

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 octamethylcyclotetrasiloxane (D₄) 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

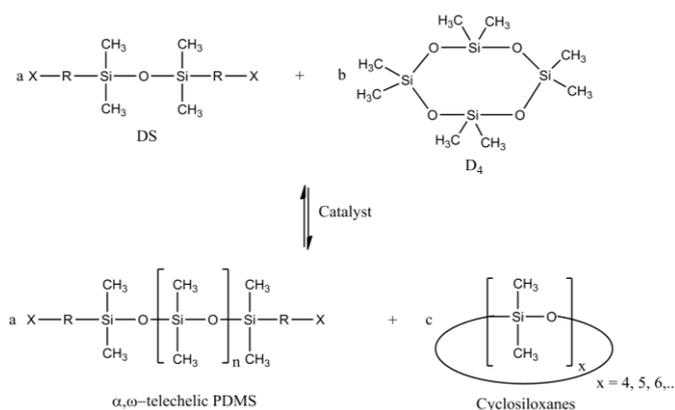
Linear polydimethylsiloxanes (PDMS) with potentially reactive functional groups at their chain ends, known as α,ω -telechelic PDMS, can be synthesized by the so-called equilibration reactions of functional disiloxanes and cyclic silox-

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



35
36

Fig. 1. Synthesis of α,ω -telechelic PDMS from disiloxane (DS) and D_4 .

37 Functional disiloxanes (DS in Fig. 1) are the key starting reactants for the
38 synthesis of α,ω -telechelic PDMS, since they not only determine the type of the
39 end-groups, but also play the role of molecular weight regulator. The most commonly
40 used cyclic siloxane is octamethylcyclotetrasiloxane (D_4 in Fig. 1). The
41 catalyst can be an acid or base compound, which breaks siloxane bonds in linear
42 and cyclic siloxanes, while the Si-CH₃, Si-R and R-X bonds remain intact.
43 Group X in Fig. 1 is a reactive functional group until R is short organic moiety,
44 which can or cannot exist. α,ω -Telechelic PDMSs, that possess reactive X group
45 bounded over moiety R, show several advantages in comparison with their Si-X
46 analogs. First, the type and nature of the residue R has a significant effect on the
47 chemical reactivity of the functional group X. Moreover, a suitable choice of the
48 residue R may affect the solubility of Si-R-X terminated siloxanes, as well as
49 their miscibility with appropriate organic monomers or polymers.¹ Strictly
50 speaking, X does not include CH₃ groups, which are seen in "siloxane oil".
51 However, polysiloxanes with terminal methyl groups are considered as telechelic
52 PDMSs, since they often play the role of reference polymers.

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



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60 thermal, oxidative and UV stability, very low surface energy, high gas perme-
61 ability and biocompatibility (physiological inertness). Due to the mentioned pro-
62 perties, organic-siloxane copolymers have received special attention as elasto-
63 mers, protective coatings, photoresists, biomaterials, gas separation membranes,
64 emulsifiers, *etc.*¹⁻³

65 In the hitherto published papers, homogeneous catalysts, such as sulfuric,
66 trifluoromethanesulfonic and trifluoroacetic acid (acid type), or potassium and
67 tetramethylammonium hydroxide (base type), were mostly used for the prepara-
68 tion of α,ω -telechelic PDMS,⁴⁻⁶ with very few exceptions. On the other hand, it
69 has long been known that siloxane equilibration polymerization can also be cat-
70 alyzed by catalysts which are insoluble in the respective reaction mixture, such
71 as, for example, ion-exchange resins.⁷⁻¹² The resulting heterogeneous catalysts
72 exhibit many practical advantages over the homogeneous ones.^{13,14} For example,
73 a heterogeneously-catalyzed equilibration polymerization does not require time
74 consuming and sometimes very tedious post-polymerization procedures,
75 including catalyst deactivation, neutralization and isolation, which are necessary
76 in homogeneous catalysis. Generally, these catalysts can be recuperated,
77 permitting their multiple usages after simple separation, washing and drying.
78 Among many different types of insoluble catalysts, particular attention has been
79 devoted to cation-exchange resins (CER), since they are cheap, thermally stable,
80 easy to handle and commercially available.¹⁵

81 Considering the importance of α,ω -telechelic PDMSs, a relatively small
82 number of studies dealing with the impact of the terminal groups on polymer
83 thermal and thermo-oxidative stability have been published to date.¹⁶⁻²¹ It is
84 well known that pronounced stability of polysiloxanes at elevated temperatures is
85 a direct consequence of their fundamental properties, such as inherent strength of
86 the Si-O bond, outstanding flexibility of the $-\text{[Si-O]}_x-$ chain segments and
87 higher entropic stability of the low molecular weight cyclic siloxanes than of the
88 linear siloxane polymers at degradation temperatures.^{2,3,22-25} Polysiloxanes as a
89 class are thermally more stable than their $-\text{C}-\text{C}-$ counterparts. The temperature
90 of the onset of irreversible thermal degradation of PDMS, the parent polymer of
91 the polysiloxane family, may reach 300-400 °C^{2,3} that is much higher than the
92 degradation temperatures of most organic $-\text{C}-\text{C}-$ polymers, the stability of which
93 rarely exceeds 150-200 °C. The differences in degradation behavior of PDMSs
94 result from three main factors: 1) the degradation atmosphere, 2) the type and the
95 relative concentration of polymer end-groups²⁶ and 3) the purity of the examined
96 sample, *i.e.*, the presence or absence of even catalytic amounts of ionic impur-
97 ities, including additives or residual polymerization catalyst.^{3,24} These factors
98 can completely change the mechanism of the degradation process and hence the
99 characteristic features of PDMS polymers. As a consequence, in inert atmo-
100 sphere, PDMSs may degrade by three different reaction mechanisms, including:

101 1) the “unzipping” mechanism (proposed by Alexandrova and Rode in 1968–
102 –1969),^{27,28} 2) the “random scission” mechanism (proposed by Thomas and
103 Kendrick in 1969)²⁹ and 3) the “externally catalyzed” mechanism (proposed by
104 Grassie and Macfarlane in 1978).³⁰ In dynamic thermal gravimetric analysis, in
105 the absence of oxygen, PDMSs generally degrade in a single weight-loss step. On
106 the other hand, thermo-oxidative degradation of the same PDMS is generally a
107 more complex process, which usually shows two weight-loss steps, leading to
108 pure silica at temperatures above 600 °C.

109 In this work, heterogeneous and homogeneous catalysis was combined for
110 the preparation of α,ω -telechelic PDMSs, with targeted molecular weights of
111 about 2500 g mol⁻¹. A cation-exchange resin based on macroporous sulfonated
112 crosslinked polystyrene was used as the heterogeneous catalyst for the synthesis
113 of trimethyl, hydrido, vinyl, and carboxypropyl terminated PDMS, while PDMS
114 with aminopropyl end-groups was prepared using tetramethylammonium hydroxide
115 as a homogeneous catalyst. Polymers of low molecular weight were
116 obtained in all cases, in order to be later used for the synthesis of block copoly-
117 mers. The syntheses were performed starting from D₄, while the disiloxane co-
118 reactants for functional group incorporation were hexamethyldisiloxane (HMDS),
119 1,1,3,3-tetramethyldisiloxane (TMDS), 1,3-divinyltetramethyldisiloxane
120 (DVTMDS), 1,3-bis(3-carboxypropyl)tetramethyldisiloxane (DCPTMDS) and
121 1,3-bis(3-aminopropyl)tetramethyldisiloxane (DAPTMDS). The structures of the
122 α,ω -telechelic PDMSs were examined by NMR and IR spectroscopy. Molecular
123 weights were obtained by ¹H-NMR spectroscopy, gel-permeation chromatog-
124 raphy (GPC) and dilute solution viscometry. Thermogravimetric analysis in nitro-
125 gen and air was used to examine the influence of the end-groups on thermal and
126 thermo-oxidative stability of α,ω -telechelic PDMSs. Commercial PDMS samples
127 with terminal methyl and silanol groups were also analyzed as reference polymers.

