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Characterization of siloxane copolymers by solution ^{17}O NMR spectroscopy

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Abstract

Solution ^{17}O NMR spectroscopy was used for structure elucidation of siloxane copolymers with the natural abundance of ^{17}O, i.e. without any enrichment prior to spectroscopy. Homo, co, and terpolymers, as well as linear chains, cyclic oligomers, and graft polymers were investigated. All relevant chemical shifts and corresponding linewidths were reported for siloxane polymers substituted with methyl, phenyl, 3-cyanopropyl, 2-cyanoethyl, 3,3,3-trifluoropropyl, and polyethylene glycol ligands and with the backbone stiffening groups tetramethyl-*p*-silphenylene, tetramethyl-*p*,*p*′-sildiphenylene ether, and *m*-carborane. An increment system was extended to predict the chemical shifts of substituted siloxane copolymers. ^{17}O NMR spectroscopy of polysiloxanes provided information concerning their chemical composition, average molecular weight, and microstructure.

Keywords: Siloxane copolymers; Stationary phases; ^{17}O NMR spectroscopy

1. Introduction

In NMR spectroscopy oxygen is not so popular like proton or carbon since ^{17}O is a quadrupolar nucleus with a nuclear spin quantum number of 5/2. Therefore, the efficient quadrupolar relaxation broadens the signal (in general >100 Hz) resulting in bad resolution in comparison to other nuclei [1,2]. Another unfortunate consequence is that the fast decaying time domain signals are subject to the problem of acoustic ringing leading to severe baseline distortions in the frequency domain [3]. Additionally, the low natural abundance of ^{17}O (0.037%) demands for long acquisition times. And last but not least ^{17}O NMR investigations of macromolecules are very unfavorable due to their slow molecular tumbling in solution caused by the great molecular radius, by the extended structure and flexibility of the polymer chains, and by the increased viscosity of the solutions.

There are several investigations about siloxanes, but there exists hardly any literature about high-molecular weight polymers. In a pioneering paper Scheim et al. applied solution ^{17}O NMR spectroscopy for the measurement of siloxanes [4]. The authors reported several chemical shifts of siloxanes with the structure $R_3Si–O–SiR_3$. Other works based on the enrichment of ^{17}O atoms by pretreatment of the sample with ^{17}O-enriched compounds to increase sensitivity. For example, initial condensation products and hydrolysis products of alkoxysilanes with ^{17}O-enriched water were monitored by solution ^{17}O NMR [5–8]. A similar enrichment was performed during the investigation of hydrolysis products of polysiloxanes with $H_2^{17}O$ under irradiation [9]. The investigation of siloxane-oxide hybrid materials by solid state and solution NMR techniques of siloxanes is reviewed by Babonneau [10]. However, enrichment of ^{17}O is necessary also for solid state NMR [10]. Structure elucidation of borosilicate glasses was frequently performed by magic-angle spinning (MAS) ^{17}O NMR [11–15]. Polydimethylsiloxanes incorporating metal-oxo species, which were synthesized with ^{17}O-enriched alkoxysilanes, were characterized by solid state MAS ^{17}O

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NMR [8,16,17]. To sum up, investigations of siloxanes are limited to small siloxane molecules by solution NMR and to ^{17}O-enriched polysiloxanes by solid state NMR. In contrast to that we set out to characterize high-molecular weight siloxane copolymers by solution ^{17}O NMR spectroscopy with natural abundance of ^{17}O. We investigated the potential of this technique for the characterization of polysiloxanes concerning their chemical composition, branching, small cyclic impurities, end groups and microstructure. These results are compared to the ones obtained by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and the advantages and limitations of this technique are clearly pointed out.

2. Experimental

2.1. Polymers

The siloxane polymers investigated are listed in Table 1. The polyethylene glycols PEG 400 (Aldrich), PEG 1000 (Merck, Darmstadt, Germany), and PEG 6000 (Fluka, Buchs, Switzerland), as well as diphenyl ether (Fluka) and poly-*m*-phenyl ether OS-138, six phenyl rings (Macherey–Nagel) were used as reference compounds for signal assignment.

