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Characterization of stationary phases for gas chromatography by ^{29}Si NMR spectroscopy

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Abstract

Commercially available polysiloxanes containing methyl, phenyl, and cyanoalkyl groups and most frequently used as stationary phases in gas chromatography, were characterized by ^1H and ^{29}Si nuclear magnetic resonance spectroscopy. Microstructure, molecular weight, end group characteristics, branching, and cyclic by-products were determined for all polymers. The microstructure of an alternating, symmetrically substituted dimethyl, diphenylpolysiloxane (SOP-50) determined by ^{29}Si nuclear magnetic resonance spectroscopy demonstrated few rearrangements after thermal treatment under gas chromatographic conditions at 420°C. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polysiloxanes, extensively used as stationary phases in capillary columns in gas chromatography, have up to date been characterized by ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy [1–7], UV and viscosity measurements [8], pyrolysis gas chromatography–mass spectroscopy (GC–MS) [9] and ^{29}Si NMR spectroscopy [10–22]. In ^1H and ^{29}Si NMR spectroscopy, the chemical composition, end groups, average molecular weight, branching, and microstructure of the substituents along the polysiloxane backbone can be elucidated. The technique is simple and the results reproducible.

Stationary phases with high thermal stability are required in high-temperature GC. Polysiloxanes display an excellent thermal stability, which is further improved, if (i) phenyl groups are incorporated into the polysiloxane backbone, (ii) the substitution of the polysiloxane backbone is symmetrical, and (iii) the sequence of silyl groups along the silicone backbone is alternating [23]. It has also been recently suggested that Si–O/Si–O exchanges occur at high temperatures in every polymer, i.e., an alternating sequence is randomized by thermal isomerization [19].

Since differences in phenyl content have been reported for commercially available methylphenylpolysiloxanes [4,5,8–10,21], it must also be concluded that other polymeric properties such as chemical composition, end group characteristics, average molecular weight, etc. will also depend on the brand or even the batch, resulting in varying gas

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chromatographic properties and thermal stability.

To further investigate polymeric microstructure and changes occurring during thermal treatment, we examined twelve commercially available stationary phases for GC. The chemical composition and microstructure of methyl, phenyl, cyanopropyl, and cyanoethyl substituted polysiloxanes were determined by ^1H and ^{29}Si NMR spectroscopy. In addition, a new, alternating 50% dimethyl, 50% diphenyl-polysiloxane (SOP-50) that is used as stationary phase in wall coated open tubular glass [23–29] and fused-silica capillary columns [30–33] was examined before and after thermal treatment at 420°C.

2. Experimental

2.1. Stationary phases

All stationary phases investigated were polysiloxanes with methyl, phenyl, cyanopropyl or cyanoethyl groups. All polymers were commercially obtained

(see Table 1), except for SOP-50, which was a gift from R. Aichholz [23].

2.2. NMR spectroscopy

Stationary phases were dissolved in deuterated chloroform between 5 and 24% (w/w) depending on the solubility and availability of the stationary phases.

^1H NMR spectra were recorded at 25°C with a Bruker AM 400 WB spectrometer (Bruker Analytische Messtechnik, Ettlingen, Germany) operating at 400.13 MHz. ^{29}Si NMR spectra were obtained at 25°C on a DRX 400 WB spectrometer (Bruker) equipped with a broadband inverse probe, operating at 79.49 MHz for ^{29}Si . Typical parameters included a spectral width of 16 kHz, 32 k datapoints, 5000 to 20 000 scans according to the concentration of the sample for sufficient signal to noise ratios. Proton composite pulse decoupling was applied only during acquisition to avoid distortions of the signal intensities due to NOE during the relaxation period. Small amounts of chromium acetylacetonate were added as

Table 1
Information about the investigated polysiloxanes given by their manufacturers

Polysiloxane	Description	End group	Manufacturer
OV-1	100% dimethyl	trimethyl	Chrompack (Middelburg, The Netherlands)
SE-52	95% methyl, 5% phenyl	trimethyl	Chrompack
OV-17	100% methylphenyl	trimethyl	Analabs, Inc. (North Haven, USA)
SOP-50	50% dimethyl, 50% diphenyl	methoxy	R. Aichholz (Novartis, Basel, Switzerland)
OV-25	50% methylphenyl, 50% diphenyl	trimethyl	Supelco (Bellefonte, USA)
PS-162	45–55% methylphenyl, 45–55% diphenyl	trimethyl	Gelest (ABCR, Karlsruhe, Germany)
OV-1701-OH	88% dimethyl, 5% phenyl, 7% cyanopropyl	hydroxy	Fluka (Buchs, Switzerland)
OV-225	25% cyanopropyl, 25% phenyl, 50% methyl	trimethyl	Analabs, Inc.
OV-225-OH	25% cyanopropyl, 25% phenyl, 50% methyl	hydroxy	Ohio Valley (Marietta, USA)
Silar 5CP	50% cyanopropyl, 50% phenyl	not given	Serva (Heidelberg, Germany)
XE-60	25% cyanoethyl, 75% methyl	not given	Analabs, Inc.
CP-Sil-88	100% dicyanopropyl	acetyl	Chrompack
OV-275	100% dicyanoethyl	acetyl	Ohio Valley
Hexamethylcyclotrisiloxane		cyclic	Aldrich (Milwaukee, USA)
Octaphenylcyclotetrasiloxane		cyclic	Aldrich

