Characterization of stationary phases for gas chromatography by ^{29}Si NMR spectroscopy
II. Silphenylene–siloxane copolymers

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Abstract

A series of tetramethyl-*p*-silphenylene–siloxane copolymers with dimethyl, 1*H*,1*H*,2*H*,2*H*-perfluorodecylmethyl and diphenyl siloxy groups was prepared. ^{1}H and ^{29}Si nuclear magnetic resonance spectroscopy showed that the chosen reaction conditions provided polymers with diphenyl content up to 85%. The theoretical content of the monomer units correlated well with the measured content. Signal assignments of the copolymers and their corresponding chemical shifts are summarized. Information about alternating, randomized or block sequences was obtained by ^{29}Si nuclear magnetic resonance spectroscopy. Limitations of the method for the determination of microstructure parameters are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polysiloxanes are currently the materials most predominantly used as stationary phases in gas chromatography (GC). Their favorable properties are high-temperature stability in combination with low-temperature flexibility and resistance to oxygen degradation. For further improvement of the thermal stability, phenylene or diphenylene ether groups are inserted into the polysiloxane backbone, leading to silphenylene (also called silarylene) siloxane copoly-mers. The general structure of a tetramethyl-*p*-silphenylene–siloxane copolymer with different siloxy groups and corresponding abbreviations is given in Fig. 1.
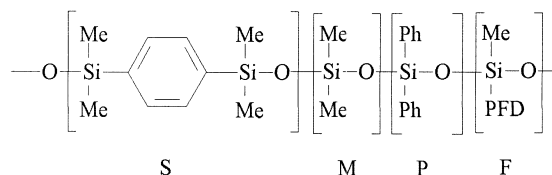

Fig. 1. The structure of silphenylene–siloxane copolymers. Abbreviations: S, tetramethyl-*p*-silphenylene; M, dimethylsiloxy; P, diphenylsiloxy; F, 1*H*,1*H*,2*H*,2*H*-perfluorodecyl (=PFD) methyl-siloxy.

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Silphenylene-modified polysiloxanes offer several advantages over conventional polysiloxane stationary phases. The silphenylene unit in the polysiloxane backbone reduces bleeding by reducing the flexibility of the polysiloxane backbone. Consequently, the main degradation pathway, i.e. the formation of small cyclic oligomers from straight chains, is suppressed. Furthermore, the thermal stability is improved due to the stronger Si–C bonds [1–3]. Reduced bleeding of the stationary phase leads to improved detection limits with detectors such as the electron capture detector, the nitrogen–phosphorus detector, and mass spectrometry, to reduced contamination of the detector, to a higher upper temperature limit, and to an extended column lifetime. Silphenylene–siloxane copolymers have been utilized as stationary phases in glass, fused-silica, and metal capillaries [4–18].

Nowadays, fused-silica capillary columns coated with numerous different silphenylene–siloxane copolymers are commercially available for GC. Almost every GC supplier offers capillary columns coated with stationary phases based on the silphenylene technique as low-bleeding or high-temperature alternatives of popular polysiloxanes, e.g., BPX-70 (SGE International, Ringwood, Australia), DB-1ms (J&W, Folsom, USA), 007-5MS (Quadrex, Woodbridge, USA), HP-35ms (Agilent Technologies, Waldbronn, Germany), CP-Sil 24 CB ''Low-Bleed''/MS (Chrompack, Middelburg, The Netherlands), MDN-12 (Supelco, Bellefonte, USA) and BGB-Silaren (BGB Analytik AG, Schlossböckelheim, Germany). Companies still introduce new capillaries coated with silphenylene polymers, which are equivalent to traditional polysiloxanes [19] and seem to replace them entirely. In contrast to conventional stationary phases, silphenylene–siloxane copolymers are hardly available in bulk. Only a few reports have been published on polymer synthesis, column deactivation and coating procedures, as column technology is a company secret and protected by patents. Most column suppliers do not give any specification of the polymers which are used for column preparation.