2.2. ^{17}O NMR spectroscopy

All samples were dissolved in toluene-h_8/toluene-d_8 (1:1 v/v) at a concentration of approximately 20–30 wt%, except XE-60, OV-210, Silar 10C, and OV-275 were dissolved in acetonitrile-d_3. The samples were measured in 10-mm-o.d. tubes (Wilmad, Buena, NJ, USA) at a temperature of 363 K in toluene or at 343 K in acetonitrile. ^{17}O NMR spectra were recorded at a frequency of 54.24 MHz on a Bruker Advance DRX 400 WB NMR spectrometer (Bruker Analytische Messtechnik, Ettlingen, Germany) equipped with a 10-mm broadband observe probe. The measurements were performed with a 90° excitation pulse (18 μs). The acquisition time was 40 ms followed by 100 ms for relaxation. Typical parameters included a spectral width of 15 kHz, 2*k* data points, 6 μs pre-scan delay, 5000–800,000 scans (total acquisition time between 1 and 40 h) to obtain sufficient signal-to-noise ratios. Data processing was performed on a silicon graphics workstation using XWINNMR version 3.1 (Bruker). As no multi-pulse sequences were used to overcome the problem of acoustic ringing, the resulting baseline distortions had to be corrected after the acquisition. For this the digital data were at first converted to analogue followed by recalculation of the first 4–16 data points by linear prediction backward using 32 filter coefficients [20]. To improve the signal-to-noise ratio the corrected free induction decay was multiplied by an exponential window function using a line broadening factor of 80–150 Hz, depending on the linewidth of the resonance lines. All chemical shifts are referenced to external H_2O ($\delta = 0$ ppm) at the appropriate temperature. For confirmation of the results ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded with the same spectrometer equipped with a 5-mm broadband observe probe with automatic tuning and matching. The polymers were dissolved in either $CDCl_3$ or acetone-d_6.

3. Results and discussion

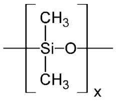
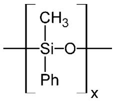
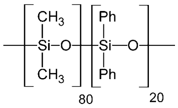
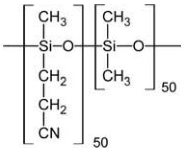
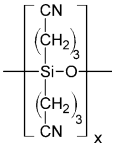
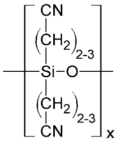
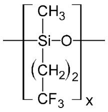
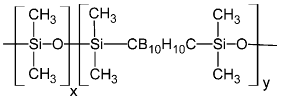
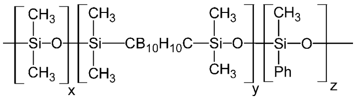
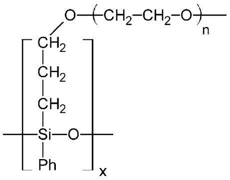
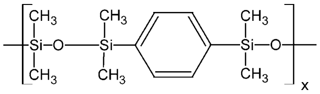
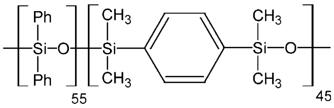
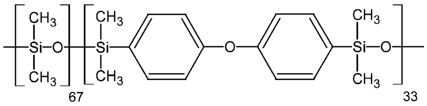
3.1. Signal assignment

Signal assignment was performed according to reference values [4], with homopolymers, where only one signal was expected (PDMS-1M, OV-1, Silar 10C, OV-210), and with reference compounds containing analogue functional groups (PEGs, diphenyl ether, polyphenyl ether).

An overlay of ^{17}O NMR spectra of SDPE-33, PDMS-1M, SM-50 and OS-138 is displayed in Fig. 1. The signals of SDPE-33 can easily be assigned with the help of the homopolymer PDMS-1M and the alternating copolymer SM-50, where in each case only one signal was expected. However, the oxygen atom of the sildiphenyl ether unit complicated signal assignment, as it could not be detected. The reference compounds diphenyl ether and a poly-*m*-phenyl ether (OS-138) resonated at 117 and 119 ppm, which corresponds roughly to values from the literature ranging from 102 to 114 ppm [21–23]. However, the linewidth increased with molecular weight: diphenyl ether (molecular weight 170) exhibits a linewidth of 330 Hz, whereas the poly-*m*-phenyl ether (molecular weight 554) has a linewidth of above 870 Hz. For neat diphenyl ether at 90 °C an even greater linewidth of 850 Hz was reported [22]. Therefore, we concluded that the sildiphenylene ether cannot be observed as the high molecular weight of SDPE-33 caused an extremely broadened signal. This increased linewidth compared to Si–O–Si bridges reveals that the sildiphenylene ether unit is very inflexible favoring its backbone stiffening property.