relaxation agent [21]. Processing was performed on a Silicon Graphics workstation using XWINNMR (Bruker), including linear prediction backwards of the first 24 datapoints to eliminate the glass peak and to obtain a flat baseline for accurate integration. All ^{29}Si chemical shifts are reported relative to internal tetramethylsilane.

2.3. Mass spectroscopy

Mass spectrometric analysis was performed on a PE Sciex API 365 triple quadrupole mass spectrometer (Perkin Elmer Sciex Instruments, Thornhill, Canada) equipped with an Electrospray Ionization Interface. Polymer OV-25 was dissolved in methanol/chloroform (1:10, HPLC grade) with 10 mM sodium acetate, and Silar 5CP was dissolved in methanol/carbon tetrachloride (1:10) with 20 mM ammonium acetate. Samples were introduced with a syringe pump at a flow rate of 5 $\mu\text{l}/\text{min}$. The interface was applied in the positive ion mode with an ionspray voltage of 5500 V. Every 5 s, a mass spectrum with a range of 30 to 3000 u was recorded. The identified compounds in the polymers were quantified by peak heights of the respective ions.

2.4. Thermal treatment of the stationary phase SOP-50

Thermal treatment of SOP-50 was performed under usual chromatographic conditions inside a wall coated open tubular fused-silica capillary column under a stream of hydrogen. The polymer was statically coated to dimethyltetraphenyldisilazane deactivated fused-silica capillaries as described previously [30]. Thermal treatment of the stationary phase was performed under a flow of hydrogen (purity $\geq 99.999\%$) on a Carlo Erba SFE 3060 gas chromatograph (Carlo Erba, Fison, Rodano, Italy). After conditioning at 380°C for three h, and 400°C and 410°C each for one h, capillary columns were heated at the maximum allowable operating temperature of 420°C for 1 h. Capillary columns were then rinsed with 5 ml dichloromethane/pentane (1:1). The soluble parts of the stationary phase eluting from three different capillary columns were collected and combined. After drying under a stream of nitrogen

the polymer was dissolved in deuterated chloroform and measured by ^{29}Si NMR spectroscopy.

2.5. Determination of microstructure parameters

The distribution of the monomer units i and j along the chain is described by the run number concept and the linkage probability [10,13]. The run number R is the average number of monomer sequences occurring in a polymer per 100 monomer units. The run number for random polymers is $R_{\text{random}} = A_i \cdot A_j / 50$. A_i and A_j are the mole fractions of the monomer units i and j .

$$R_{\text{Experimental}} = (\text{ratio } iji) \cdot A_i = (\text{ratio } jij) \cdot A_j$$

The ratio jij is derived from the signal intensity ratio of the triads, $\text{ratio } jij = 2 \cdot [jij / (jij + jii + iii)]^{0.5}$.

In the first-order Markovian model, the probability of monomer addition depends upon the event immediately preceding [13]. The linkage probability P_{ij} gives the probability of addition of the monomer i to a j chain ending.

$$P_{ii} = (A_i - R_i/2)/A_i$$

$$P_{ij} = R_i/2 \cdot A_i$$

$$P_{jj} = (A_j - R_j/2)/A_j$$

$$P_{ji} = R_j/2 \cdot A_j$$

where $P_{ii} + P_{ij} = 1$ and $P_{jj} + P_{ji} = 1$

for random distribution: $P_{ii} = P_{ij} = P_{jj} = P_{ji} = 0.5$

for alternating polymer: $P_{ii} = P_{jj} = 0$ and $P_{ij} = P_{ji} = 1$

for blocky co-polymer: $P_{ii} = P_{jj} = 1$ and $P_{ij} = P_{ji} = 0$

3. Results and discussion

3.1. ^1H NMR spectroscopy

The methyl, phenyl, cyanopropyl, and cyanoethyl content of the stationary phases were calculated from areas obtained from ^1H NMR spectra. The substituents attached to the silicon atoms are expressed as percentages in Table 2.

Table 2
Chemical composition of the stationary phases calculated from ^1H NMR data

Polymer	Methyl (%)	Phenyl (%)	Cyanopropyl (%)
OV-1	100	0	0
SE-52	93.1	6.9	0
OV-17	57.7	42.3	0
SOP-50	50.4	49.6	0
OV-25	31.8	68.2	0
PS-162	30.5	69.5	0
OV-1701-OH	86.8	6.2	7.0
OV-225	52.8	21.9	25.3
OV-225-OH	57.2	20.2	22.6
Silar 5CP	8.1 ^a	43.4	48.5
CP-Sil-88	0	0	100
OV-275	0	0	100 ^b

^a Due to the trimethylsilyl end group, resulting in an average molecular weight of 6700.