In the first part of this work, [29]Si nuclear magnetic resonance (NMR) spectroscopy was applied for the characterization of numerous polysiloxanes used as stationary phases in GC [20]. In this part, we describe the preparation and analysis of sil-phenylene–siloxane copolymers with dimethyl, perfluorodecylmethyl, and diphenyl siloxy groups. ^{1}H and ^{29}Si NMR spectroscopy was used to obtain information about the chemical composition and microstructure parameters. Limitations of the method in structure elucidation are discussed.

2. Experimental

2.1. Preparation of silphenylene–siloxane copolymers

The monomers bis(dimethylamino)dimethylsilane (1), bis(dimethylamino)diphenylsilane (2), diphenyl-silanediol (3), and 1,4-bis(hydroxydimethyl-silyl)benzene (5) were purchased from ABCR (Karlsruhe, Germany). Bis(dimethylamino)-1H,1H,2H,2H-perfluorodecyl (=PFD) methylsilane (4) was prepared from the corresponding dichloro-silane as described in Ref. [21].

Pike's reaction of diaminosilanes and silandiols was used to prepare high-molecular-mass polymers by a step-growth polymerization reaction [22]. A generalized scheme of the condensation reaction is given in Fig. 2. The reaction conditions reported in the literature [15] were modified slightly. The monomers 1–5 were mixed in different ratios (see Tables 1 and 2) and dissolved in toluene in gas-tight screwed vials. The condensation reaction was performed at 110°C for 48 h. Chain elongation was terminated by adding an excess of 2. After removal of the solvent at 110°C the polymer was heated in 10° steps from 140 to 200°C, maintaining the temperature at every level for 15 min. For purification, the polymer was dissolved in toluene at 100°C and precipitated with five volumes of methanol. This procedure was repeated five times. Finally, solvent residues were removed under reduced pressure at 100°C.

2.2. NMR spectroscopy

All polymers were dissolved in deuterated chloroform at concentrations of around 3–7.5% (w/w). NMR spectra were recorded at 25°C with a Bruker DRX 400 WB spectrometer (Bruker Analytische Messtechnik, Ettlingen, Germany) using a 5-mm
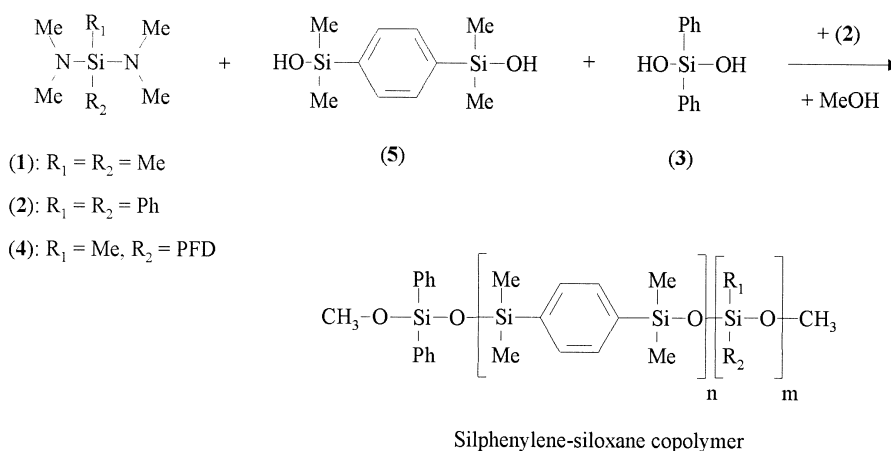
Fig. 2. Generalized scheme of the condensation reaction of bis(dimethylamino)silanes **1**, **2**, and **4** with 1,4-bis(hydroxydimethyl-silyl)benzene (**5**) to form methoxy-terminated silphenylene–siloxane copolymers.