Fig. 2 displays the ^{17}O NMR spectrum of another polymer where signal assignment was complicated due to several different signals: OV-330 is a graft polymer with a polysiloxane backbone and a polyethylene glycol (PEG) side chain. The propylene, phenyl-polysiloxane backbone (at 60.5 ppm) was identified in comparison with OV-17, which is a methyl, phenyl-polysiloxane and exhibited a chemical shift of 66.9 ppm. PEGs with molecular weights of 400, 1000, and 6000 were used as reference compounds to confirm the signal for $-(CH_2CH_2-O)_n$ about -1 ppm, see PEG 400 in Fig. 2. The signal at -10 ppm reflects internal water, which is associated with the polymer. This signal is also present when acetonitrile was used as solvent, as it contained a minute amount of water, which can be observed due to the long acquisition times. The signal at -21.6 ppm is assumed to be the terminal methoxy group of the polyethylene glycol side chain. This chemical shift is

Table 1
Names, description and structure of siloxane polymers investigated

Polymer	Description	Supplier	Chemical structure
PDMS-1M	100% Dimethyl-polysiloxane	Sigma, St Louis, MO, USA	
OV-17	100% Methylphenyl-polysiloxane	Analabs, North Haven, CT, USA	
PS090	80% Dimethyl, 20% diphenyl-polysiloxane	ABCR, Karlsruhe, Germany	
XE-60	50% 2-Cyanoethylmethyl, 50% dimethyl-polysiloxane	Supelco, Bellefonte, PA, USA	
Silar 10C	100% 3-Cyanopropyl-polysiloxane	Alltech Associates, Deerfield, IL, USA	
OV-275	100% Cyanoalkyl-polysiloxane	Pierce Eurochemie, Rotterdam, The Netherlands	
OV-210	100% 3,3,3-Trifluoropropyl-methyl-polysiloxane	Macherey-Nagel, Düren, Germany	
Dexsil 300	Carborane-methylsilicone	Alltech Associates	
Dexsil 400	Carborane-methylphenyl silicone	Supelco	
OV-330	Phenylsiloxane-carbowax copolymer	Macherey-Nagel; Ohio Valley Specialty Chemical, Marietta, OH, USA	
SM-50	45% Tetramethyl-*p*-silphenylene-55% dimethylsiloxane copolymer	Laboratory-made [18]	
SP-43	45% Tetramethyl-*p*-silphenylene-55% diphenylsiloxane copolymer	Laboratory-made [18]	
SDPE-33	34.5% Tetramethyl-*p*,*p*′-sildiphenylene ether-65.5% dimethylsiloxane copolymer	Laboratory-made [19]	