^b 40% Cyanoethyl, 60% Cyanopropyl substitution, 50:50 is reported in the literature [1].

The information obtained from ^1H NMR is limited, because it is not possible to clarify whether silicon atoms are symmetrically or asymmetrically substituted with the ligands, or whether cyclic by-products are present. Furthermore no details of microstructure can be derived from this method.

Table 3
Chemical composition of methylphenyl-polysiloxanes derived from ^{29}Si NMR spectra

Polymer	Dimethyl (%)	Methylphenyl (%)	Diphenyl (%)
OV-1	100	0	0
SE-52	94.1	0	5.9
OV-17	0	100	0
SOP-50	48.6	0	51.4
OV-25	0	45.6	54.4
PS-162	0	47.9	52.1

3.2. ^{29}Si NMR spectroscopy

Peak assignment was performed with pure polymers like OV-1, OV-17, and CP-Sil-88 and according to literature [14,21,34]. Chemical shifts of methyl, phenyl, and cyanoalkyl substituted polysiloxanes are summarized in Fig. 1.

No signals at -66 or -79 ppm for $-\text{Si}(\text{O})_3$ are detected in any of the polymers, demonstrating that none of the stationary phases investigated are branched [11].

3.2.1. Methylphenyl-polysiloxanes

The percentages of silicon atoms of methylphenyl-polysiloxanes substituted with different ligands are given in Table 3.

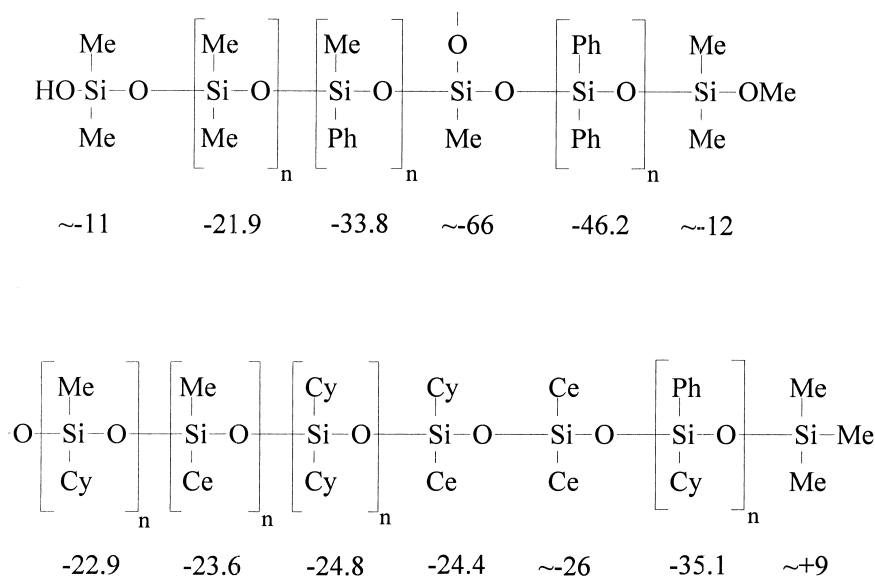


Fig. 1. Chemical shifts of methyl (=Me), phenyl (=Ph), cyanopropyl (=Cy), and cyanoethyl (=Ce) substituted polysiloxanes.

OV-1: Only one peak at -21.9 ppm is present in the spectrum (not shown) which correlates to dimethyl substituted silicon atoms. No peaks for cyclic by-products are present. The end group $-\text{O}-\text{Si}(\text{CH}_3)_3$ around $+8$ ppm is not visible indicating a high average chain length which is in agreement with published data, where an average molecular weight of 300 000–400 000 has been reported [35].

SE-52: The NMR spectrum of SE-52 clearly shows a dimethyl, diphenyl-polysiloxane. Dimethyl groups ranging from -20.0 to -21.9 ppm and diphenyl groups around -48.4 ppm are found. No methylphenyl groups are visible at -33.8 ppm. The chemical shift of -48.4 ppm reflects an isolated diphenyl group which is surrounded by dimethyl groups (see also Fig. 3, peak No 2). Neither cyclic impurities nor the end group are traceable.

Microstructure parameters: Since the run number

for the diphenyl unit (11.8) is very close to the run number of a random distribution (11.1) this indicates that the diphenyl groups are randomly distributed along the polysiloxane backbone.

OV-17: The spectrum of OV-17 shows only one peak corresponding to a 100% methylphenyl-polysiloxane. No cyclic impurities were detected. The trimethylsilyl end group is found at $+8.8$ ppm. An average chain length of 14.4 can be calculated from the signal area ratio of end to chain groups, resulting in an average molecular weight of 2200. This value is distinctly lower than the molecular weight of 4000 given in the literature [35].