Table 1
The amount of monomer used for the preparation of a series of silphenylene–diphenylsiloxane copolymers and the silphenylene content measured by ^{1}H and ^{29}Si NMR spectroscopy. The run numbers calculated from the P-centered triads are compared to R_{random} for a random sequence

Polymer	Monomers used for synthesis (mol%)			Silphenylene content measured (mol%)		Run number	
	2	**3**	**5**	^{1}H NMR	^{29}Si NMR	R_{random}	R
SP-50	50.0	0.0	50.0	49.3	51.4	50.0	89.9
SP-43	50.0	7.5	42.5	44.6	45.3	49.6	95.2
SP-25	50.0	25.0	25.0	25.5	25.7	38.2	38.2
SP-20	50.0	30.0	20.0	24.8	24.4	36.9	51.1
SP-10	50.0	40.0	10.0	14.6	14.5	24.8	28.1
SP-5	50.0	45.0	5.0	14.7	12.9	22.5	34.4

broadband inverse probe operating at 400.13 and 79.49 MHz for ^{1}H and ^{29}Si NMR spectroscopy, respectively. Typical parameters for ^{29}Si NMR spectroscopy included a spectral width of 16 kHz, 32 k datapoints, and 3000 to 30 000 scans to obtain sufficient signal-to-noise ratios. Proton composite pulse decoupling was applied only during acquisition to avoid distortions of the signal intensities due to

unwanted NOE influences during the relaxation period. Small amounts of chromium acetylacetonate were added as relaxation agent. 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 thereby obtaining a flat baseline for accurate integration. All [29]Si chemical shifts are

Table 2
Expected and measured compositions of a silphenylene–dimethyldiphenylsiloxane copolymer

Monomer unit:	**1**	**2**	**3**	**5**
% used for synthesis:	20.0	30.0	45.0	5.0
Content measured by	Dimethylsiloxy	Diphenylsiloxy		Silphenylene
^{1}H NMR	20.9	70.6		8.5
^{29}Si NMR	22.0	70.6		7.4

reported relative to internal tetramethylsilane. External calibration was used in cases where signals around 0 ppm were expected.

2.3. Determination of microstructure parameters

The copolymer microstructure can be expressed in terms of the run number concept, where the run number R describes the average number of monomer sequences in 100 repeating units of a copolymer chain [20,23,24]. R is related to the ^{29}Si NMR signal intensities:

$$R = A_i \cdot ratio \ jij = A_j \cdot ratio \ iji$$

where A_i and A_j refer to the mole fractions of monomer units i and j. The *ratio jij* is derived from the signal intensity areas of the i-centered triads in the ^{29}Si NMR spectrum:

$$ratio \ jij = 2 \cdot [area_{jij}/(area_{jij} + area_{iij} + area_{iii})]^{0.5}$$

where $area_{jij}$, $area_{iij}$, and $area_{iii}$ are the integral areas of the indicated i-centered triads. The run number for a randomized polymer is:

$$R_{random} = A_i \cdot A_j / 50$$

3. Results

A series of tetramethyl-p-silphenylene–siloxane copolymers with variable dimethyl, PFD methyl, and diphenyl content was synthesized and analyzed by

^{1}H and ^{29}Si NMR spectroscopy. The ^{29}Si NMR signal assignments of the different sequences are based on the literature, where ^{29}Si NMR analyses of silphenylene–dimethylsiloxane copolymers [24–27] and a poly(tetramethyl-p-silphenylene–siloxane) homopolymer have been reported [28]. The chemical shifts are summarized in Fig. 3.

3.1. Silphenylene–dimethylsiloxane copolymers

The copolymer SM-50 was prepared by reaction of equimolar amounts of **1** and **5**. The ^{29}Si NMR spectrum (not shown) consists of two singlets, corresponding to the methylsiloxy and silphenylene unit at −19.6 and −2.5 ppm, respectively. Additionally, the polymer contains a short sequence of a dimethyl-silicone at −21.9 ppm with a content of 4.3%. The silphenylene content measured by ^{1}H and ^{29}Si NMR spectroscopy is 48.5 and 45.3%, respectively, consistent with the theoretical values. The chemical shifts show that the two singlets in the spectrum at −19.6 and −2.5 ppm correspond to the sequences SMS and MSM. The run number $R = 97.5$ indicates a truly alternating polymer. Different synthetic approaches resulted in similar alternating copolymers previously characterized by ^{29}Si NMR spectroscopy [25–27].