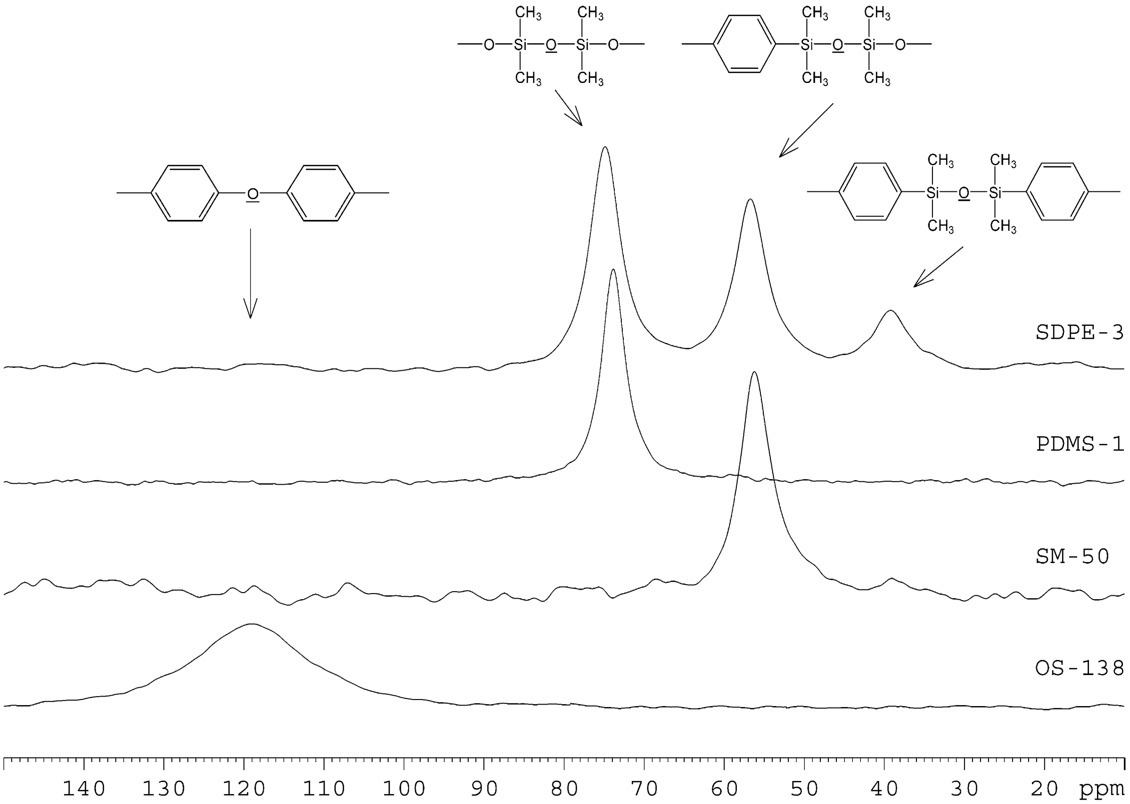


Fig. 1. Overlays of ^{17}O NMR spectra of SDPE-33, PDMS-1M, SM-50, and OS-138. Recorded in toluene at 90 °C, referenced to external water. Number of scans are 457591, 180950, 20186 and 310706 for SDPE-33, PDMS-1M, SM-50 and OS-138, respectively. Note that the sildiphenylene ether expected at approximately 117 ppm cannot be observed.

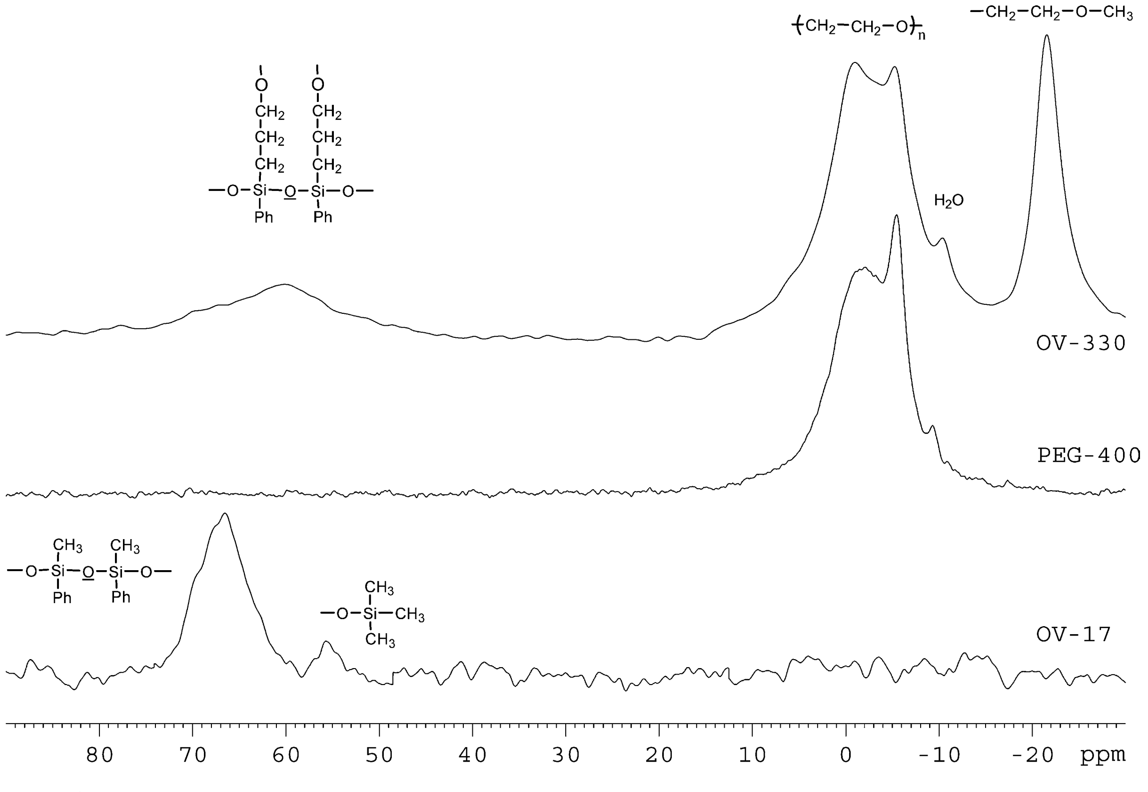


Fig. 2. Overlays of ^{17}O NMR spectra of OV-330, PEG 400, and OV-17. Recorded in toluene at 90 °C, referenced to external water. Number of scans are 167001, 81257 and 179336 for OV-330, PEG 400 and OV-17, respectively.

consistent with that one of ethyl methyl ether, where a chemical shift of −22.5 ppm was reported [21]. The relatively low linewidth of 130 Hz reflects the more steric freedom. It could not be excluded that another low molecular weight impurity caused this signal, although both OV-330 polymers obtained from two different suppliers exhibited this signal. From the abundance of the end group vs. the linear PEG chain, an unexpectedly short side chain length between 2 and 3 could be calculated for the two OV-330 polymers. These data were confirmed by ^{1}H NMR spectroscopy, although signal assignment is not so clear as in ^{17}O NMR spectroscopy due to signal overlap.