OV-25: The ^{29}Si NMR spectrum of OV-25 is given in Fig. 2. Signals for methylphenyl ($=\text{O}$, around -33 ppm) and diphenyl ($=\text{P}$, around -46 ppm) substituted silicon atoms are present. Due to the neighboring effect, each group is split into triads.

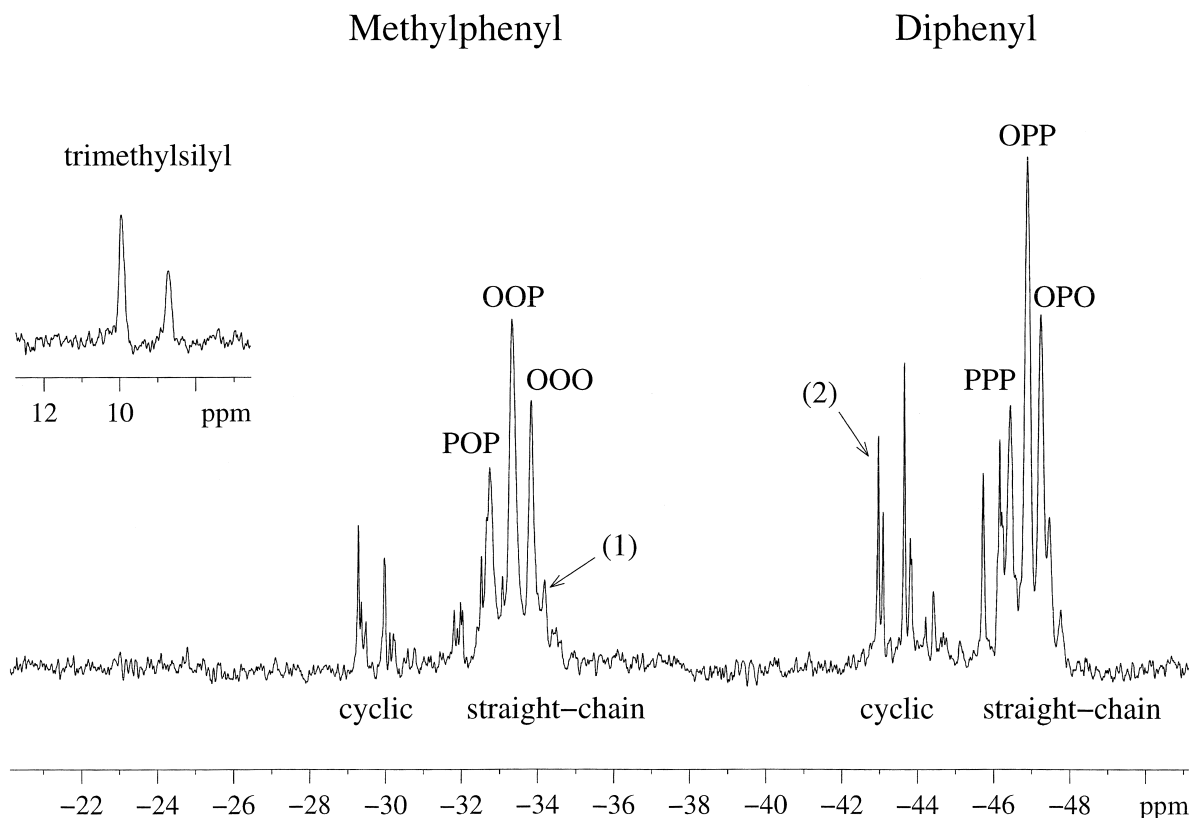


Fig. 2. ^{29}Si NMR spectrum of the methylphenyl ($=\text{O}$), diphenyl ($=\text{P}$) polysiloxane OV-25. (1) at -33.8 is for OOOOO like OV-17, (2) at -42.9 ppm indicates octaphenylcyclotetrasiloxane.

The exact peak assignment of the triads is given in Fig. 2.

Microstructure: The run number for a random distribution should be 49.6. The run number for the methylphenyl group R_O is 53.0 and for the diphenyl group R_P is 64.5, resulting in linkage probabilities of $P_{OO}=0.42$, $P_{OP}=0.58$, $P_{PP}=0.41$, and $P_{PO}=0.58$. As the linkage probabilities P_{OP} and P_{PO} are higher than for a randomized polymer ($P_{ij}=0.5$), it can be concluded that OV-25 is slightly alternating.

Additional, signals ranging from -29.0 to -30.0 ppm and from -42.8 to -43.8 ppm reflecting cyclic polysiloxanes can be detected. For example, the cyclic tetramer octaphenylcyclotetrasiloxane gives rise to a singlet at -42.9 ppm, this peak is marked with (2) in Fig. 2. No cyclic trimers are detectable whose methylphenyl groups are expected to have a chemical shift more downfield (around -20 ppm), because trimeric rings are more strained than tetrameric rings.

It is possible that higher oligomers are present, but these compounds are not distinguishable from linear chains. Cyclic impurities have already been identified in OV-17 and OV-25 by size exclusion chromatography [4].

