at 26.20 ppm arises from methyne carbons, while the signal at 40.08 ppm is from CH$_2$ carbons connected to amino groups. Based on the two-dimensional DEPT spectrum of DAPTMDS (Fig. S-4 of the Supplementary material), it was concluded that four different methyl groups exist showing signals at –1.47, –1.10, 0.10 and 11.37 ppm, as well as three methylene (CH$_2$) groups at 15.14, 21.00, 27.45 and 45.21 ppm and one methyne (CH) group at 26.21 ppm.

Gas chromatogram of DAPTMDS confirmed the presence of three types of very similar molecular species. DAPTMDS participated with 61.8 %, while the isopropyl structural isomers with one or two branched groups participated with 28.0 and 10.2 %.

The polymer sample PDMS-NH$_2$, and the mixture of cyclosiloxanes obtained as by-products in the synthesis were characterized by IR spectroscopy. The IR spectrum of PDMS-NH$_2$ showed characteristic peaks at 2963 and 2905 cm$^{-1}$ (asymmetric and symmetric C–H stretching), 1584 (NH$_2$ bending), 1412 (SiMe asymmetric), 1261 (SiMe symmetric), 1083 and 1024 cm$^{-1}$ (SiOSi asymmetric stretching, broad band with two absorption maxima) and 800 cm$^{-1}$ [Si(CH$_3$)$_2$ rocking]. The bands of very low intensity at about 3500 cm$^{-1}$ arise from the asymmetric and symmetric stretching of NH$_2$ groups. The IR spectrum of the cyclosiloxanes obtained after equilibrate distillation (Synthesis No. 5), showed

characteristic bands at 2963 and 2905 cm$^{-1}$ (asymmetric and symmetric C–H stretching), 1412 and 1261 cm$^{-1}$ (SiMe asymmetric and SiMe symmetric), as well as a broad band with one absorption maximum at 1074 cm$^{-1}$ (SiOSi asymmetric). Bands from NH$_2$ groups, about 3500 cm$^{-1}$, were not detected in this spectrum. This was indirect confirmation that all the structural amino-disiloxane isomers were completely incorporated in PDMS-NH$_2$.

*Molecular weights of the α,ω-telechelic PDMSs*

All the relevant molecular weight values of the $\alpha,\omega$-telechelic PDMSs, both calculated and experimentally determined, are listed in Table II. The first column gives the $\overline{M}_{n(calc)}$, obtained from experimentally determined reaction mixture compositions at equilibrium. The number-average molecular weights of the obtained linear polymers were experimentally determined using different techniques. First, the $\overline{M}_{nNMR}$ values were calculated from the $^1$H-NMR spectra, *via* the experimentally obtained ratio of the signal integrals for the methyl group and the end-group protons. Second, from GPC, which gave both the number-average, $\overline{M}_{nGPC}$, and the weight-average, $\overline{M}_{wGPC}$, molecular weights and finally from the intrinsic viscosities, [$\eta$], which gave viscosity average values, $\overline{M}\eta$.

The $\overline{M}_{nNMR}$ values of the samples PMDS-COOH and PDMS-NH$_2$ (3100 and 3720 g mol$^{-1}$, respectively) were in relatively good agreement with the calculated values, $\overline{M}_{n(calc)}$, (2560 and 2440 g mol$^{-1}$, respectively). The $\overline{M}_{nNMR}$ values of the samples PMDS-CH=CH$_2$ and PDMS-H (5170 and 8170 g mol$^{-1}$, respectively) were significantly higher in comparison with the $\overline{M}_{n(calc)}$ values (2410 and 2340 g mol$^{-1}$, respectively). One of the possible reasons for this might be a significant difference in the intensity of the protons of a methyl group and the protons of the end-groups. The higher $\overline{M}_{nNMR}$ value of the sample PDMS-H could also be explained by lower purity of TMDS, *i.e.*, the presence of 1,1,1,3,3-pentamethyldisiloxane. Except for the terminal hydrido groups, that also causes the presence of (trimethylsilyl)oxy groups and, consequently higher intensity of the methyl group integral, leading to a false higher $\overline{M}_{nNMR}$ value of PDMS-H. Furthermore, TMDS possesses the lowest boiling point of all the disiloxanes used in this work, and hence, a deviation of $\overline{M}_{nNMR}$ from $\overline{M}_{n(calc)}$ could be the consequence of its higher volatility during the synthesis, which again causes an increased ratio of Si(CH$_3$)$_2$ to end-group protons. The molecular weight of the sample PDMS-CH$_3$ could not be determined by $^1$H-NMR, since it was very difficult to distinguish protons from the terminal Si(CH$_3$)$_3$ groups and protons from Si(CH$_3$)$_2$ groups within the chain.