The chemical shifts of all polysiloxanes investigated are listed in Table 2. Unfortunately, signal assignment is not unambiguous in ^{17}O NMR. First, symmetrical substitution cannot be distinguished from asymmetrical substitution e.g. the chemical shift of O–MePhSi–*O*–SiMePh–O (in OV-17) and of O–Me$_2$Si–*O*–SiPh$_2$–O (in PS090) are very similar: 66.9 and 67.3 ppm, respectively. Therefore, it cannot be concluded from the ^{17}O spectrum whether PS090 consists of diphenyl or methylphenyl groups. Additional information is required to assign signals and to calculate the chemical composition, e.g. ^{29}Si NMR spectroscopy is a suitable complimentary technique for structure elucidation. A second limitation of ^{17}O NMR spectroscopy for the structure elucidation of polysiloxanes is that a distinction between 2-cyanoethyl and 3-cyanopropyl ligands is not possible due to their similar chemical shifts. For example, OV-275, a 45% dicyanoethyl, 55% dicyanopropyl-polysiloxane (derived from ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy data), exhibited only one signal at 60 ppm in the ^{17}O NMR spectrum (not shown), and closely resembles the spectrum of Silar 10C, which is a truly 100% dicyanopropyl-polysiloxane.

Derived from the chemical shift data an increment system was established by Scheim et al. [4]. This system was extended by several units of siloxane copolymers, see Table 3. The values derived by Scheim et al. for small siloxanes are listed for comparison. The influence of the Si substituent on the chemical shift of oxygen is partly very low. If a phenyl group replaces a methyl group, the shift is changed by only 3 ppm. Therefore, it is reasonable that the tetramethyl-*p*-silphenylene and the tetramethyl-*p*,*p*′-sildiphenylene ether units cannot be distinguished by their chemical shifts (19.8 vs. 19.5 ppm) as the difference is six bindings apart and has too less influence on the chemical environment. However, the chemical shift of a carborane unit (21.2 ppm) is by accident similar to the above-described backbone stiffening groups.

3.2. Quantitation of ^{17}O NMR spectra

The chemical composition of the polymers can be calculated from the ^{17}O NMR spectra. Good agreement

Table 2
Chemical shifts of siloxane polymers and corresponding linewidths in ^{17}O NMR spectroscopy

Group[a]	Chemical shift (ppm)[b]	Linewidth (Hz)	Polymer
O–Me$_2$Si–*O*–SiMe$_2$–O	73.9	195	PDMS-1M
	74.9	225	PS090
	74.4	210	Dexsil 300
	74.9	230	SDPE-33
	75.3	40	Hexamethylcyclotrisiloxane
	75.4	56	Octamethylcyclotetrasiloxane
	74.3[c]	n.d.	XE-60
O–Me$_2$Si–*O*–SiPh$_2$–O	67.3	270	PS090
O–Ph$_2$Si–*O*–SiPh$_2$–O	60.2	470	Octaphenylcyclotetrasiloxane
O–MePhSi–*O*–SiMePh–O	66.9	405	OV-17
O–(CH$_2$CH$_2$CN)MeSi–*O*–SiMe$_2$–O	70.7[c]	490	XE-60
O–[(CH$_2$)$_{2–3}$CN]$_2$Si–*O*–Si[(CH$_2$)$_{2–3}$CN]$_2$–O	61.0[c]	480	OV-275
	60.5[c]	500	Silar 10C
O–Me(CH$_2$CH$_2$CF$_3$)Si–*O*–Si(CH$_2$CH$_2$CF$_3$)Me–O	66.0[c]	610	OV-210
O–[–(CH$_2$)$_3$–PhSi]–*O*–[SiPh(CH$_2$)$_3$–]–O	60.5	550	OV-330
Si–C$_6$H$_4$–Me$_2$Si–*O*–SiMe$_2$–O	56.3	205	SM-50
Si–C$_6$H$_4$–Me$_2$Si–*O*–SiPh$_2$–O	50.8	450	SP-43
C$_6$H$_4$–O–C$_6$H$_4$–Me$_2$Si–*O*–SiMe$_2$–O	56.7	240	SDPE-33
C$_6$H$_4$–O–C$_6$H$_4$–Me$_2$Si–*O*–SiMe$_2$–C$_6$H$_4$–	39.2	290	SDPE-33
B$_{10}$H$_{10}$–C–Me$_2$Si–*O*–SiMe$_2$–O	58.2	200	Dexsil 300
	56.0	<430	Dexsil 400
O–CH$_2$–CH$_2$–*O*–CH$_2$–CH$_2$–O	−1.0	<470	OV-330
O–CH$_2$–CH$_2$–*O*–CH$_3$	−21.6	130	OV-330
O–MePhSi–*O*–SiMe$_3$	55.9	200	OV-17