3.2. Silphenylene-1H,1H,2H,2H-perfluorodecyl methylsiloxane copolymers
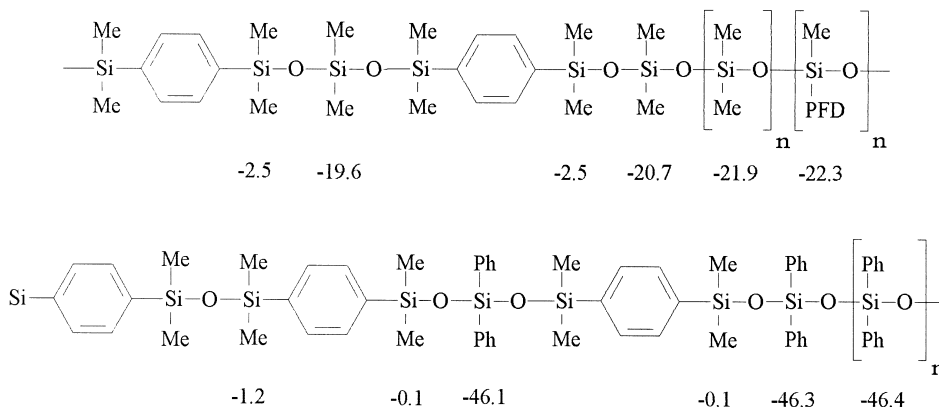
A silphenylene–PFD methyl siloxane copolymer

Fig. 3. ^{29}Si NMR chemical shifts (ppm) of silphenylene–siloxane copolymers with dimethyl, 1H,1H,2H,2H-perfluorodecyl (=PFD) methyl, and diphenyl siloxy groups relative to tetramethylsilane.

was synthesized by reaction of equimolar amounts of **4** and **5**. The silphenylene content measured by ^{1}H and ^{29}Si NMR spectroscopy was 47.6 and 48.9%, respectively, which is consistent with the theoretical values. The ^{29}Si NMR spectrum consists of two singlets at -1.2 and -22.3 ppm corresponding to the block copolymers SS and FFF.

3.3. Silphenylene–diphenylsiloxane copolymers

The diphenyl monomers **2** and **3** and the silphenylene unit **5** were mixed in different ratios, resulting in a series of silphenylene–diphenylsiloxane copolymers. The ratios of monomer units used for the preparation and the silphenylene content measured by NMR spectroscopy are listed in Table 1. There is a good correlation between the expected and measured silphenylene content. Nevertheless, the content of the silphenylene unit is higher than expected in all polymers. This is attributed to the formation of cyclic diphenyl oligomers, which are removed via reprecipitation.

Some of the polymers contain short block sequences of dimethylpolysiloxane (analogous to OV-1 at -21.9 ppm), e.g. the content in the polymers SP-5 and SP-50 is 2.6 and 4.1%, respectively. It is assumed that the diphenylsilane **2** is contaminated with the corresponding dimethylsilane **1**, leading to an undesirable side reaction. As **1** reacts very fast, it forms a homopolymer analogous to OV-1. Other batches of monomer **2** did not show this side reaction.