128 EXPERIMENTAL

129 *Materials*

130 D₄ (98.9 %), HMDS (100 %), TMDS (82.7 %), DVTMDS (98.7 %), DCPTMDS and
131 DAPTMDS (61.8 %), are purchased from ABCR (Germany). In parentheses are shown the
132 purities of the liquid chemicals, which were determined by gas chromatography, while the
133 molecular structure was confirmed by NMR spectroscopy. DAPTMDS was also analyzed by
134 IR spectroscopy.

135 A commercial grade macroporous cation-exchange resin Duolite C26 (CER), strong acid
136 type, from Diamond Shamrock (USA), having a total ion-exchange acid capacity of 1.85 eq L⁻¹,
137 was used as the reaction catalyst after overnight drying by warming at 50 °C in a vacuum
138 dryer. An aqueous solution of tetramethylammonium hydroxide, TMAH, concentration of 25
139 %, purchased from Fisher Scientific (England), was used as received. Chloroform from Lach-
140 ema (Czech Republic), was distilled at atmospheric pressure, and the fraction boiling at 61 °C
141 was collected. Toluene, from Alkaloid-Skopje, was distilled at atmospheric pressure, and the
142 fraction boiling at 110 °C was collected.

143 Constant viscosity PDMS standards (B1–B7, Brookfield Laboratories, USA), terminated
144 entirely with methyl groups were used for calibration of the GPC system. Cyclosiloxanes, D₄,
145 and decamethylcyclopentasiloxane, D₅ (ABCR, Germany) were also used for the construction
146 of a calibration curve. The average molecular weights of the Brookfield standards were calculated
147 from their zero shear viscosities.³¹ The zero shear viscosities and the molecular weights
148 of the Brookfield standards are given in Table S-I of the Supplementary material. The standard
149 sample B3, with η_0 of 50.5 cSt and molecular weight of 3270 g mol⁻¹ (Table S-I of the
150 Supplementary material to this paper), was used for thermogravimetric analysis, as well as a
151 commercial α,ω -disilanol-polydimethylsiloxane, PDMS-OH (ABCR, Germany). The molecular
152 mass of the sample PDMS-OH, according to the producer specification, was 2000–3500
153 g mol⁻¹, with η_0 of 45–85 cSt.

154 *Synthesis of α,ω -telechelic PDMSs*

155 All siloxane equilibration reactions were performed in a 100 cm³, four-necked, round-
156 bottomed flask equipped with a mechanical stirrer, reflux condenser, gas inlet and a thermo-
157 meter. The compositions of the reaction mixtures are given in Table I.

158 In syntheses No. 1, 3 and 4, the appropriate amount of D₄, disiloxane (DS) and the catal-
159 yst (CER) were charged into the reactor flask, and the flask was placed in a constant temper-
160 ature oil bath at 50 °C. The amount of CER catalyst was in all cases 22 meq per 100 g of
161 reaction mixture. The reaction mixture was stirred for 2 h at 50 °C, and then 22 h at 95 °C.
162 After stirring the reaction mixture for 24 h, at a speed of 500 rpm, it was filtered through a
163 stainless steel net filter to remove the catalyst. The filtrate was fractionated by distillation
164 under a reduced pressure of 0.5 mm Hg (66.7 Pa) to remove the volatiles. The equilibrate was
165 gradually heated to a temperature of 200 °C and then this temperature held constant for 30
166 min. From the weight of the separated fractions of cyclics and linear polymers, the
167 quantitative composition of equilibrates was calculated. The catalyst was washed with three
168 portions of dichloromethane and then dried 24 h at 50 °C before the next use.

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

173 Synthesis No. 5 was performed using tetramethylammonium hydroxide as a homogen-
174 eous catalyst, in the following way: appropriate amounts of D₄, DAPTMDS and TMAH (0.5 g
175 of TMAH per 100 g of reaction mixture) were charged into the reaction flask and the mixture
176 was stirred 2 h at 50 °C, then 22 h at 95 °C and finally 1 h at 150 °C. Heating at 150 °C
177 provokes thermal degradation of TMAH catalyst. The remaining procedure was completely
178 the same as previously described for the polymers obtained with CER catalyst.

179 *Measurements*

180 *NMR spectroscopy.* ¹H- (200 MHz), ¹³C- (50 MHz) and DEPT-NMR spectra were
181 obtained on a Varian Gemini-200 instrument. The samples were solutions in CDCl₃, with tet-
182 ramethylsilane (TMS) as the internal standard.

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

187 *Infrared spectroscopy, IR.* A Perkin–Elmer Model 1725X spectrophotometer was used to
188 record the IR spectra of the DAPTMDS and PDMS-NH₂ samples as films on KBr pellets.



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Comment [S.T.4]: Not an SI unit!

189 *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 (η_{sp}) was calculated as $\eta_{sp} = \eta_r - 1$.

195 The reduced, η_{red} , and inherent, η_{inh} , viscosities were calculated by Eq (1) and (2):

$$196 \quad \eta_{red} = \eta_{sp}/c \quad (1)$$

$$197 \quad \eta_{inh} = \ln \eta_r/c \quad (2)$$

198 where c is concentration, in g dL⁻¹.

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

$$202 \quad [\eta] = K \overline{M}_\eta^a \quad (3)$$

203 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

205 *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 cm³ min⁻¹. The system was calibrated with Brookfield PDMS standards (Table S-1), D₄ and D₅. 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.

214 *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 cm³ min⁻¹. The sample mass was around 10 mg.

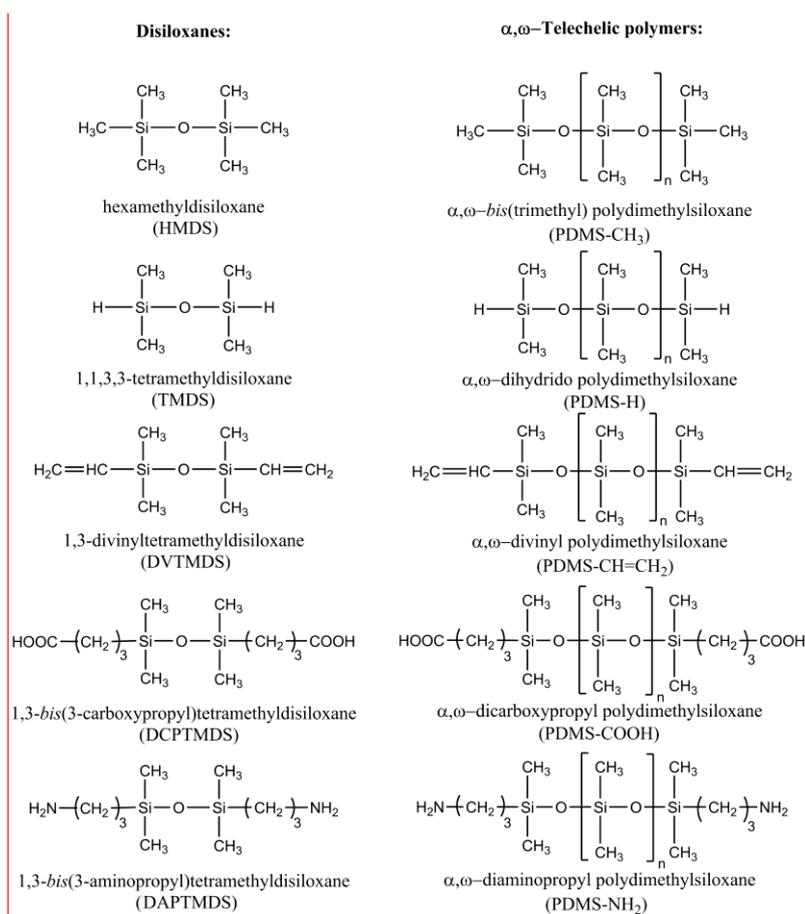
219 RESULTS AND DISCUSSION

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

221 Four heterogeneously and one homogeneously catalyzed siloxane equilibrium reaction are performed to obtain α,ω -telechelic PDMSs with targeted molecular weight of 2500 g mol⁻¹. The syntheses were performed starting from D₄ and the required disiloxane. The reaction scheme is shown in Fig. 1.