[a] The respective oxygen atom is italic.

[b] The chemical shifts are reported in toluene, referenced to external water ($\delta = 0$ ppm).

[c] Reported in acetonitrile.

Table 3
Increments of chemical shift of siloxane copolymers R_1–O–R_2

Groups R_1, R_2	Increment (ppm)[a]	Increment (ppm)[b] [4]
O–Me_2Si–	37.0	35.5
O–$[(CH_2)_{2-3}CN]_2Si$–	30.2[c]	–
O–$Me(CH_2CH_2CN)Si$–	33.7[c]	–
O–$Me(CH_2CH_2CF_3)Si$–	33.0[c]	–
O–MePhSi–	33.5	32.7
O–Ph_2Si–	30.3	29.1
Me_2Si–C_6H_4–Me_2Si–	19.8	–
C_6H_4–O–C_6H_4–Me_2Si–	19.5	–
$B_{10}H_{10}$–C–Me_2Si–	21.2	–
Me_3Si–	22.4	21.4
O–CH_2–CH_2–	−0.5	–

[a] Reported in toluene at 90 °C, referenced to external water.
[b] Measured at 60 °C.
[c] Reported in acetonitrile at 70 °C.

can be obtained in comparison to data from ^{1}H and ^{29}Si NMR spectroscopy, see SDPE-33, Dexsil 300 and Dexsil 400 in Table 4. However, quantitation is very inaccurate for some polymers, see, e.g. PS090 in Table 4. In this case the chemical composition is deviating, as a small amount of a diphenyl-*O*-diphenly unit cannot be detected due to a broadened signal. Therefore, quantitative data derived from ^{17}O NMR spectra must be treated very carefully.

3.3. Line broadening

Broad signals have to be expected in ^{17}O NMR spectroscopy, as quadrupolar relaxation is almost always the most effective relaxation pathway for the ^{17}O nucleus. It is reasonable to assume this quadrupolar interaction is in the same order of magnitude for all of the investigated siloxane polymers, as the electric field gradient tensor as well as the asymmetry parameter will be quite similar. Thus the discussion of the observed line broadening may be focused on the rotational correlation time τ_c, which is first of all a function of the solvent viscosity and the temperature, both parameters being interdependent [1]. The easiest way to reduce the linewidth is to elevate the temperature and hence shorten τ_c, but even then the resonance lines tend to be rather broad. Secondly τ_c is a function of the molecular radius with the complication, that most of the polymers will not have a globular shape, so extended structures as well as local motions within an elongated chain have to be considered.

Only small cyclic oligosiloxanes having a short τ_c exhibit relatively narrow signals: hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane exhibited linewidths of 56 and 40 Hz, respectively. In comparison to that a dimethyl-polysiloxane with a molecular weight of 24,000 (PDMS-1M) exhibited a linewidth of 195 Hz, this is a fourfold increase in linewidth in comparison to small molecules. Both the tetramethyl-*p*-silphenylene and the tetramethyl-*p*,*p*′-sildiphenylene ether unit did not significantly increase the linewidth in comparison to a dimethyl siloxy group, although these units are used as backbone stiffening groups. If the second unit is a dimethylsiloxy group, the linewidth (SM-50: 205 Hz and SDPE-33: 230 Hz) is similar to a –Me_2Si–O–$SiMe_2$– unit (195 Hz). Also the carborane unit does not increase the linewidth in comparison to –Me_2Si–O–$SiMe_2$–, e.g. Dexsil 300 exhibited a linewidth of 200 Hz. Hence the observed moderate line broadening for these siloxanes indicates sufficient rotational freedom within the polymer chain for this arrangement of the ligands, thus lengthening the overall rotational correlation time not too much.