Gel-permeation chromatograms of the examined samples are given in Fig. 5. The GPC measurements gave relative molecular weight values of the $\alpha,\omega$-telechelic PDMSs according to siloxane viscosity standards. Number and weight average molecular weights ($\overline{M}_{nGPC}$ and $\overline{M}_{wGPC}$) were obtained, as well as

polydispersity indices ($I = \overline{M}_{wGPC} / \overline{M}_{nGPC}$). The values corresponding to the top of the peaks, $M_{peak}$, were also determined. The results are given in Table II. Matching between $\overline{M}_{n(calc)}$ and $\overline{M}_{nGPC}$ was good for the samples PDMS-CH$_3$, PDMS-COOH and PDMS-NH$_2$. Deviation of $\overline{M}_{nGPC}$ from $\overline{M}_{n(calc)}$ was again the highest for the samples PDMS-H (5240 g mol$^{-1}$) and PDMS-CH=CH$_2$ (4430 g mol$^{-1}$), but still less in comparison with deviation of its $\overline{M}_{nNMR}$ values from $\overline{M}_{n(calc)}$. It is not surprising that the experimental points obtained using $^1$H--NMR spectroscopy and GPC measurements are more or less scattered about the expected (calculated) values but, in general, it seems that, in this particular case and the examined molecular weights range, the GPC method might be the more useful and reliable experimental technique for determination of the number average molecular weights.
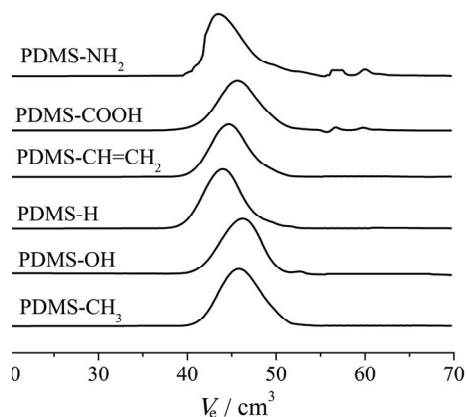


Fig. 5. GPC curves for the $\alpha,\omega$-telechelic PDMSs.

The results of the GPC measurements were used to calculate the polydispersity indices $I$, a measure of the molecular weight distribution width and their values are also given in the Table II. The polydispersity indices were in range from 1.75 (PDMS-CH=CH$_2$) to 2.49 (PDMS-NH$_2$), indicating the "most probable" molecular weight distribution, characteristic for polymers obtained by step polymerization (Fig. 5). It should be mentioned that the polydispersities obtained here are in fair agreement with the results established for samples of comparable molecular weights.[10] The highest $I$ value of 2.49 was shown by PDMS-NH$_2$, which might be explained by the presence of disiloxane isomers and their different reactivity, which leads to the spread of the molecular weight distribution.