225 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-CH₃), (dimethylsilyl)oxy (PDMS-H), (dimethylvinylsilyl)oxy (PDMS-CH=CH₂), [(3-carboxypropyl)dimethylsilyl]oxy (PDMS-COOH) and [(3-aminopropyl)

231 dimethylsilyloxy (PDMS-NH₂). As the siloxy residue exists in all structures
 232 shown, simplified titles were assigned to the polymers and are used in Fig. 2.



233
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Fig. 2. The structure of disiloxanes and α,ω -telechelic PDMSs.

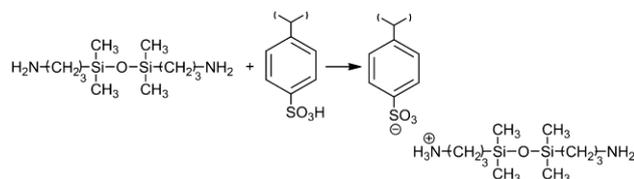
235 In heterogeneously catalyzed reactions, where HMDS, TMDS, DVTMDS
 236 and DCPTMDS were used as the disiloxane, the catalyst was CER, while in
 237 homogeneously catalyzed reaction, where DAPTMDMS was used as the disilox-
 238 ane, the catalyst was TMAH. The synthesis of α,ω -diaminopropyl PDMS could
 239 not be realized with an acid catalyst such as CER, because the amino groups of
 240 DAPTMDMS are strong proton-acceptors. The protons, which catalyze siloxane
 241 redistribution reaction, are “caught” by the free electron pairs of the nitrogen of



Comment [V5]: Please correct:

- 1) All “ α,ω –” should be in *italic*
- Changes for α,ω -Telechelic polymers nomenclature
- a) α,ω -bis(trimethyl)polydimethylsiloxane (“bis” should not be in *italic*)
- b) α,ω -dihydropolydimethylsiloxane
- c) α,ω -divinylpolydimethylsiloxane
- d) α,ω -bis(3-carboxypropyl)polydimethylsiloxane
- e) α,ω -bis(3-aminopropyl)polydimethylsiloxane

242 amino groups. As shown in Fig. 3, salt formation occurs in the presence of
 243 DAPTMS, which leads to inactivation of the CER catalyst.³³ Therefore, for the
 244 synthesis of α,ω -diaminopropyl PDMS, a base-type catalyst, such as for example
 245 an anion-exchange resin, should be used.⁹ As a suitable anion exchange resin is
 246 not available at the moment, it was decided to use TMAH, a homogeneous cat-
 247 alyst, but very easy to handle, which is not usual for this type. TMAH is unstable
 248 at higher temperatures, and simple heating at 150 °C provokes its complete ther-
 249 mal degradation, which means there was no need for further neutralization and
 250 purification of the reaction mixture. The only drawback of TMAH in comparison
 251 with heterogeneous catalysts is the impossibility of its recycling and reuse.



252
 253

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

254 The mole ratio of D₄ and disiloxane determines the degree of polymerization,
 255 *i.e.*, the molecular weight of linear telechelic PDMSs. The ratio of D₄ and
 256 disiloxane was selected to obtain molecular weights of 2500 g mol⁻¹ in all syn-
 257 theses (*i.e.*, degree of polymerization \cong 30). In the calculation of the initial
 258 reaction mixture compositions, it was assumed that 90 wt. % of the starting silox-
 259 ane units, [Si(CH₃)₂O], originating from D₄, would be incorporated in the linear
 260 polymer, considering that the usual proportion of cyclics in equilibrates is about
 261 10 wt. %.^{1,2}

262 After completion of the equilibration reaction, the cyclics were separated
 263 from the linear polymer by distillation under the reduced pressure, as described
 264 in Experimental. The weight of the cyclics was calculated from the weight of
 265 equilibrate before distillation and the weight of linear polymer after distillation.
 266 The composition of the initial reaction mixtures and the compositions with respect
 267 to linear polymers and cyclics (D₄ and higher) after completion of the reactions,
 268 *i.e.*, at assumed equilibrium, are given in Table I. It could be seen that the
 269 found fractions of cyclics at assumed equilibrium varied from 8.2 wt. % for the
 270 sample PDMS-COOH to 10.6 wt. % for the sample PDMS-NH₂. The content of
 271 cyclosiloxanes in the equilibrates was in agreement with literature data.¹⁻³
 272 Simultaneously, the calculated degrees of polymerization, $\bar{X}_{n(\text{calc})}$, which are
 273 given in Table I, varied from 29.6 (PDMS-COOH) to 30.4 (PDMS-NH₂).

274 The calculated degrees of polymerization and the molecular weights of the
 275 polymers were obtained by a procedure shown for the sample PDMS-CH₃. From
 276 the difference in the weight of D₄ and of the cyclics after distillation (2.8 g), the

277 weight of the siloxane units, $[(\text{CH}_3)_2\text{SiO}]$ incorporated into the linear chains were
 278 calculated: $28.05 \text{ g} - 2.80 \text{ g} = 25.25 \text{ g}$.

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

$$280 \quad 1 \text{ mol} : 74 \text{ g} = x : 25.25 \text{ g}, x = 0.3412 \text{ mol}$$

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

282 TABLE I. Composition of the initial and equilibrium mixtures and the calculated average
 283 number degree of polymerization, $\bar{X}_{n(\text{calc})}$ of α,ω -telechelic PDMSs

Synthesis No.	Type of polymer	Initial mixtures		Equilibrium mixtures		Polymer $\bar{X}_{n(\text{calc})}$
		$m_{\text{DS}} / \text{g}^a$	$m_{\text{D}_4} / \text{g}^b$	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

284 ^aMole fraction of DS was in all cases 0.11; ^bmole fraction of D₄ was in all cases 0.89

285 From the mole ratio of siloxane units that are incorporated in the linear poly-
 286 mer chains and the number of moles of HMDS ($1.85 \text{ g} \Rightarrow 0.0114 \text{ mol}$), the
 287 number average degree of polymerization, $\bar{X}_{n(\text{calc})}$ was calculated:

$$288 \quad \bar{X}_{n(\text{calc})} = \frac{0.3412 \text{ mol}}{0.0114 \text{ mol}} = 29.9$$

289 The number average molecular weight, $\bar{M}_{n(\text{calc})}$, was calculated based on
 290 $\bar{X}_{n(\text{calc})}$:

$$291 \quad \bar{M}_{n(\text{calc})} = 74 \bar{X}_{n(\text{calc})} + 162 = 2380 \text{ g mol}^{-1}$$

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

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

296 TABLE II. Molecular weights of α,ω -telechelic PDMSs

Polymer	$\bar{M}_{n(\text{calc})}$ g mol ⁻¹	$\bar{M}_{n\text{NMR}}$ g mol ⁻¹	$\bar{M}_{n\text{GPC}}$ g mol ⁻¹	$\bar{M}_{w\text{GPC}}$ g mol ⁻¹	<i>I</i>	M_{peak} g mol ⁻¹	$[\eta]$ dL g ⁻¹	\bar{M}_{η} 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

297 ^aGiven in the producer's specifications

298 The structures of the disiloxanes and D₄, and of the assumed structures of
299 the polymers, given in Fig. 2, were confirmed by ¹H-, ¹³C- and 2D-NMR
300 spectroscopy. The spectra are depicted in Figs. S-2 (¹H-NMR), S-3 (¹³C-NMR)
301 and S-4 (two-dimensional DEPT spectrum) of the Supplementary material.