Contrary to that, larger ligands like phenyl attached to both silicon atoms surrounding the respective ^{17}O nucleus cause dramatic line broadening: –MePhSi–O–SiMePh– has a linewidth of 405 Hz (see OV-17). Even small molecules with phenyl groups exhibit a broadened linewidth, e.g. octaphenylcyclotetrasiloxane with Ph_2Si–O–$SiPh_2$ units has a linewidth of 470 Hz. The linewidth is influenced rather by the large ligand than by the cyclic strained structure, as the homologous octamethylcyclotetrasiloxane and the even more strained hexamethylcyclotrisiloxane exhibited relatively narrow signals (56 and 40 Hz, respectively). In the same way the diphenylsiloxy group increased the linewidth of a silphenylene–diphenylsiloxane copolymer to 450 Hz (for SP-43), whereas a silphenylene–dimethylsiloxane copolymer (SM-50) exhibited a linewidth of 205 Hz. Also alkyl substituents, such as cyanopropyl, cyanoethyl, and trifluoropropyl cause broadened signals with linewidths

Table 4
Chemical composition of selected siloxane copolymers determined by NMR spectroscopy

Polymer	^{1}H NMR	^{29}Si NMR	^{17}O NMR
SDPE-33	32.8% tetramethyl-*p*,*p*′-sildiphenylene ether–67.2% methylsiloxane copolymer [19]	34.5% tetramethyl-*p*,*p*′-sildiphenylene ether–65.5% dimethylsiloxane copolymer [19]	34.1% tetramethyl-*p*,*p*′-sildiphenylene ether–65.9% dimethylsiloxane copolymer
Dexsil 300	33.3% bis(dimethylsilyl)carborane–66.7% methylsiloxane copolymer	34.5% bis(dimethylsilyl)carborane–65.5% dimethylsiloxane copolymer	32.0% bis(dimethylsilyl)carborane–68.0% methylsiloxane copolymer
Dexsil 400	23.5% bis(dimethylsilyl)carborane–65.3% methylsiloxane, 11.2% phenylsiloxane terpolymer	24.9% bis(dimethylsilyl)carborane–24.3% methylphenylsiloxane, 50.8% dimethylsiloxane terpolymer	24.4% bis(dimethylsilyl)carborane–75.6% methylphenylsiloxane copolymer
PS090	78.7% methyl, 21.3% phenyl-polysiloxane	76.3% dimethyl, 23.7% diphenyl-polysiloxane	87.8% dimethyl, 12.2% diphenyl-polysiloxane

about 500 Hz, see OV-275, Silar 10C, and OV-210 in Table 2. So the accumulation of these space-demanding ligands on the polysiloxane backbone seems to introduce much rigidity into the structure, may be due to π–π interactions in the case of the aromates or due to apolar interactions in the case of the alkyl side chains. As a result the overall τ_c is increased and the ^{17}O NMR resonance lines become rather broad.

In general, linewidths of >100 Hz are expected due to the electric quadrupole moment of ^{17}O [1,2]. Linewidths of 375–450 Hz were reported for small hydrolytic products of dimethyl, diphenyl-polysiloxanes [9]. Lower linewidths of ∼100 Hz were found for short dimethylsiloxy chains and cyclic species [8]. However, poor resolution due to broadened signals was observed when higher polymeric condensation products of tetramethoxysilane were monitored by ^{17}O NMR in solution [7]. Even the linewidths of short aliphatic *n*-alcohols range from 90 to 200 Hz [24]. Solid state MAS ^{17}O NMR spectroscopy of polydimethylsiloxane hybrid materials provided larger linewidths of approximately 2000 Hz [16,17]. Therefore, a linewidth of 200 Hz for polymers is acceptable, since both the high molecular weight and the high viscosity of the sample solutions broaden the signals. The highly concentrated polymer solutions have high viscosity even at elevated acquisition temperatures; therefore, spin–spin relaxation time (T_2) is very short resulting in signal broadening. However, the linewidth is moreover dramatically increased by large substituents such as phenyl, obviously due to an extended structure and higher rigidity of the polymer.

3.4. Acquisition times

An adequate signal-to-noise ratio demands for relatively long acquisition times. To decrease experiment times, high sample concentrations (∼20–30%) and large i.d. NMR tubes (10 mm) were applied. Homopolymers (OV-17, PDMS-1M) or alternating copolymers (SM-50, SP-43) where only one signal is expected can be measured within reasonable times (1–8 h). However, extremely long measuring times (up to 40 h) were necessary for terpolymers, where several signals are expected.