Regarding the molecular weights, the $\alpha,\omega$-telechelic PDMSs were finally characterized by dilute solution viscometry. The intrinsic viscosities were determined, as described in the Experimental, and then the average viscosity values, $\overline{M}_\eta$, were calculated using the Mark–Houwink equation. The $\overline{M}_\eta$ values were in range from 3590 to 6090 g mol$^{-1}$ (Table II). The $\overline{M}_\eta$ values were between

$\overline{M}_{\mathrm{nGPC}}$ and $\overline{M}_{\mathrm{wGPC}}$ (closer to $\overline{M}_{\mathrm{wGPC}}$) in all cases, as was expected for step polymerizations.

*Thermogravimetric analysis of α,ω-telechelic PDMSs*

The influence of the type of end-groups on the thermal and thermo-oxidative stability of $\alpha,\omega$-telechelic PDMSs was examined by thermogravimetric analysis in nitrogen and air. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of the synthesized $\alpha,\omega$-telechelic PDMSs and the commercial samples – B3 ((trimethylsilyl)oxy-terminated PDMS) and PDMS-OH (silanol-terminated PDMS) are presented in Fig. 6. The characteristic results are given in Tables III and IV.

The literature data suggest that during the thermogravimetric analysis, in the absence of oxygen, polysiloxanes generally degrade by a single weight-loss step. The characteristic temperatures of this process – the onset of degradation, the maximal rate of degradation, the end of degradation, *etc.*, depend primarily on the type of the polymer side groups and on the purity of the sample examined. On the other hand, if the side groups in all samples are entirely $CH_3$, as in this study, then the influence of the end-groups on the degradation mechanism could be examined. Additionally, the relatively low molecular weights of the examined polymers allow this effect to be easily registered.

From results obtained herein, it is obvious that the end-groups significantly affect the thermal and thermo-oxidative stability as well as the degradation mechanisms of $\alpha,\omega$-telechelic PDMSs. The temperatures at which the weight loss was 5 wt. % ($T_{5\%}$) were taken as indicators of the onset of degradation. In addition, the temperatures at which the weight loss was 50 wt. % ($T_{50\%}$), as well as the temperatures of the maximal rate of degradation ($T_{\mathrm{max}}$) and corresponding residue upon degradation at 700 °C were taken as characteristic degradation parameters.

It could be seen that all $\alpha,\omega$-telechelic PDMSs started to lose weight at somewhat lower temperatures in air (236–352 °C) than in nitrogen (265–360 °C). The $T_{5\%}$ values were highest for the samples PDMS-H and PDMS-CH=CH$_2$ both in nitrogen (360 and 332 °C, respectively) and air (352 and 314 °C, respectively) atmosphere, which was somehow surprising result. The possible cause of this behavior might be the initial addition reactions, which are possible thanks to the presence of Si–H or Si–CH=CH$_2$ groups, without the generation of volatile products. If no volatile compounds are formed in PDMS-H and PDMS-CH=CH$_2$, then there is no weight loss below and about 300 °C, when the other samples started to degrade.