In order to investigate these cyclic impurities, the polymer was analyzed by high-temperature GC. More than 10 peaks eluted between 220°C and 330°C from an SE-52 high-temperature capillary column (chromatogram not shown). Further investigations were done with electrospray-MS. Ion formation was supported with sodium acetate resulting in sodium adduct ions of the oligomers. All five possible tetramers (m/z 567.0, 629.0, 690.9, 752.9, and 815.9) and all six possible pentamers (m/z 702.9, 764.9, 827.9, 887.9, 949.9, and 1011.9) were identified in the mass spectrum, as were some hexamers

(m/z 839.9, 901.9, and 963.9). No trimers were seen. According to these data 75% of the cyclic oligomers are tetramers, around 20% pentamers and 5% hexamers.

The trimethylsilyl end group is visible in the ^{29}Si NMR spectrum around $+9$ ppm with a calculated average chain length of 25. The average molecular weight of the linear polymer is 4000 and lies between the two values (2100 and 10 000) reported in the literature [4,35].

PS-162: The spectrum of PS-162 is similar to that of OV-25, except that the content of cyclic impurities is higher (over 50%).

3.2.2. Cyanoalkyl substituted polysiloxanes

In contrast to a previous report [21], it is possible to distinguish between methyl and cyanopropyl substitution from the chemical shifts because a cyanopropyl group exhibits a more upfield shift than a methyl group. A dimethyl group (OV-1) gives rise to a signal at -21.9 ppm, a methylcyanopropyl group (OV-225) at -22.9 ppm, and a dicyanopropyl group (CP-Sil-88) at -24.8 ppm (see Fig. 1). The cyanoethyl group is reflected by a further upfield shift, therefore, the methylcyanoethyl group shows a signal at -23.6 ppm (XE-60) and the dicyanoethyl group at approximately -26 ppm.

By accurate peak assignment in ^{29}Si NMR spectra it is possible to derive the chemical composition (see Table 4) and other microstructure parameter of cyanoalkyl substituted polysiloxanes.

OV-1701-OH: The spectrum (not shown) is very similar to that shown by Scholten [21,36]. There are two groups of signals, one around -21 ppm corresponding to dimethyl groups, and a second ranging from -36.9 to -38.0 ppm corresponding to cyanopropylphenyl substituted silicon atoms.

Table 4

Chemical composition of cyanopropyl and cyanoethyl substituted polysiloxanes calculated from ^{29}Si NMR data

Polymer	Methyl (%)	Phenyl (%)	Cyanopropyl (%)	Cyanoethyl (%)
OV-1701-OH	88.8	5.6	5.6	0
OV-225	50	26.9	23.1	0
OV-225-OH	58.2	22.4	19.4	0
Silar 5CP	0	50.0	50.0	0
XE-60	77.5	0	0	22.5
CP-Sil-88	0	0	100	0
OV-275	0	0	71.0	29.0

The signal of the silanol end group is at -11 ppm. The signal area ratio of end to chain groups is 1:65, reflecting an average chain length of 130 siloxane units and an average molecular weight of 12 000. This mass is similar to the molecular weight of 17 400, which has been reported by Scholten [21].

Microstructure: The run number is very similar to the run number of a randomized polymer indicating that the methyl and cyanopropylphenyl groups are randomly distributed along the polysiloxane chain.

Compared to the NMR spectrum described by Scholten [21,36] there is a small but significant additional signal at -45.6 ppm reflecting diphenyl substituted silicon atoms. In view of its chemical shift an isolated diphenyl group can be excluded (-48.3 ppm similar to SE-52). This probably reflects blocky diphenyl groups or an unknown cyclic tetrameric impurity, where a chemical shift around -43 to -46 ppm would be expected.

OV-225: Only two peaks were observed, which are hardly split. One peak at -22.9 ppm arises from methylcyanopropyl-polysiloxane and the second peak at -33.88 ppm from methylphenyl-polysiloxane (analog to OV-17 at -33.84 ppm). Therefore, OV-225 is a blocky co-polymer.

OV-225-OH: The OV-225-OH spectrum is similar to that of OV-225, apart from one additional signal around -21 ppm reflecting dimethyl substituted silicon atoms. Because of this, OV-225-OH has a higher methyl content than OV-225. In conclusion, OV-225-OH consists of three monomer units, i.e., dimethyl, methylcyanopropyl, and methylphenyl siloxy groups.

Silar 5CP: Cyanopropylphenyl substituted silicon atoms give rise to signals around -35.4 ppm. Further compounds (50%) reflected by signals around -32.2 to -32.9 ppm were assumed to be cyclic oligomers due to their chemical shifts which was unambiguously confirmed by electrospray-MS. Ion formation was supported with ammonium acetate resulting in ammonium adduct ions at m/z 773.9, 963.9, and 1152.9. These ions corresponded to the cyclic tetramer (96% of the cyclic impurities), and to the cyclic pentamer and hexamer with distinctly smaller abundance ($<4\%$).