302 The ¹H-NMR spectrum of PDMS-CH₃ (Fig. S-2 of the Supplementary
303 material) showed a signal at 0.06 ppm of the protons of the methyl groups bound
304 to silicon. The ¹H-NMR spectrum of PDMS-H (Fig. S-2) showed a signal at 0.14
305 ppm of the Si-CH₃ protons and a signal at 4.71 ppm of the protons connected
306 directly to silicon, Si-H. The signal at 0.07 ppm indicates the presence of mono-
307 functional polymer, *i.e.*, arises from the methyl groups of 1,1,1-trimethyl-sub-
308 stituted silicon atoms. GC of TMDS also confirmed the presence of two disilox-
309 ane compounds. The contribution of TMDS in gas chromatogram was 82.7 %
310 while the contribution of 1,1,1,3,3-pentamethyl-disiloxane was 12.9 %. There
311 was also found a small fraction of other compounds (4.4 %).

312 The ¹H-NMR spectrum of PDMS-CH=CH₂ (Fig. S-2) showed a signal at
313 0.15 ppm of the protons from the methyl groups bound to silicon, as well as a
314 multiplet at 5.95 ppm of the vinyl-group protons, CH=CH₂. The ¹³C-NMR spec-
315 trum of PDMS-CH=CH₂ (Fig. S-3) showed signals at 131.66 and 139.40 ppm of
316 the CH and CH₂ carbons of the vinyl groups respectively, while the signal at 1.00
317 ppm arises from the carbons of the methyl groups connected to silicon.

318 The ¹H-NMR spectrum of PDMS-COOH (Fig. S-2) showed signals at 0.59,
319 1.69 and 2.38 ppm of the protons from the propane-1,3-diyl CH₂ groups (closer
320 to the carboxyl group have higher δ shift), while at 0.05 ppm, the signal of Si-
321 CH₃ protons is observed. In the spectrum of DCPTMDS disiloxane, the signal of
322 the protons from the carboxyl-groups, COOH was found at 11.42 ppm. This
323 signal was not found in the spectrum of PDMS-COOH because of the low
324 concentration of terminal COOH groups. The ¹³C-NMR spectrum of PDMS-
325 COOH (Fig. S-3) showed signals at 17.84, 18.85 and 37.38 ppm of the carbon
326 atoms from CH₂ groups. The signal at 1.00 ppm is of the carbon atoms from the
327 methyl groups bound to silicon, while the signal at 179.72 ppm comes from the
328 carbon atoms of the carboxyl groups, COOH.

329 The ¹H-NMR spectrum of PDMS-NH₂ (Fig. S-2) showed a signal at 0.07
330 ppm of the protons of the methyl groups bound to silicon. The signals at 0.52,
331 1.50 and 2.66 ppm are from the CH₂ protons from the propane-1,3-diyl groups,
332 while the signal at 1.38 ppm arises from NH₂ protons. The signal at 0.96 ppm is
333 from the protons of methyl groups bound to the methyne (CH) groups. Analysis
334 of the ¹H-NMR spectrum showed that the commercial DAPTMDs product is a
335 mixture of structural isomers (Fig. 4). As all three compounds participate in the equilib-
336 ration reactions, the resulting PDMS-NH₂ polymers may contain both propane-1,3-
337 diyl (-CH₂-CH₂-CH₂-, Fig. 4-I) or both propylene (-CH(CH₃)CH₂-, Fig. 4-II)
338 moieties, as well as one propane-1,3-diyl and one propylene group (Fig. 4-III).

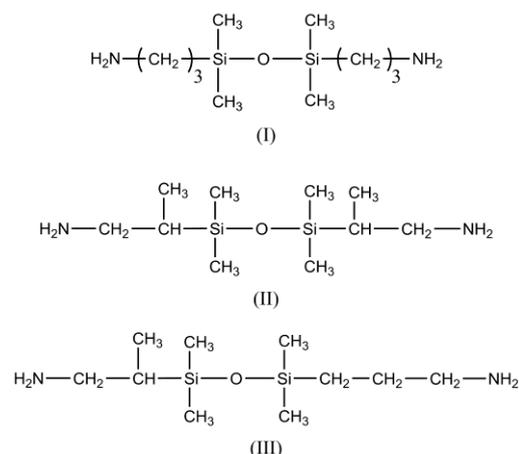


Fig. 4. Structural isomers of DAPTMDs.

339
340

341 The ^{13}C -NMR spectrum of PDMS-NH₂ (Fig. S-3 of the Supplementary
342 material) showed a signal at 0.09 ppm of carbons from the methyl groups bound
343 to silicon. The signals at 15.14, 27.44 and 45.21 ppm arise from CH₂ carbons of
344 the propane-1,3-diyl groups. The signal of carbon from the methyl groups bound
345 to a methyne group appears at 11.36 ppm. The signal at 26.20 ppm arises from
346 methyne carbons, while the signal at 40.08 ppm is from CH₂ carbons connected
347 to amino groups. Based on the two-dimensional DEPT spectrum of DAPTMDs
348 (Fig. S-4 of the Supplementary material), it was concluded that four different
349 methyl groups exist showing signals at -1.47, -1.10, 0.10 and 11.37 ppm, as well
350 as three methylene (CH₂) groups at 15.14, 21.00, 27.45 and 45.21 ppm and one
351 methyne (CH) group at 26.21 ppm.

352 Gas chromatogram of DAPTMDs confirmed the presence of three types of
353 very similar molecular species. DAPTMDs participated with 61.8 %, while the
354 isopropyl structural isomers with one or two branched groups participated with
355 28.0 and 10.2 %.

356 The polymer sample PDMS-NH₂, and the mixture of cyclosiloxanes obtained
357 as by-products in the synthesis were characterized by IR spectroscopy. The IR
358 spectrum of PDMS-NH₂ showed characteristic peaks at 2963 and 2905 cm⁻¹
359 (asymmetric and symmetric C-H stretching), 1584 (NH₂ bending), 1412 (SiMe
360 asymmetric), 1261 (SiMe symmetric), 1083 and 1024 cm⁻¹ (SiOSi asymmetric
361 stretching, broad band with two absorption maxima) and 800 cm⁻¹ [Si(CH₃)₂
362 rocking]. The bands of very low intensity at about 3500 cm⁻¹ arise from the
363 asymmetric and symmetric stretching of NH₂ groups. The IR spectrum of the
364 cyclosiloxanes obtained after equilibrate distillation (Synthesis No. 5), showed

365 characteristic bands at 2963 and 2905 cm^{-1} (asymmetric and symmetric C–H
366 stretching), 1412 and 1261 cm^{-1} (SiMe asymmetric and SiMe symmetric), as
367 well as a broad band with one absorption maximum at 1074 cm^{-1} (SiOSi asym-
368 metric). Bands from NH_2 groups, about 3500 cm^{-1} , were not detected in this
369 spectrum. This was indirect confirmation that all the structural amino-disiloxane
370 isomers were completely incorporated in PDMS- NH_2 .

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

372 All the relevant molecular weight values of the α,ω -telechelic PDMSs, both
373 calculated and experimentally determined, are listed in Table II. The first column
374 gives the $\overline{M}_{n(\text{calc})}$, obtained from experimentally determined reaction mixture
375 compositions at equilibrium. The number-average molecular weights of the
376 obtained linear polymers were experimentally determined using different tech-
377 niques. First, the $\overline{M}_{n\text{NMR}}$ values were calculated from the $^1\text{H-NMR}$ spectra, via
378 the experimentally obtained ratio of the signal integrals for the methyl group and
379 the end-group protons. Second, from GPC, which gave both the number-average,
380 $\overline{M}_{n\text{GPC}}$, and the weight-average, $\overline{M}_{w\text{GPC}}$, molecular weights and finally from
381 the intrinsic viscosities, $[\eta]$, which gave viscosity average values, \overline{M}_η .