The commercial samples B3 and PDMS-OH (terminated with SiCH$_3$ and Si–OH groups, respectively) start to degrade at very similar temperatures in both nitrogen and air atmospheres (Tables III and IV). However, the degradation mechanisms were completely different, which could be seen from the shape of their DTG
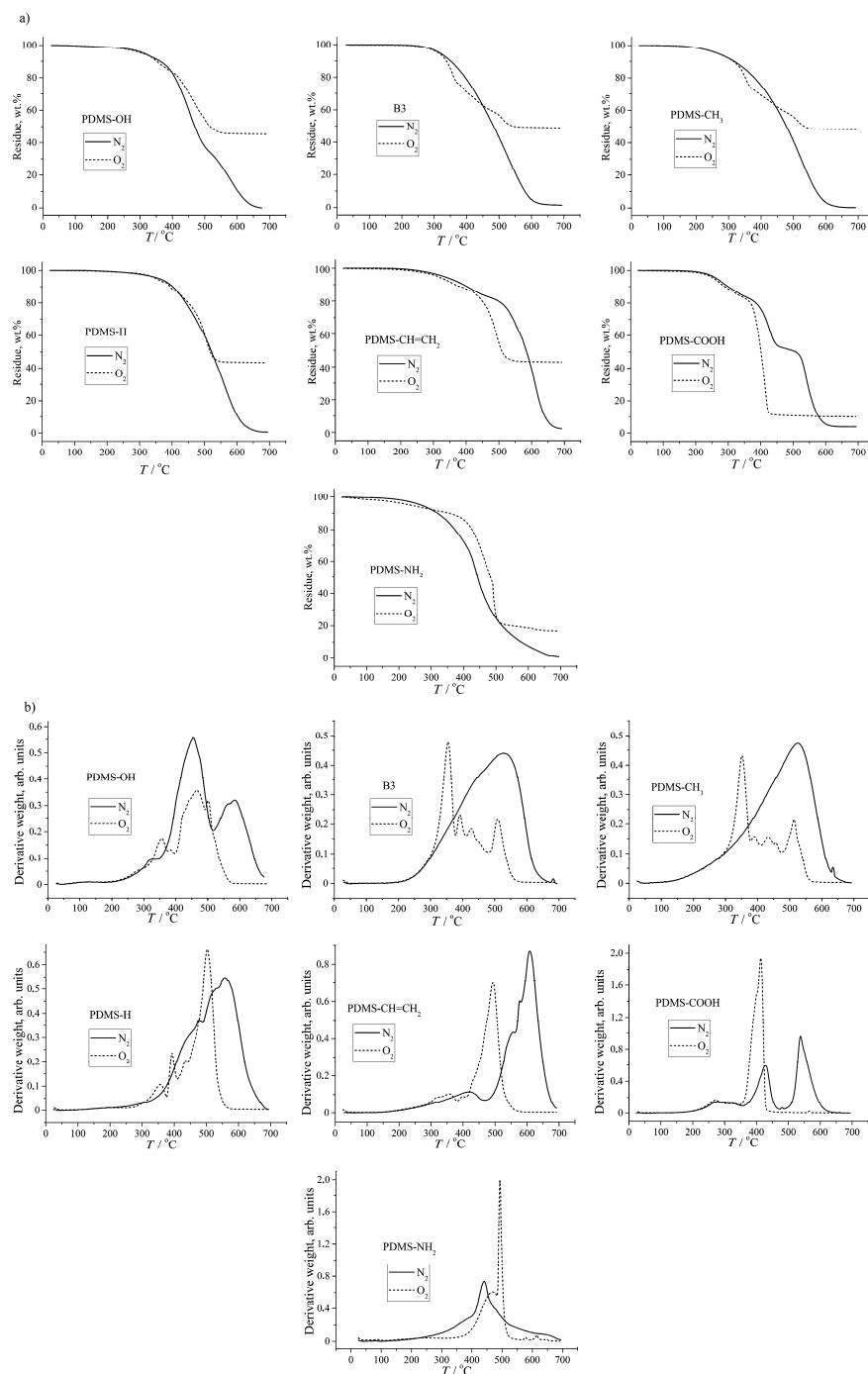
a)



b)



Fig. 6. TG (left) and DTG (right) curves of the α,ω-telechelic PDMSs in nitrogen and air.

TABLE III. The data of the thermogravimetric analysis of the $\alpha,\omega$-telechelic PDMSs in nitrogen

| Sample | $T_{5\%}$ / °C | $T_{50\%}$ / °C | $T_{max.}$ / °C | Residue at 700 °C, wt. % |
|---|---|---|---|---|
| PDMS-OH | 312 | 469 | 320/456/582 | 0 |
| B3 | 316 | 482 | 528 | 1.5 |
| PDMS-CH$_3$ | 266 | 478 | 526 | 0.3 |
| PDMS-H | 360 | 522 | 440/478/526/558 | 0.6 |
| PDMS-CH=CH$_2$ | 332 | 583 | 420/556/578/608 | 2.2 |
| PDMS-COOH | 265 | 507 | 278/430/538 | 4.0 |
| PDMS-NH$_2$ | 268 | 442 | 386/440 | 0.8 |