The signal area of the trimethylsilyl end group (at $+10.3$ ppm) in the NMR spectrum indicates an average chain length of 17 and an average molecular

weight of 3300. This is only half of the value determined by ^1H NMR, because cyclic impurities are excluded.

XE-60: The spectrum contains triads for dimethyl (around -20 ppm) and methylcyanoethyl (around -24 ppm) groups. The cyanoethyl substitution is calculated with 22.5%, what is in good agreement with the specification (25% cyanoethyl substitution) given by the manufacturer and the literature [9]. The microstructure indicates a randomized polymer.

CP-Sil-88: The dicyanopropyl group gives rise to a signal at -24.8 ppm. An unknown impurity at -22.3 ppm was assumed to be the cyclic tetramer due to its chemical shift. Neither the trimethylsilyl end group at around $+8$ ppm nor the acetyl end group reported in the literature [1] was visible.

OV-275: The polymer consists of three monomer units, that is, dicyanopropyl, cyanopropylcyanoethyl, and dicyanoethyl, reflected by peaks at -23.4 ppm, -24.2 ppm, and around -25.5 ppm, respectively. Neither the trimethylsilyl nor the acetyl end group could be identified.

3.3. Microstructure of SOP-50

The ^{29}Si NMR spectrum is given in Fig. 3. The silicon atoms are substituted either with two methyl or two phenyl groups. Peaks for dimethyl substituted silicon atoms (=M) range from -18.7 to -21.9 ppm, peaks for diphenyl substituted silicon atoms (=P) from -46.4 to -48.3 ppm. The end group $-\text{Si}(\text{CH}_3)_2-\text{O}-\text{CH}_3$ is not visible at -12 ppm due to low concentrations indicating a high molecular weight.

The microstructure parameters of SOP-50 were determined according to Engelhardt et al. [10] and are summarized in Table 5. The signals for dimethyl substituted silicon atoms are divided into 3 groups corresponding to the ligands of the neighboring silicon atoms, PMP, PMM, and MMM (see Fig. 3). These three M-centered triads are further divided into 3 signals according to the neighbors of the triads, resulting in pentads. For example, the pentad MMMMM at -21.9 ppm, the only signal of OV-1, is marked with (1) in Fig. 3.

The spectrum of an exactly alternating polymer should exhibit two sole peaks at -19.2 ppm for MPMPM and -48.1 ppm for PMPMP (peaks mark-