382 The $\overline{M}_{n\text{NMR}}$ values of the samples PMDS-COOH and PDMS- NH_2 (3100
383 and 3720 g mol^{-1} , respectively) were in relatively good agreement with the
384 calculated values, $\overline{M}_{n(\text{calc})}$, (2560 and 2440 g mol^{-1} , respectively). The
385 $\overline{M}_{n\text{NMR}}$ values of the samples PMDS- $\text{CH}=\text{CH}_2$ and PDMS-H (5170 and 8170 g
386 mol^{-1} , respectively) were significantly higher in comparison with the $\overline{M}_{n(\text{calc})}$
387 values (2410 and 2340 g mol^{-1} , respectively). One of the possible reasons for this
388 might be a significant difference in the intensity of the protons of a methyl group
389 and the protons of the end-groups. The higher $\overline{M}_{n\text{NMR}}$ value of the sample
390 PDMS-H could also be explained by lower purity of TMDS, *i.e.*, the presence of
391 1,1,1,3,3-pentamethyldisiloxane. Except for the terminal hydrido groups, that
392 also causes the presence of (trimethylsilyl)oxy groups and, consequently higher
393 intensity of the methyl group integral, leading to a false higher $\overline{M}_{n\text{NMR}}$ value of
394 PDMS-H. Furthermore, TMDS possesses the lowest boiling point of all the
395 disiloxanes used in this work, and hence, a deviation of $\overline{M}_{n\text{NMR}}$ from $\overline{M}_{n(\text{calc})}$
396 could be the consequence of its higher volatility during the synthesis, which
397 again causes an increased ratio of $\text{Si}(\text{CH}_3)_2$ to end-group protons. The molecular
398 weight of the sample PDMS- CH_3 could not be determined by $^1\text{H-NMR}$, since it
399 was very difficult to distinguish protons from the terminal $\text{Si}(\text{CH}_3)_3$ groups and
400 protons from $\text{Si}(\text{CH}_3)_2$ groups within the chain.

401 Gel-permeation chromatograms of the examined samples are given in Fig. 5.
402 The GPC measurements gave relative molecular weight values of the α,ω -tele-
403 chelic PDMSs according to siloxane viscosity standards. Number and weight
404 average molecular weights ($\overline{M}_{n\text{GPC}}$ and $\overline{M}_{w\text{GPC}}$) were obtained, as well as

405 polydispersity indices ($I = \overline{M}_{wGPC} / \overline{M}_{nGPC}$). The values corresponding to the
 406 top of the peaks, M_{peak} , were also determined. The results are given in Table II.
 407 Matching between $\overline{M}_{n(calc)}$ and \overline{M}_{nGPC} was good for the samples PDMS-CH₃,
 408 PDMS-COOH and PDMS-NH₂. Deviation of \overline{M}_{nGPC} from $\overline{M}_{n(calc)}$ was again
 409 the highest for the samples PDMS-H (5240 g mol⁻¹) and PDMS-CH=CH₂ (4430
 410 g mol⁻¹), but still less in comparison with deviation of its \overline{M}_{nNMR} values from
 411 $\overline{M}_{n(calc)}$. It is not surprising that the experimental points obtained using ¹H-
 412 -NMR spectroscopy and GPC measurements are more or less scattered about the
 413 expected (calculated) values but, in general, it seems that, in this particular case
 414 and the examined molecular weights range, the GPC method might be the more
 415 useful and reliable experimental technique for determination of the number
 416 average molecular weights.

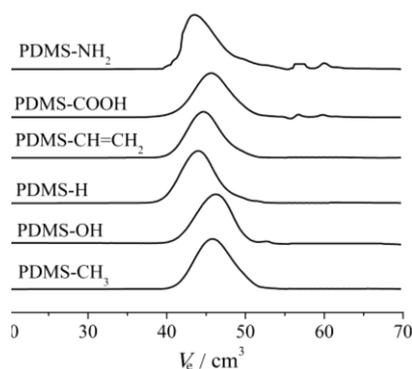


Fig. 5. GPC curves for the α,ω -telechelic PDMSs.

417 The results of the GPC measurements were used to calculate the polydis-
 418 persity indices I , a measure of the molecular weight distribution width and their
 419 values are also given in the Table II. The polydispersity indices were in range
 420 from 1.75 (PDMS-CH=CH₂) to 2.49 (PDMS-NH₂), indicating the “most pro-
 421 bable” molecular weight distribution, characteristic for polymers obtained by step
 422 polymerization (Fig. 5). It should be mentioned that the polydispersities obtained
 423 here are in fair agreement with the results established for samples of comparable
 424 molecular weights.¹⁰ The highest I value of 2.49 was shown by PDMS-NH₂,
 425 which might be explained by the presence of disiloxane isomers and their differ-
 426 ent reactivity, which leads to the spread of the molecular weight distribution.

427 Regarding the molecular weights, the α,ω -telechelic PDMSs were finally
 428 characterized by dilute solution viscometry. The intrinsic viscosities were deter-
 429 mined, as described in the Experimental, and then the average viscosity values,
 430 $\overline{M} \eta$, were calculated using the Mark-Houwink equation. The $\overline{M} \eta$ values were in
 431 range from 3590 to 6090 g mol⁻¹ (Table II). The $\overline{M} \eta$ values were between

432 $\overline{M}_{n\text{GPC}}$ and $\overline{M}_{w\text{GPC}}$ (closer to $\overline{M}_{w\text{GPC}}$) in all cases, as was expected for step
433 polymerizations.

434 *Thermogravimetric analysis of α,ω -telechelic PDMSs*

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

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

451 From results obtained herein, it is obvious that the end-groups significantly
452 affect the thermal and thermo-oxidative stability as well as the degradation mech-
453 anisms of α,ω -telechelic PDMSs. The temperatures at which the weight loss was
454 5 wt. % ($T_{5\%}$) were taken as indicators of the onset of degradation. In addition,
455 the temperatures at which the weight loss was 50 wt. % ($T_{50\%}$), as well as the
456 temperatures of the maximal rate of degradation (T_{max}) and corresponding resi-
457 due upon degradation at 700 °C were taken as characteristic degradation parameters.

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

468 The commercial samples B3 and PDMS-OH (terminated with SiCH_3 and
469 Si-OH groups, respectively) start to degrade at very similar temperatures in both
470 nitrogen and air atmospheres (Tables IV and V). However, the degradation mech-
471 anisms were completely different, which could be seen from the shape of their DTG



Comment [N6]: Too small font in Fig. 6. Should be rearranged.