TABLE IV. The data of the thermogravimetric analysis of the $\alpha,\omega$-telechelic PDMSs in air

| Sample | $T_{5\%}$ / °C | $T_{50\%}$ / °C | $T_{max.}$ / °C | Residue at 700 °C, wt. % |
|---|---|---|---|---|
| PDMS-OH | 306 | 516 | 356/464/500 | 45.2 |
| B3 | 312 | 543 | 354/392/424/508 | 49.0 |
| PDMS-CH$_3$ | 266 | 536 | 352/388/432/510 | 48.2 |
| PDMS-H | 352 | 517 | 356/392/436/502 | 43.3 |
| PDMS-CH=CH$_2$ | 314 | 508 | 320/356/398/494 | 42.9 |
| PDMS-COOH | 257 | 401 | 270/414 | 10.1 |
| PDMS-NH$_2$ | 236 | 483 | 468/492 | 16.9 |

curves (Fig. 6). It is known that PDMS with SiOH end-groups degrades by depolymerization in an inert atmosphere.[27] Thanks to the great flexibility of –[SiO]$x$– segments of the siloxane chains, the terminal SiOH groups can initiate intramolecular rearrangement by the so-called "back-biting" or "unzipping" process, which results in the formation of cyclic siloxanes (Fig. 7).
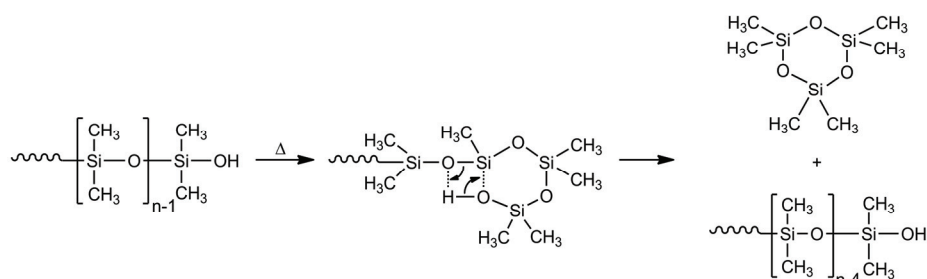


Fig. 7. Thermal degradation of silanol-terminated PDMS – "unzipping" mechanism.

The similar shape of TG and DTG curves of the PDMS-CH$_3$ and the commercial B3 of analogous molecular weight was expected, as both samples were terminated entirely by methyl groups. The lower $T_{5\%}$ value of the sample PDMS-CH$_3$ (266 °C for both N$_2$ and air atmosphere), in comparison with $T_{5\%}$ value of B3 (316 °C in N$_2$ and 312 °C in air) could be attributed to the presence of linear siloxanes of lower molecular weights and also maybe the presence of residual cyclics, that are not completely removed during the vacuum distillation. The

initial weight loss of the PDMS-CH$_3$ could be caused by the evaporation of lower linear and cyclic siloxanes during the thermogravimetric analysis. As a precondition for intramolecular depolymerization in an inert atmosphere, which begins from the chain-ends, is the presence of SiOH groups, it could be concluded that PDMSs terminated with different kinds of functional groups cannot degrade in this way. It is well known that the stability of the Si–O bonds is countered by the characteristic flexibility of the siloxane chain segments, which enables easy formation of local configurations that facilitate inter- and intramolecular siloxane redistribution reactions.[23] These reactions lead to fragmentation of linear siloxane chains into the smaller cyclosiloxanes that are volatile and thermodinamically more stable at the degradation temperatures. Consequently, the stability of linear PDMSs at elevated temperatures is reduced, and their degradation occurs at temperatures lower than would be expected based on Si–O dissociation energies.[2,3]