A ^{29}Si NMR spectrum of a representative silphenylene–diphenylsiloxane copolymer is shown in Fig. 4. The spectrum consists of two multiplets, corresponding to the silphenylene and diphenylsiloxy groups at -0.1 to -1.2 ppm and -46.1 to -46.4 ppm, respectively. Considering the silphenylene region first, only the two diads SP and SS are observed. Although the alternating diad SP dominates, the block diad SS at -1.2 ppm is found in almost every polymer (see Fig. 4). The content of block S ranges from 0 to 3%, indicating that no block copolymers were formed. Fine splitting due to long-range influences can be observed, but the individual signals cannot be assigned due to small differences in the chemical shifts.
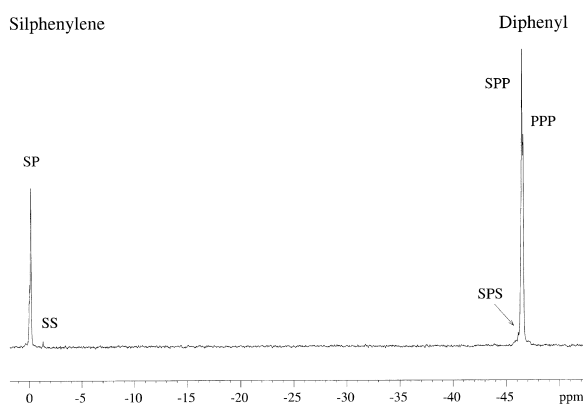
Analysis of the diphenyl-centered triad region

Fig. 4. ^{29}Si NMR spectrum of the silphenylene–diphenylsiloxane copolymer SP-10. SP and SS represent the silphenylene diads; SPS, SPP, and PPP represent the diphenylsiloxy-centered triads.

shows that the difference in the chemical shifts between the sequences SPP (at -46.3 ppm) and PPP (at -46.4 ppm) is small (Figs. 3 and 4). Only the chemical shift of the alternating sequence SPS (at -46.1 ppm) is distinctly different from that of SPP and PPP. Polymers with a diphenylsiloxy content of about 50% have a high content of the alternating sequence SPS, whereas SPP and PPP sequences are less abundant. In contrast, the SPP and PPP sequences predominate in polymers with very high diphenylsiloxy content (e.g., in SP-20 and SP-10), whereas the alternating triad SPS is less abundant. Although the differences in the chemical shifts of the triads SPS, SPP, and PPP are small, the microstructure parameters can be estimated (see Table 1). The run numbers indicate that our silphenylene–diphenylsiloxane copolymers have sequences which are between a randomized and an alternating polymer, where $R = 100$ is expected.

3.4. Silphenylene–dimethyldiphenylsiloxane copolymers

In the ^{29}Si NMR spectrum of a silphenylene–dimethyldiphenylsiloxane copolymer (Fig. 5) dimethyl- and diphenyl-centered triads can be observed around -20 and -46 ppm, whereas only diads are found for the silphenylene region around 0 ppm. The amount of monomer units used for the synthesis and the composition of the polymer measured by NMR spectroscopy are given in Table 2. Again, the
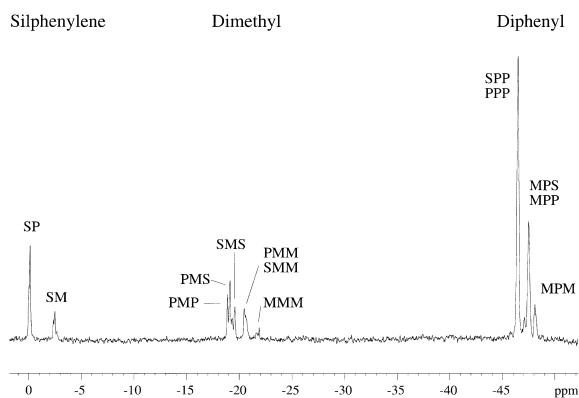
Fig. 5. ^{29}Si NMR spectrum of a silphenylene–dimethyldiphenylsiloxane copolymer. SP and SS represent the silphenylene diads; PMP, PMS, SMS, PMM, SMM, and MMM represent the dimethylsiloxy-centered triads; PPP, SPP, MPS, MPP, and MPM represent the diphenylsiloxy-centered triads.

theoretical and measured values for the chemical composition are in good agreement. The microstructure cannot be determined exactly, since three different monomers were used for the polymerization reaction. However, the sequence seems to be randomized, as no dimeric structures of S at -1.2 ppm could be observed.