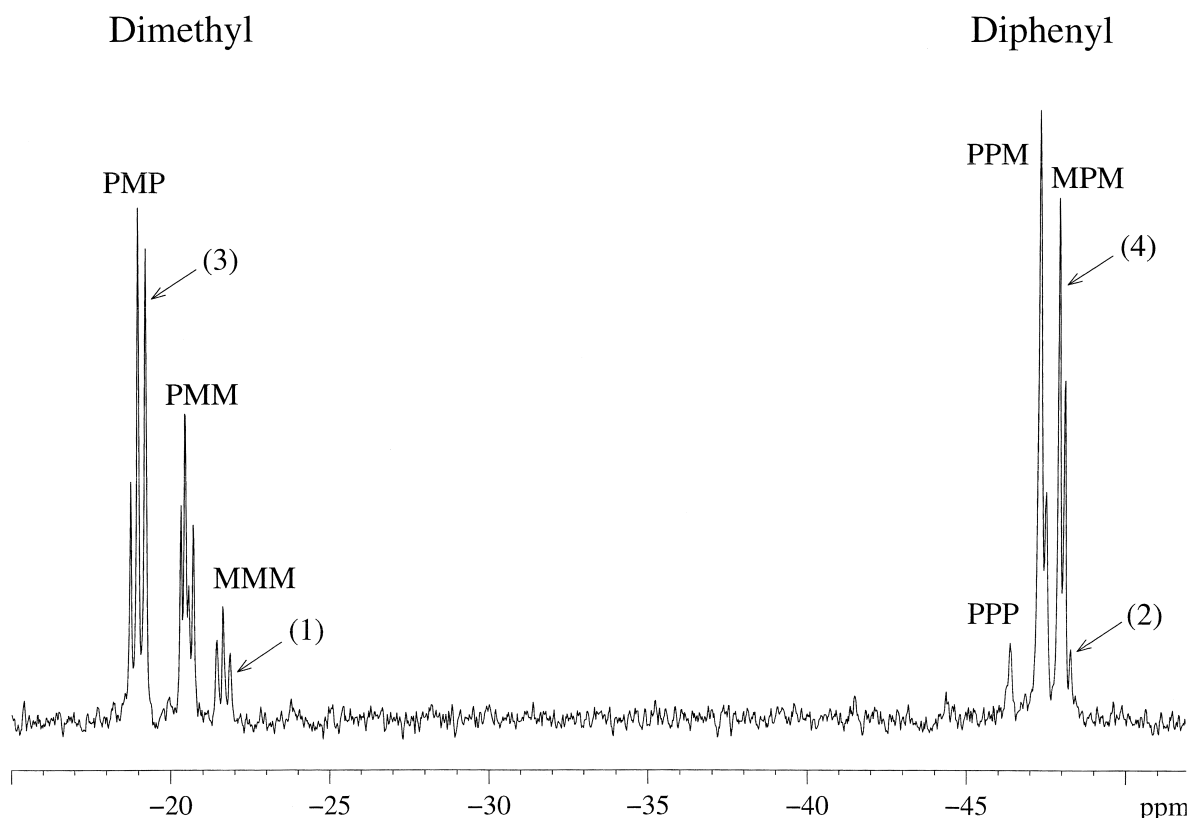


Fig. 3. ^{29}Si NMR spectrum of the dimethyl (=M), diphenyl (=P) polysiloxane SOP-50 showing triad assignment. (1) indicates the pentad MMMMM at -21.9 ppm (like OV-1), (2) at -48.4 ppm is for MMPMM, an isolated diphenyl group like in SE-52. (3) and (4) are for the exactly alternating pentads MPMPM at -19.2 ppm and PMPMP at -48.1 ppm.

ed with (3) and (4) in Fig. 3). From the complex structure of the spectrum it can be concluded that the polymer is not exactly alternating as proposed by

Table 5
Microstructure parameter of SOP-50

	SOP-50	After thermal treatment	For a random polymer	For an alternating polymer
$^a A_M$	48.6	50.0		
$^a A_P$	51.4	50.0		
R_M	71.5	70.2	50	100
R_P	68.3	65.4	50	100
P_{MM}	0.265	0.298	0.5	0
P_{MP}	0.735	0.702	0.5	1
P_{PP}	0.337	0.346	0.5	0
P_{PM}	0.663	0.654	0.5	1

^a Monomer units: M=dimethylsiloxy, P=diphenylsiloxy.

Blum [23]. Nevertheless, a clear tendency towards an alternating polymer can be derived from the microstructure parameters. The linkage probabilities P_{MP} and P_{PM} are much higher than P_{MM} and P_{PP} and the run number lies between a randomized and an alternating polymer. For comparison, microstructure parameters of an exactly alternating and a randomized polymer are given in Table 5. This indicates that SOP-50 has a sequence which is more randomized than alternating [13].

3.4. Isomerization after thermal treatment

Thermal stability of polymers is usually investigated by thermogravimetric analysis. Polysiloxanes are generally thermally treated in a crucible, either

under a stream of inert gas or under vacuum [2,3,15,19]. Here, the polymer SOP-50 was used as a stationary phase in high-temperature GC and was heated to 420°C inside a capillary column. The mass to surface ratio of the polymer was distinctly higher than in thermal gravimetric analysis, since the polymer was only a thin film on the wall of the capillary column. A second difference to thermogravimetric analysis was the difference in surface. The deactivated fused-silica surface was possibly more inert than the surface of a metal crucible. A third difference is the fact that only the soluble part of the stationary phase was rinsed with solvent and analyzed by NMR spectroscopy. No information about the immobilized part of the polymer was obtained, because it was not possible to investigate the immobilized part of the stationary phase inside a capillary column by means of this technique.

Microstructure parameters are given in Table 5. No significant changes are observed. The run number decreases slightly, indicating that the polymer is only redistributed to a limited extent. Redistribution reactions lead to a more randomized sequence. Nevertheless, the randomization reactions are slow.

Some conclusions can be derived from these data:

(i) No cross linking occurs in the soluble part of the stationary phase, because no peaks for $-\text{Si}(\text{O})_3$ (at -66 or -79 ppm) or $-\text{O}-\text{Si}(\text{CH}_3)_3$ (at $+7$ ppm) were observed. Therefore, the exchange of Si–C and Si–O bonds is slow at temperatures applied in high-temperature GC. This is in good agreement with Corriu et al. [19], who heated a dimethyl polysilphenylene-siloxane in sealed tubes to 360°C for 400 min.

(ii) No methylphenyl silyl groups are generated during thermal treatment. Therefore, no rearrangements of dimethyl and diphenyl to methylphenyl substituted silicon atoms occurred. This is obvious as the binding between silicon and carbon is very strong.

(iii) The reaction of intramolecular and intermolecular Si–O/Si–O exchanges is slow, otherwise the polymer would be completely randomized after thermal treatment. Intramolecular Si–O/Si–O exchange is the commonly accepted mechanism for the thermal degradation of polysiloxanes resulting in a decrease of molecular weight [37]. Corriu et al. assumed that intermolecular Si–O/Si–O exchanges

often occur unnoticed in polysiloxanes, although the molecular weight does not decrease [19]. Both exchange reactions should change an alternating to a randomized polymer.

Exactly alternating polymers should be useful for high-temperature applications, because an alternating structure stabilizes the polysiloxane backbone against nucleophilic attack. This is due to the fact that thermal rearrangement reactions are slow at temperatures applied in high-temperature GC.