PDMS-CH$_3$ and B3 samples terminated with CH$_3$ groups may degrade by inter- and intramolecular redistribution reactions, which occur randomly between the siloxane bonds located within the polymeric chains, whereby cyclics reoccur. This is the so-called "random scission" mechanism, shown in Fig. 8.[29,34]
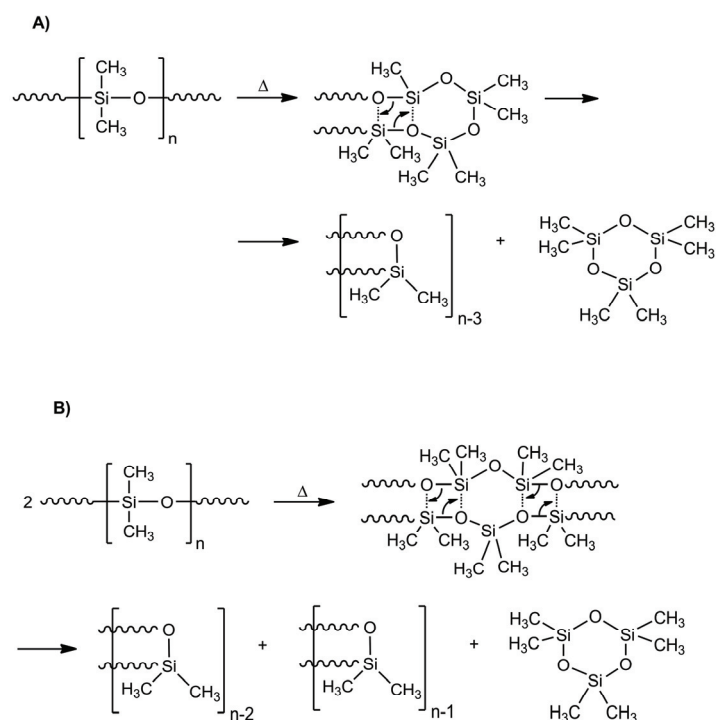


Fig. 8. Thermal degradation of PDMS – "random scission" mechanism; A) intramolecular redistribution and B) intermolecular redistribution.

The samples PDMS-COOH and PDMS-NH$_2$ were the most thermally unstable in both N$_2$ and air atmospheres, in comparison with the other telechelic PDMSs. The $T_{5\%}$ values were 265 °C for the sample PDMS-COOH and 268 °C for PDMS-NH$_2$ in nitrogen, whereas the corresponding temperatures in air amounted to 257 °C (PDMS-COOH) and 236 °C (PDMS-NH$_2$). The degradation mechanisms of these two samples are completely different in both nitrogen and air atmosphere, which was confirmed by the DTG curves shown in Fig. 6.

The degradation of PDMS-COOH in N$_2$ occurs in three steps, of which the first one is probably decarboxylation, followed by unzipping and/or random scission. It can be seen that the same sample in air degrades by a two-stage mechanism.

Based on the DTG curves, it could be concluded that majority of the examined α,ω-telechelic PDMSs degrade according to complex mechanism, with the maximal weight loss rates occurring in at least two temperatures intervals. The sample PDMS-OH shows two-step degradation processes, with $T_{max}$ at 456 and 582 °C. A "knee" at the TG curve of the PDMS-OH sample can be clearly seen, which signifies where the first degradation step ends and the second step begins. Most probably, the degradation of PDMS-OH in N$_2$ begins from the chain-ends by "back-biting" (the first step of degradation) and then proceeds by "random scission" (the second step of degradation). The exception is the degradation of the samples B3 and PDMS-CH$_3$ in N$_2$, where one maximum on the DTG curves occurs in both cases (528 and 526 °C, respectively). The one-step degradation process of these samples involves only "random scission". A $T_{max}$, corresponding to "random scission" also occurs in the DTG curves of the samples PDMS-H, PDMS--CH=CH$_2$ and PDMS-COOH at 558, 601 and 538 °C, respectively (Table III).