4. Discussion

The synthesized silphenylene–siloxane copolymers are assumed to be analogous to the silphenylene polymers used as stationary phases in gas chromatography. Capillary columns coated with similar silphenylene polymers are commercially available as the so-called low-bleed, MS or high-temperature versions of conventional stationary phases, e.g., HP-35MS (Agilent Technologies), CP-Sil 24 CB ''Low-bleed''/MS (Chrompack), DB-17ms (J&W), and BPX-50 (SGE International). All these silphenylene–siloxane copolymers are claimed to be equivalent to 65–50% methyl, 35–50% phenyl polysiloxanes.

With our polymerization conditions, we were able to synthesize silphenylene–diphenylsiloxane copolymers with diphenyl contents up to 85%, which distinctly exceed the phenyl content of commercially available silphenylene polymers. This high phenyl

content in combination with excellent thermal stability and high molecular mass makes these polymers well suited as new stationary phases in high-temperature GC. In preliminary experiments the copolymers were coated on glass capillary columns and used up to 360°C in high-temperature GC. Unique selectivity during the separation of steroids and triacylglycerols was obtained due to the high polarity of the stationary phase (unpublished results).

4.1. Polymer preparation

4.1.1. Reaction yield

The yield of the polymerization reaction decreased from 90% (SP-25) to 50% (SP-10) with increasing content of diphenylsiloxy groups. The yield decreased to 12% if the content of the silphenylene unit **5** was lowered to 5% (SP-5). At least 15% of silphenylene units seems to be necessary to obtain high-molecular-mass polymers with a high phenyl content. If the diphenyl monomers bis(dimethylamino)diphenylsilane (**2**) and diphenylsilanediol (**3**) were mixed, only cyclic oligomers and no polymer were obtained, providing evidence that it is not possible to prepare copolymers with more than 85% diphenyl content under these reaction conditions.

4.1.2. Reaction time

Bis(dimethylamino)dimethylsilane (**1**) reacts much faster than the corresponding diphenylsilane (**2**). Mixing **1** and **5** in equimolar amounts produced the exactly alternating copolymer SM-50. In contrast, the analogous copolymerization reaction between **2** and **5** led to the more randomized copolymer SP-50, as the starting material was less reactive. In conclusion, it can be stated that fast condensation reactions provide alternating polymers, while moderate reactions result in alternating or randomized polymers and slow condensation reactions lead to entirely randomized or block polymers. In other words, decreasing condensation reaction rate increases the amount of redistribution products leading to randomized copolymers.

4.1.3. Cyclic impurities

No cyclic compounds were found in any of the polymers. This is different from the case of several commercially available polysiloxanes, e.g. OV-25,

PS-162 and Silar 5CP, where large amounts of cyclic impurities have been found [20]. It can be concluded that reprecipitation is very efficient for removing small cyclic impurities.

4.1.4. End group

The terminal methoxysiloxy group, expected approximately at -12 or -35 ppm in ^{29}Si NMR spectroscopy, could not be detected in any of the polymers. This provides evidence that the step-growth polymerization reaction provides polymers with relatively high molecular mass, resulting in a low abundance of terminal methoxysiloxy groups.

4.1.5. Flexibility

All prepared polymers are gums with a high viscosity at room temperature. With increasing phenyl content, the polymers have a higher crystalline character due to the more rigid polysiloxane chain. Usually, the silphenylene unit is incorporated into methylphenyl-polysiloxanes to reduce the flexibility of the main chain. In contrast, more flexible polymers with lower glass transition temperatures are obtained when silphenylene units are incorporated into a diphenylpolysiloxane chain. The increased flexibility is necessary, as viscous liquids are required as stationary phases for gas liquid chromatography.