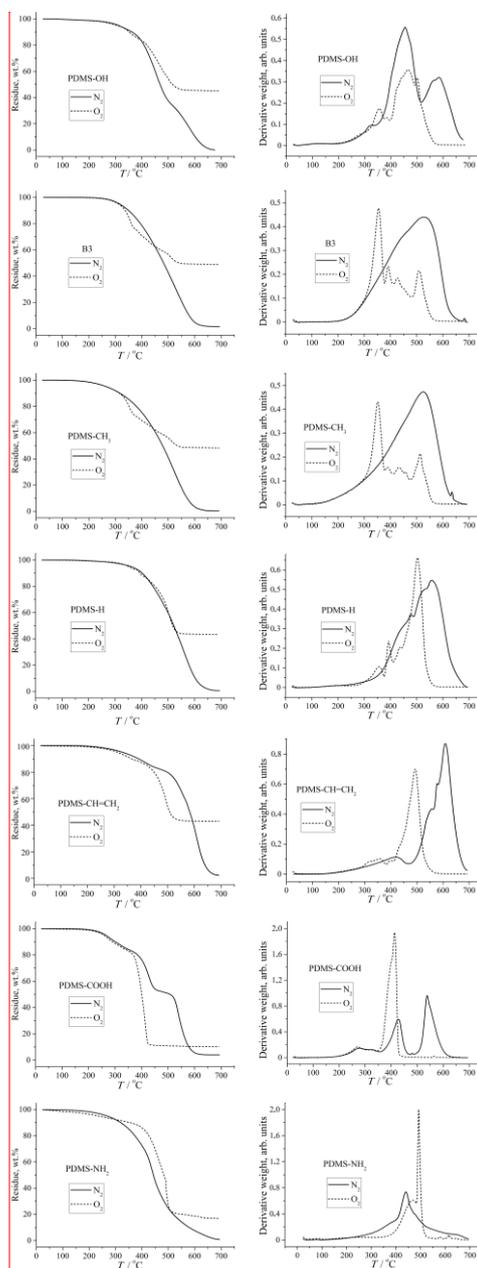


Fig. 6. TG (left) and DTG (right) curves of the α,ω -telechelic PDMSs in nitrogen and air.

ected proof

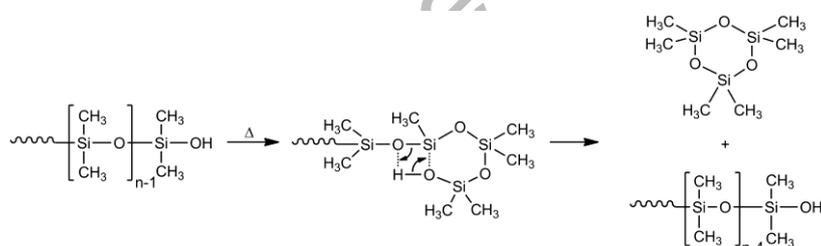
472 TABLE III. The data of the thermogravimetric analysis of the α,ω -telechelic PDMSs in nitrogen

Sample	$T_{5\%} / ^\circ\text{C}$	$T_{50\%} / ^\circ\text{C}$	$T_{\text{max.}} / ^\circ\text{C}$	Residue at 700 $^\circ\text{C}$, 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

473 TABLE IV. The data of the thermogravimetric analysis of the α,ω -telechelic PDMSs in air

Sample	$T_{5\%} / ^\circ\text{C}$	$T_{50\%} / ^\circ\text{C}$	$T_{\text{max.}} / ^\circ\text{C}$	Residue at 700 $^\circ\text{C}$, 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

474 curves (Fig. 6). It is known that PDMS with SiOH end-groups degrades by
 475 depolymerization in an inert atmosphere.²⁷ Thanks to the great flexibility of
 476 $-\text{[SiO]}_x-$ segments of the siloxane chains, the terminal SiOH groups can initiate
 477 intramolecular rearrangement by the so-called “back-biting” or “unzipping”
 478 process, which results in the formation of cyclic siloxanes (Fig. 7).



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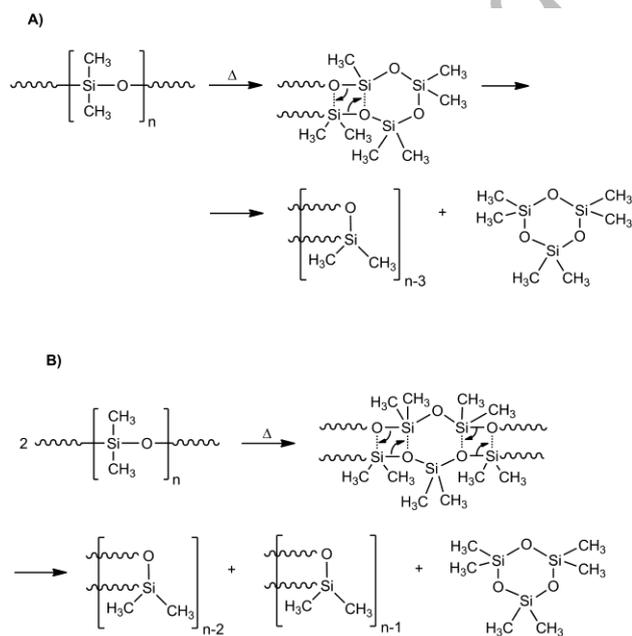
480

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

481 The similar shape of TG and DTG curves of the PDMS-CH₃ and the com-
 482 mercial B3 of analogous molecular weight was expected, as both samples were
 483 terminated entirely by methyl groups. The lower $T_{5\%}$ value of the sample PDMS-
 484 -CH₃ (266 $^\circ\text{C}$ for both N₂ and air atmosphere), in comparison with $T_{5\%}$ value of
 485 B3 (316 $^\circ\text{C}$ in N₂ and 312 $^\circ\text{C}$ in air) could be attributed to the presence of linear
 486 siloxanes of lower molecular weights and also maybe the presence of residual
 487 cyclics, that are not completely removed during the vacuum distillation. The

488 initial weight loss of the PDMS-CH₃ could be caused by the evaporation of lower
 489 linear and cyclic siloxanes during the thermogravimetric analysis. As a precondition
 490 for intramolecular depolymerization in an inert atmosphere, which begins
 491 from the chain-ends, is the presence of SiOH groups, it could be concluded that
 492 PDMSs terminated with different kinds of functional groups cannot degrade in
 493 this way. It is well known that the stability of the Si–O bonds is countered by the
 494 characteristic flexibility of the siloxane chain segments, which enables easy
 495 formation of local configurations that facilitate inter- and intramolecular siloxane
 496 redistribution reactions.²³ These reactions lead to fragmentation of linear siloxane
 497 chains into the smaller cyclosiloxanes that are volatile and thermodynamically
 498 more stable at the degradation temperatures. Consequently, the stability of
 499 linear PDMSs at elevated temperatures is reduced, and their degradation occurs
 500 at temperatures lower than would be expected based on Si–O dissociation
 501 energies.^{2,3}

502 PDMS-CH₃ and B3 samples terminated with CH₃ groups may degrade by
 503 inter- and intramolecular redistribution reactions, which occur randomly between
 504 the siloxane bonds located within the polymeric chains, whereby cyclics re-
 505 occur. This is the so-called “random scission” mechanism, shown in Fig. 8.^{29,34}



506
 507
 508

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

509 The samples PDMS-COOH and PDMS-NH₂ were the most thermally
510 unstable in both N₂ and air atmospheres, in comparison with the other telechelic
511 PDMSs. The $T_{5\%}$ values were 265 °C for the sample PDMS-COOH and 268 °C
512 for PDMS-NH₂ in nitrogen, whereas the corresponding temperatures in air
513 amounted to 257 °C (PDMS-COOH) and 236 °C (PDMS-NH₂). The degradation
514 mechanisms of these two samples are completely different in both nitrogen and
515 air atmosphere, which was confirmed by the DTG curves shown in Fig. 6.

516 The degradation of PDMS-COOH in N₂ occurs in three steps, of which the
517 first one is probably decarboxylation, followed by unzipping and/or random
518 scission. It can be seen that the same sample in air degrades by a two-stage
519 mechanism.

520 Based on the DTG curves, it could be concluded that majority of the exam-
521 ined α,ω -telechelic PDMSs degrade according to complex mechanism, with the
522 maximal weight loss rates occurring in at least two temperatures intervals. The
523 sample PDMS-OH shows two-step degradation processes, with T_{\max} at 456 and
524 582 °C. A “knee” at the TG curve of the PDMS-OH sample can be clearly seen,
525 which signifies where the first degradation step ends and the second step begins.
526 Most probably, the degradation of PDMS-OH in N₂ begins from the chain-ends by
527 “back-biting” (the first step of degradation) and then proceeds by “random scis-
528 sion” (the second step of degradation). The exception is the degradation of the
529 samples B3 and PDMS-CH₃ in N₂, where one maximum on the DTG curves
530 occurs in both cases (528 and 526 °C, respectively). The one-step degradation pro-
531 cess of these samples involves only “random scission”. A T_{\max} , corresponding to
532 “random scission” also occurs in the DTG curves of the samples PDMS-H, PDMS-
533 -CH=CH₂ and PDMS-COOH at 558, 601 and 538 °C, respectively (Table III).