In contrast to thermal degradation in N$_2$, the literature data suggest that thermo-oxidative degradation of the same PDMSs is generally a more complex process, which leads to pure silica at temperatures above 600 °C. The data obtained here confirmed this suggestion in the case of the samples PDMS-CH$_3$ and B3, with terminal methyl groups, where four $T_{max}$ can be seen at each DTG curve. The thermo-oxidative degradation of the other samples proceeds through at least two steps (Fig. 6, left panel), but compared to the thermal degradation of the same samples in nitrogen, their mechanisms cannot be denoted as more complex.

The residue after degradation was very low or even it was not present at all in N$_2$ (from 0 to 4 wt.%, Table III), while in air, the amount of residue ranged from 10.1 wt. % (PDMS-COOH) to 49.0 wt.% (B3, Table IV. The explanation for this behavior can be found again in different degradation mechanisms of PDMS chains in inert and oxidative atmosphere. In inert N$_2$ atmosphere, regardless of whether degradation occurs by unzipping or random scission, cyclosiloxanes as thermally more stable products in comparison with linear PDMSs are

formed, and because of this, the residual weights were very small (Table III). In a thermo-oxidative atmosphere, degradation of the PDMS chains starts with formation of peroxy structures in the side-chains, which leads to the occurrence of different free radical reactions and results in the formation of CO, $CO_2$, $H_2$, $H_2O$, HCHO and HCOOH, leaving a significant amount of residual $SiO_2$ above 600 °C (Fig. 9). The amount of the resulting residue in air was usually smaller than what would be expected from the relative content of silicon in the original polymer, meaning that volatile organosilicon compounds were also formed.[3,23,24]



Fig. 9. Thermo-oxidative degradation of PDMS by the free-radical mechanism.

Taking into account all the observations described for the thermo-oxidative degradation of PDMSs, the free-radical mechanism is proposed until 350–400 °C, followed by siloxane redistribution reactions at higher temperatures.[35] A slightly surprising result was the relatively small residue that was found in the samples PDMS-COOH and PDMS-NH$_2$ (10.1 and 16.9 wt. %, Table IV). This indicates that during oxidative degradation of PDMS-COOH and PDMS-NH$_2$, a large quantity of volatile organosilicon compounds were produced in comparison with other examined samples, where the residues in air were between 40 and 50 wt. %.