3.5. Cyclic oligosiloxanes

It was not possible to distinguish cyclic impurities from linear chains on the basis of their chemical shifts, e.g. the chemical shifts of linear $-Me_2Si-O-SiMe_2-$ sequences ranged from 73.9–74.9 ppm (Table 2), whereas the chemical shifts of the corresponding cyclic tri- and tetrasiloxanes are only slightly higher, i.e. 75.3 and 75.4 ppm, respectively. Similarly, the linear chain of $-Ph_2Si-O-SiPh_2-$ (expected at ∼60 ppm) is not distinguishable from octaphenylcyclotetrasiloxane (at 60.2 ppm). This finding is contradictory to a recent report, where two different ^{17}O NMR signals of dimethylpolysiloxane (at 66.7 and 71.1 ppm) were attributed to short linear chains and cyclic species [8].

3.6. Determination of average molecular weight

Only if a relatively low molecular weight is expected, the molecular weight can be calculated from the ^{17}O NMR spectra. For example, the end group $-OSiMe_3$ can be detected at 55.9 ppm in the spectrum of OV-17 (Fig. 2). With the ratio of the abundance of the end group vs. linear chain, an average chain length of 16 and an average molecular weight of 2500 could be calculated. This correlates very well with the molecular weight of 2200 for the same lot of OV-17 determined by ^{29}Si NMR spectroscopy [25]. Molecular weights in a similar range between 2300 and 4000 were reported for analogue OV-17 polymers from other manufacturers [26–28]. Another example, where the average molecular weight could be determined, is OV-330. The average chain length of the polyethylene glycol side chain could be calculated from the ratio of the area of the side chain end group (methoxy) and the polyethylene glycol chain. Obviously, OV-330 contains only a short side chain with an average molecular weight approximately half as much as PEG 400. However, the average chain length of the side chain could be calculated from the ratio of the area of the polysiloxane backbone and the polyethylene glycol side chain. The average chain length of the polyethylene glycol side chain was found to be 3.5 resulting in an average molecular weight of 210. These values were confirmed by proton NMR spectroscopy: an average chain length of 3.7 and an average molecular weight of 225 could be calculated from the abundance of the methylene protons of the ethylene glycol unit versus the phenyl protons of the siloxane backbone.

3.7. Determination of the microstructure

^{17}O NMR spectroscopy provides only limited information about the microstructure of siloxane copolymers. For example, both alternating and blocky sequences can be observed in SDPE-33, see Fig. 1. Another example is SM-50, an alternating tetramethyl-*p*-silphenylene-dimethylsiloxane copolymer [18], which exhibits only one signal at 56.3 ppm. A blocky or randomized copolymer would exhibit additional signals at 74 ppm for blocky dimethylsiloxy units and 40 ppm for blocky tetramethyl-*p*-silphenylene units. Nevertheless, ^{17}O NMR spectroscopy is clearly inferior to ^{29}Si NMR spectroscopy, where triads and even pentads of polysiloxanes can be assigned [18,25,29].

4. Conclusion

^{17}O NMR spectroscopy provides important information about the structure of polysiloxanes: The chemical composition can be calculated from the ^{17}O NMR spectra.

As the two siloxy neighbors of the oxygen atom can be assigned, limited information about the microstructure of the polymer can be obtained. For low-molecular weight polymers, the average molecular weight can be calculated from the abundance of a trimethylsilyl end group, which cannot be quantified by ^{1}H NMR spectroscopy due to signal overlap. However, ^{17}O NMR spectroscopy is not a so powerful tool for structure elucidation of siloxane polymers such as ^{1}H or ^{29}Si NMR spectroscopy. Broad resonance lines lead to low signal-to-noise ratios, e.g. units with low abundance or end groups of higher molecular weight polymers may not be detected. Broadened lines also cause signal overlap, complicate signal assignment and reduce the accuracy of quantitative data. Furthermore, only two neighboring units can be assigned, in contrast to ^{29}Si NMR spectroscopy, where up to five siloxy groups can be assigned. Additionally, peak assignment is not unambiguous, as symmetrical substitution of the siloxane backbone cannot be distinguished from an asymmetrical one. Despite of these limitations, ^{17}O NMR spectroscopy is a complimentary technique to confirm results obtained by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. Furthermore, ^{17}O NMR spectroscopy will gain in importance in the future, when improved instrumentation is accessible to reduce acquisition times and to improve signal-to-noise ratios.

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