534 In contrast to thermal degradation in N₂, the literature data suggest that
535 thermo-oxidative degradation of the same PDMSs is generally a more complex
536 process, which leads to pure silica at temperatures above 600 °C. The data ob-
537 tained here confirmed this suggestion in the case of the samples PDMS-CH₃ and
538 B3, with terminal methyl groups, where four T_{\max} can be seen at each DTG
539 curve. The thermo-oxidative degradation of the other samples proceeds through
540 at least two steps (Fig. 6, left panel), but compared to the thermal degradation of
541 the same samples in nitrogen, their mechanisms cannot be denoted as more
542 complex.

543 The residue after degradation was very low or even it was not present at all
544 in N₂ (from 0 to 4 wt.%, Table III), while in air, the amount of residue ranged
545 from 10.1 wt. % (PDMS-COOH) to 49.0 wt.% (B3) (Table IV). The explanation
546 for this behavior can be found again in different degradation mechanisms of
547 PDMS chains in inert and oxidative atmosphere. In inert N₂ atmosphere, regard-
548 less of whether degradation occurs by unzipping or random scission, cyclosilox-
549 anes as thermally more stable products in comparison with linear PDMSs are



Comment [L7]: It would seem that this polymer ignited in air

CONCLUSIONS

568

569 A series of α,ω -telechelic PDMS with hydrido, vinyl, carboxypropyl and
570 aminopropyl functional groups at the polymer chain-ends, with target molecular
571 weight of about 2500 g mol^{-1} , were prepared by siloxane equilibration reactions.
572 The number average molecular weights of the samples PDMS-COOH and
573 PDMS-NH₂, calculated from their ¹H-NMR spectra (3100 and 3720 g mol^{-1} , res-
574 pectively), agreed very well with the values predetermined by the compositions
575 of the reaction mixtures. The $\overline{M}_{n\text{NMR}}$ values of the samples PDMS-CH=CH₂
576 and PDMS-H (5170 and 8170 g mol^{-1} , respectively), were significantly higher in
577 comparison with the calculated values (2410 and 2340 g mol^{-1} , respectively).
578 Except of the meaningful difference in the intensities of the proton signals from
579 terminal groups, and the protons from the methyl groups, the reasons for the
580 higher $\overline{M}_{n\text{NMR}}$ value of the PDMS-H sample could be the lower purity and
581 higher volatility of the TMDS reactant, which has the lowest boiling temperature
582 of all the disiloxanes used in this work. Regarding the size of polymer molecules,
583 the synthesized polymers were also characterized by GPC and dilute solution
584 viscometry. Agreement between $\overline{M}_{n(\text{calc})}$ and $\overline{M}_{n\text{GPC}}$ was very good for the
585 samples PDMS-CH₃, PDMS-COOH and PDMS-NH₂. The maximal deviation
586 between $\overline{M}_{n\text{GPC}}$ and $\overline{M}_{n(\text{calc})}$ was again for the sample PDMS-H. The polydis-
587 persity index of the synthesized samples ranged from 1.75 (PDMS-CH=CH₂) to
588 2.49 (PDMS-NH₂), which suggested the „most probable“ molecular weights dis-
589 tribution. The \overline{M}_η values obtained from dilute solutions viscometry lay between
590 $\overline{M}_{n\text{GPC}}$ and $\overline{M}_{w\text{GPC}}$, as was to be expected for the „most probable“ distribution.
591 The results of thermogravimetric analysis in nitrogen and air showed that the
592 terminal functional groups influenced significantly the thermal and thermo-oxi-
593 dative stability of the α,ω -telechelic PDMSs, as well as the degradation mech-
594 anism. Degradation of all polymer samples started at lower temperatures in an
595 oxidative atmosphere than in an inert nitrogen atmosphere. The highest tempe-
596 ratures of the onset of degradation were shown by the samples PDMS-H and
597 PDMS-CH=CH₂, in both a nitrogen and an air atmosphere. It is believed that this
598 behavior pattern of the PDMS-H and PDMS-CH=CH₂ is the consequence of
599 initial addition reactions, without the generation of volatile products at tempe-
600 ratures below and about $300 \text{ }^\circ\text{C}$, which were possible thanks to the presence of
601 the Si-H or Si-CH=CH₂ groups. The samples PDMS-COOH and PDMS-NH₂
602 were the most unstable in both nitrogen and air atmosphere in comparison with
603 the other investigated telechelic PDMSs. The shape of the DTG curves having at
604 least two weight loss peaks showed that the majority of the α,ω -telechelic
605 PDMSs degrade by complex mechanisms. The residue after degradation was
606 very low in nitrogen (0 to $4 \text{ wt. } \%$), while in the air, it was significantly higher
607 (10 to $49 \text{ wt. } \%$). In order to obtain more details about the degradation products
608 and degradation mechanism of α,ω -telechelic PDMSs, thermogravimetric ana-

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

611 SUPPLEMENTARY MATERIAL

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

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617 Science and Technological Development of the Republic of Serbia (Project No. 172062).

618

ИЗВОД

619 СИНТЕЗА, СТРУКТУРА И ТЕРМОГРАВИМЕТРИЈСКА АНАЛИЗА α,ω -ТЕЛЕХЕЛИЧНИХ
620 ПОЛИДИМЕТИЛСИЛОКСАНА МАЛЕ МОЛСКЕ МАСЕ

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625 Серија α,ω -телехеличних полидиметилсилоксана (PDMS), предодређене молске
626 масе од око 2500 g mol^{-1} , синтетисана је реакцијом силоксанске еквилибрације. Синтеза
627 су изведене полазећи од октаметилциклотетрасилоксана (D_4) и различитих дисилокса-
628 на, као што су: хексаметилдисилоксан (HMDS), 1,1,3,3-тетраметилдисилоксан (TMDS),
629 1,3-дивинилтетраметилдисилоксан (DVTMDS), 1,3-бис(3-карбоксипропил)тетраметил-
630 дисилоксан (DCPTMDS) и 1,3-бис(3-аминопропил)тетраметилдисилоксан (DAPTMDMS).
631 Дисилоксани су служили за увођење функционалних група на крајеве полимерних
632 ланаца, а такође су имали улогу регулатора молске масе полимера. Полидиметил-
633 силоксани са триметил, хидридо, винил, карбоксипропил и аминопропил завршним
634 групама су добијени на овај начин. Структура α,ω -телехеличних PDMS је потврђена
635 NMR и IR спектроскопијом. Молске масе полимера су одређене ^1H -NMR спектроскопи-
636 јом, гел-пропусном хроматографијом (GPC) и вискозиметријом разблажених раствора.
637 Термограмметријска анализа (TGA) у азоту и ваздуху је показала да природа завршних
638 група значајно утиче на термичку и термо-оксидативну стабилност, као и на механизам
639 деградације α,ω -телехеличних PDMS.

640 (Примљено 27 априла, ревидирано 19 јуна, прихваћено 28. јуна 2017)

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Comment [V8]: Please check!