CONCLUSIONS

A series of $\alpha,\omega$-telechelic PDMS with hydrido, vinyl, carboxypropyl and aminopropyl functional groups at the polymer chain-ends, with target molecular weight of about 2500 g mol$^{-1}$, were prepared by siloxane equilibration reactions. The number average molecular weights of the samples PMDS-COOH and PDMS-NH$_2$, calculated from their ^{1}H-NMR spectra (3100 and 3720 g mol$^{-1}$, respectively), agreed very well with the values predetermined by the compositions of the reaction mixtures. The $\overline{M}_{nNMR}$ values of the samples PMDS-CH=CH$_2$ and PDMS-H (5170 and 8170 g mol$^{-1}$, respectively), were significantly higher in comparison with the calculated values (2410 and 2340 g mol$^{-1}$, respectively). Except of the meaningful difference in the intensities of the proton signals from terminal groups, and the protons from the methyl groups, the reasons for the higher $\overline{M}_{nNMR}$ value of the PDMS-H sample could be the lower purity and higher volatility of the TMDS reactant, which has the lowest boiling temperature of all the disiloxanes used in this work. Regarding the size of polymer molecules, the synthesized polymers were also characterized by GPC and dilute solution viscometry. Agreement between $\overline{M}_{n(calc)}$ and $\overline{M}_{nGPC}$ was very good for the samples PDMS-CH$_3$, PDMS-COOH and PDMS-NH$_2$. The maximal deviation between $\overline{M}_{nGPC}$ and $\overline{M}_{n(calc)}$ was again for the sample PDMS-H. The polydispersity index of the synthesized samples ranged from 1.75 (PDMS-CH=CH$_2$) to 2.49 (PDMS-NH$_2$), which suggested the „most probable" molecular weights distribution. The $\overline{M}_\eta$ values obtained from dilute solutions viscometry lay between $\overline{M}_{nGPC}$ and $\overline{M}_{wGPC}$, as was to be expected for the „most probable" distribution. The results of thermogravimetric analysis in nitrogen and air showed that the terminal functional groups influenced significantly the thermal and thermo-oxidative stability of the $\alpha,\omega$-telechelic PDMSs, as well as the degradation mechanism. Degradation of all polymer samples started at lower temperatures in an oxidative atmosphere than in an inert nitrogen atmosphere. The highest temperatures of the onset of degradation were shown by the samples PDMS-H and PDMS-CH=CH$_2$, in both a nitrogen and an air atmosphere. It is believed that this behavior pattern of the PDMS-H and PDMS-CH=CH$_2$ is the consequence of initial addition reactions, without the generation of volatile products at temperatures below and about 300 °C, which were possible thanks to the presence of the Si–H or Si–CH=CH$_2$ groups. The samples PDMS-COOH and PDMS-NH$_2$ were the most unstable in both nitrogen and air atmosphere in comparison with the other investigated telechelic PDMSs. The shape of the DTG curves having at least two weight loss peaks showed that the majority of the $\alpha,\omega$-telechelic PDMSs degrade by complex mechanisms. The residue after degradation was very low in nitrogen (0 to 4 wt. %), while in the air, it was significantly higher (10 to 49 wt. %). In order to obtain more details about the degradation products and degradation mechanism of $\alpha,\omega$-telechelic PDMSs, thermogravimetric ana-

lysis with mass detection (TG−MS), as well as pyrolysis-gas chromatography-mass spectrometry analysis (Py−GC−MS) are planned for further research.

## SUPPLEMENTARY MATERIAL

The data of PDMS Brookfield standards and GPC calibration curve, as well as ^{1}H-, ^{13}C- and DEPT-NMR spectra are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

И З В О Д

### СИНТЕЗА, СТРУКТУРА И ТЕРМОГРАВИМЕТРИЈСКА АНАЛИЗА $\alpha,\omega$-ТЕЛЕХЕЛИЧНИХ ПОЛИДИМЕТИЛСИЛОКСАНА МАЛЕ МОЛСКЕ МАСЕ

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Серија $\alpha,\omega$-телехеличних полидиметилсилоксана (PDMS), предодређене молске масе од око 2500 g mol$^{-1}$, синтетисана је реакцијом силоксанске еквилибрације. Синтезе су изведене полазећи од октаметилциклотетрасилоксана (D$_4$) и различитих дисилоксана, као што су: хексаметилдисилоксан (HMDS), 1,1,3,3-тетраметилдисилоксан (TMDS), 1,3-дивинилтетраметилдисилоксан (DVTMDS), 1,3-бис(3-карбоксипропил)тетраметилдисилоксан (DCPTMDS) и 1,3-бис(3-аминопропил)тетраметилдисилоксан (DAPTMDS). Дисилоксани су служили за увођење функционалних група на крајеве полимерних ланаца, а такође су имали улогу регулатора молске масе полимера. Полидиметилсилоксани са триметил, хидридо, винил, карбоксипропил и аминопропил завршним групама су добијени на овај начин. Структура $\alpha,\omega$-телехеличних PDMS је потврђена NMR и IR спектроскопијом. Молске масе полимера су одређене $^1$H-NMR спектроскопијом, гел-пропусном хроматографијом (GPC) и вискозиметријом разблажених раствора. Термогравиметријска анализа (TGA) у азоту и ваздуху је показала да природа завршних група значајно утиче на термичку и термо-оксидативну стабилност, као и на механизам деградације $\alpha,\omega$-телехеличних PDMS.

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