4.1.6. Catalysis

In one separate experiment, a polymer analogous to SP-25 (25% silphenylene, 75% diphenyl siloxane) was prepared in an open reaction vial [15]. NMR analyses showed that the diphenylsiloxy content was reduced from 75 to 63%. Again, it is assumed that cyclic diphenylsiloxy oligomers are formed in a side reaction. In contrast, we performed the condensation reaction in a gas-tight screwed vial preventing the volatile dimethylamine evaporating from the reaction mixture. Under these conditions the reaction was more complete, indicating that dimethylamine acted as a basic catalyst by increasing the rate of the condensation reaction and by reducing side reactions.

4.2. Determination of the microstructure

^{29}Si NMR spectroscopy has been successfully applied to the characterization of polysiloxanes with methyl, phenyl, cyanopropyl, and cyanoethyl ligands [20,23,24]. Information was derived about the chemical composition, end groups, average molecular mass, cyclic impurities, branching, and microstructure parameters.

When analyzing silphenylene–siloxane copolymers with ^{29}Si NMR spectroscopy, two different effects complicate the exact determination of the microstructure parameters.

(i) The structure of the tetramethyl-*p*-silphenylene unit reduces the information obtained about the microstructure compared to polysiloxanes. One neighboring group of the silphenylene unit is two bonds apart via a siloxane bond (see Fig. 6). This neighboring group can be determined as in polysiloxanes. On the other hand, the second neighboring group of a silphenylene group is seven bonds apart from the investigated silicon nucleus. The transmission of shift information along the seven bonds is to small to be observed, leading to small differences of the chemical shifts. This small influence of the second neighboring group is marked by a canceled arrow in Fig. 6. Consequently, only one neighboring group can be determined, resulting in dimeric structures (diads) of the silphenylene unit, e.g. SS or SP, of silphenylene–diphenylsiloxane copolymers in Fig. 4. It is not possible to determine triads or pentads as in polysiloxanes. Furthermore, microstructure parameters cannot be calculated from diads of the silphenylene unit.

(ii) In the case of silphenylene–diphenylsiloxane copolymers, a second factor prevents the accurate determination of microstructure parameters. Unfortunately, the silphenylene and diphenylsiloxy groups have a very similar influence on the chemical shift of the adjacent silicon nucleus. Replacement of a
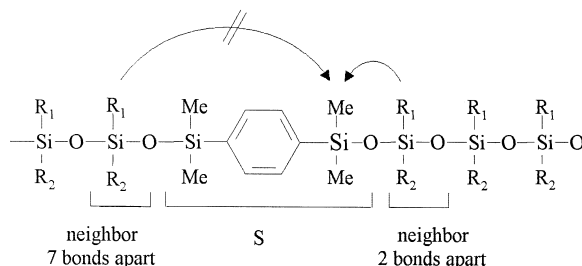

Fig. 6. Influence of the two neighboring groups on a tetramethyl-*p*-silphenylene (=S) unit.

dimethylsiloxy group by both a diphenylsiloxy group and a silphenylene unit causes a similar downfield shift, leading to low spectral dispersion. Therefore, it is hardly possible to distinguish between SPP (at −46.3 ppm) and PPP (at −46.4 ppm) (see Figs. 3 and 4). Only the alternating sequence SPS (at −46.1 ppm) is sufficiently separated from the other sequences. However, the determination of the microstructure is inaccurate, as the integration is imprecise due to signal overlapping.

4. Conclusion

The chosen polymerization conditions provided silphenylene–siloxane copolymers with dimethyl, PFD methyl, and diphenyl siloxy groups. High-molecular-mass polymers with diphenyl contents up to 85% were obtained. ^{29}Si NMR spectroscopy in combination with ^{1}H NMR spectroscopy yielded various structural information, such as the chemical composition, cyclic impurities, branching, and microstructure parameters. Some limitations complicated the structure elucidation of silphenylene–siloxane copolymers by ^{29}Si NMR spectroscopy, since the microstructure parameters could not be determined from diads of the silphenylene unit.

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