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Supplementary material

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SUPPLEMENTARY MATERIAL TO

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

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12, Belgrade 11000, Serbia and ³University of Belgrade, Faculty of Agriculture,

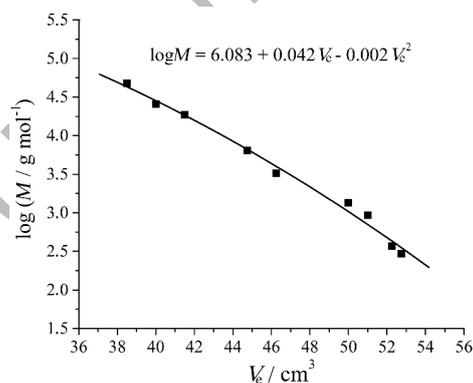
Nemanjina 6, Zemun, Belgrade 11080, Serbia

J. Serb. Chem. Soc. 82 (0) (2017) 000–000

TABLE S-I. Bulk viscosities and calculated molecular weights of PDMS standards

Standard sample	η_o / cSt	$\bar{M} \eta_o / \text{g mol}^{-1}$
B1	5.4	940
B2	10.1	1360
B3	50.5	3270
B4	98	6490
B5	480	18680
B6	955	25910
B7	4860	47710

Comment [V9]: Not an SI unit!



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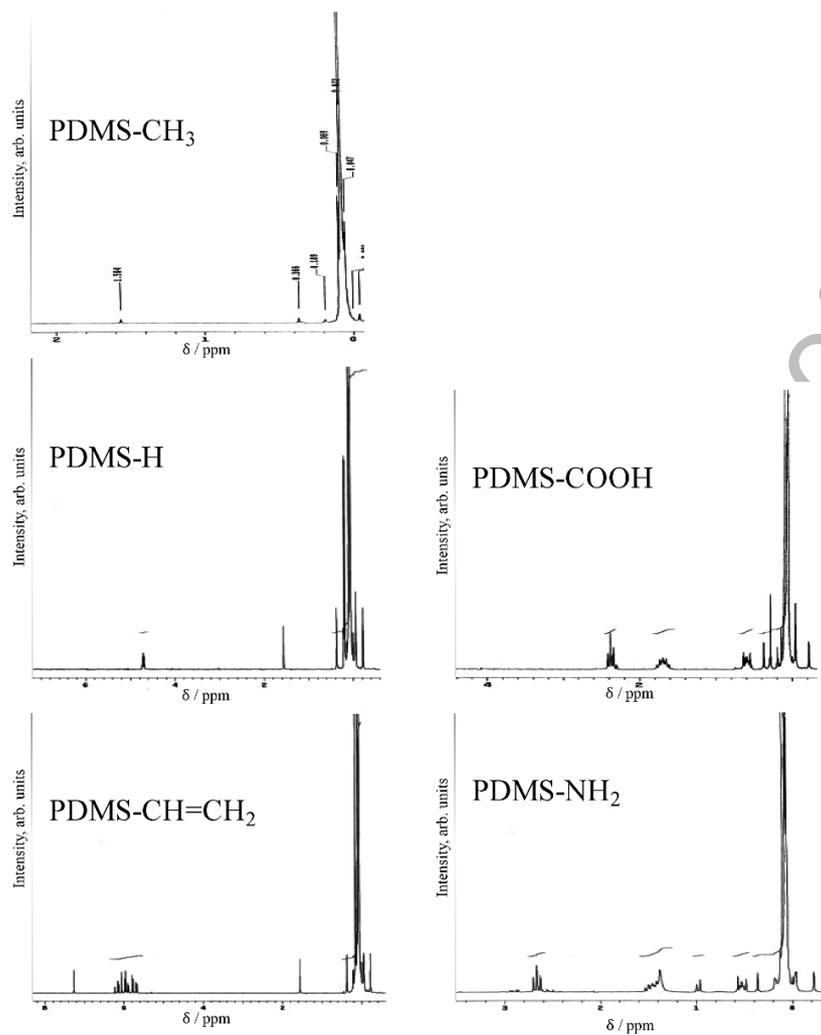
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Fig. S-1. Calibration curve for GPC.

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Fig. S-2. ¹H-NMR spectra of α,ω -telechelic PDMSs.

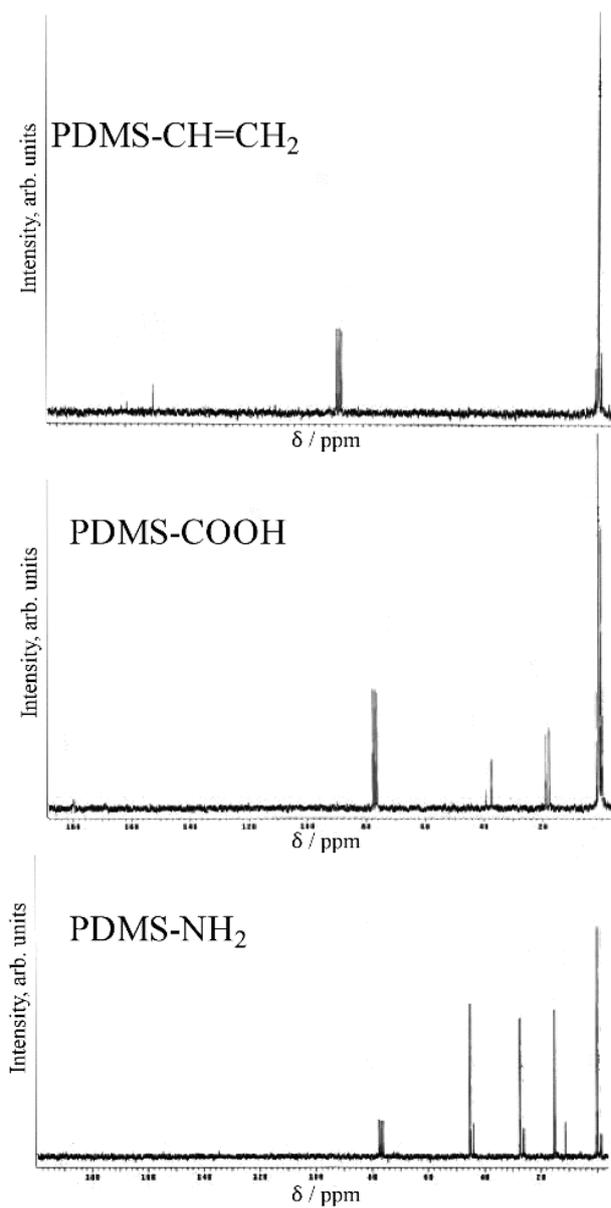
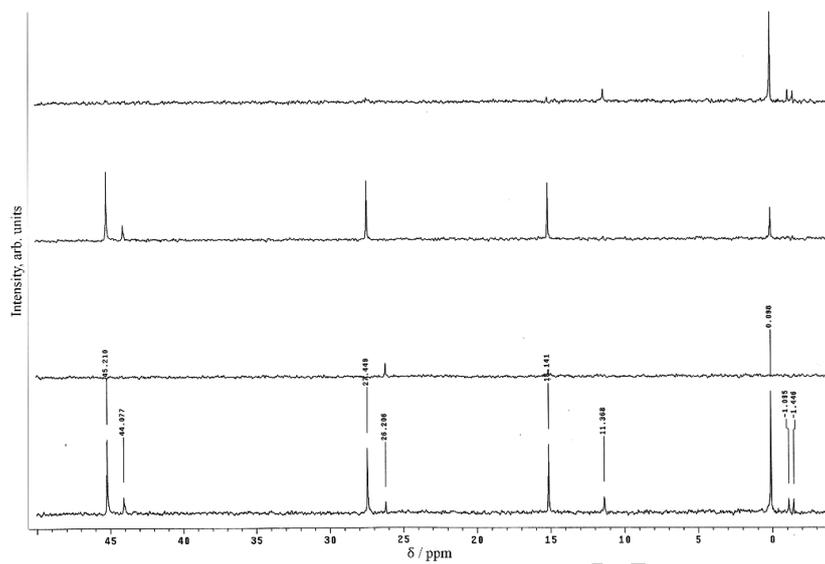


Fig. S-3. ¹³C-NMR spectra of α, ω -telechelic PDMSs.

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Fig. S-4. DEPT spectrum of 1,3-bis(3-aminopropyl)tetramethyldisiloxane.

Uncorrected