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References

- [1] H. Heckers, K. Dittmar, F.W. Melcher, H.O. Kalinowski, *J. Chromatogr.* 135 (1977) 93.
- [2] N. Grassie, I.G. Macfarlane, *Eur. Polym. J.* 14 (1978) 875.
- [3] N. Grassie, I.G. Macfarlane, K.F. Francey, *Eur. Polym. J.* 15 (1979) 415.
- [4] L.B. Itsikson, V.G. Berezkin, J.K. Haken, *J. Chromatogr.* 334 (1985) 1.
- [5] A. Gracia-Raso, P. Ballester, R. Bergueiro, I. Martínez, J. Sanz, M.L. Jimeno, *J. Chromatogr.* 402 (1987) 323.
- [6] B. Boutevin, B. Youssef, *Macromolecules* 24 (1991) 629.
- [7] P.R. Dvornic, R.W. Lenz, *Macromolecules* 27 (1994) 5833, and references cited therein.
- [8] T.J. Stark, P.A. Larson, R.D. Dandeneau, *J. Chromatogr.* 279 (1983) 31.
- [9] S. Fujimoto, H. Ohtani, S. Tsuge, *Fresenius Z. Anal. Chem.* 331 (1988) 342.
- [10] G. Engelhardt, H. Jancke, *Polym. Bull.* 5 (1981) 577.
- [11] G. Engelhardt, H. Jancke, E. Lippmaa, S. Samoson, *J. Organomet. Chem.* 210 (1981) 295.
- [12] P.J. Andolino-Brandt, R. Subramanian, P.M. Sormani, T.C. Ward, J.E. McGrath, *Polym. Prepr.* 26 (1985) 213.
- [13] I.R. Herbert, A.D.H. Clague, *Macromolecules* 22 (1989) 3267.
- [14] G. Wu, M. Hetem, C.A. Cramers, J.A. Rijks, *J. High Resolut. Chromatogr.* 13 (1990) 811.

- [15] V. Belot, R.J.P. Corriu, D. Leclercq, P.H. Mutin, A. Vioux, J. Polym. Sci. A, Polym. Chem. 30 (1992) 613.
- [16] H. Jancke, Fresenius J. Anal. Chem. 342 (1992) 846.
- [17] J.R. Brewer, K. Tsuchihara, R. Morita, J.R. Jones, J.P. Bloxside, S. Kagoa, T. Otsuki, S. Fujishige, Polym. 35 (1994) 5109.
- [18] J.R. Brewer, K. Tsuchihara, R. Morita, J.R. Jones, J.P. Bloxside, S. Fujishige, Polym. 35 (1994) 5118.
- [19] R. Corriu, D. Leclercq, P.H. Mutin, H. Samson, A. Vioux, J. Polym. Sci. 32 (1994) 187.
- [20] R.J.P. Corriu, D. Leclercq, P.H. Mutin, H. Samson, A. Vioux, J. Organomet. Chem. 466 (1994) 43.
- [21] A.B. Scholten, J.W. deHaan, H.G. Janssen, L.J.M. vandeVen, C.A. Cramers, J. High Resolut. Chromatogr. 20 (1997) 17.
- [22] A. Benouargha, B. Boutevin, G. Caporiccio, E. Essassi, F. Guida-Pietrasanta, A. Ratsimihety, Eur. Polym. J. 33 (1997) 1117.
- [23] W. Blum, R. Aichholz, J. Microcol. Sep. 5 (1993) 297.
- [24] V. Spitzer, R. Aichholz, J. High Resolut. Chromatogr. 19 (1996) 497.
- [25] R. Aichholz, E. Lorbeer, J. Microcol. Sep. 8 (1996) 553.
- [26] R. Aichholz, V. Spitzer, E. Lorbeer, J. Chromatogr. A 787 (1997) 181.
- [27] V. Spitzer, W. Tomberg, R. Hartmann, R. Aichholz, Lipids 32 (1997) 1189.
- [28] R. Aichholz, V. Spitzer, E. Lorbeer, J. High Resolut. Chromatogr. 21 (1998) 152.
- [29] R. Aichholz, E. Lorbeer, J. High Resolut. Chromatogr. 21 (1998) 363.
- [30] B.X. Mayer, E. Lorbeer, J. High Resolut. Chromatogr. 18 (1995) 504.
- [31] B.X. Mayer, E. Lorbeer, J. Chromatogr. A 758 (1997) 235.
- [32] B.X. Mayer, C. Reiter, T.L. Bereuter, J. Chromatogr. B 692 (1997) 1.
- [33] B. Mayer, Dissertation, University of Vienna, 1997.
- [34] N. Satyanarayana, H. Alper, Macromolecules 28 (1995) 281.
- [35] J.K. Haken, J. Chromatogr. 300 (1984) 1.
- [36] A.B. Scholten, personal communication (1997).
- [37] T.H. Thomas, T.C. Kendrick, J. Polym. Sci. A2 (1969) 537.