Tetramethyl-*p,p′*-sildiphenylene ether–dimethyl, diphenylsiloxane copolymers as stationary phases in gas chromatography

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Abstract

A 33% tetramethyl-*p,p′*-sildiphenylene ether (SDPE)–67% dimethylsiloxane copolymer was prepared and characterized by ^{1}H and ^{29}Si NMR spectroscopy. The random copolymer was coated on fused-silica capillary columns and used as stationary phase in GC. Highly deactivated capillary columns with high separation efficiency and a working range from -10 to $400\,°C$ were obtained. For comparison, a commercially available capillary column with an SDPE–diphenyl, dimethylsiloxane terpolymer was tested. The selectivity of SDPE phases is best described by the assumption that an SDPE unit is equivalent to two dimethylsiloxy and one diphenylsiloxy group. Both capillary columns exhibited low column bleed in combination with seriously increased elution temperatures.
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1. Introduction

The high thermal stability of polysiloxanes is further improved by incorporating backbone stiffening groups into the polysiloxane backbone. This so-called silarylene technique uses carborane, phenylene, diphenylene ether, and biphenylene groups to replace oxygen atoms of the backbone. The thermal stability is improved by steric hindrance of the formation of small cyclic oligomers. The first use of tetramethyl-*p*-silphenylene–dimethylsiloxane copolymers as stationary phases for GC was described by Buijten et al. [1]. Nowadays, almost every column manufacturer offers so-called low-bleed or MS columns, which are based on the silarylene technique [2]. However, only one manufacturer offers a capillary column, which is explicitly specified to contain an SDPE unit, i.e. BGB-Silaren from BGB Analytik AG (Schlossböckelheim, Germany).

The synthesis of SDPE–dimethylsiloxane copolymers and their excellent stability were first reported by Breed et al. [3]. Dvornic and Lenz described in detail the preparation of alternating SDPE–dimethylsiloxane and SDPE–methylvinylsiloxane copolymers and their thermal properties, such as glass transition temperature and thermal stability [4–8]. Three SDPE–siloxane copolymers with methyl, phenyl and trifluoropropyl groups were coated on glass capillary columns and applied in high-temperature GC [9,10] and the usefulness for triacylglycerol (TAG) analysis was investigated [11]. These capillary columns exhibited an excellent thermal stability with an upper working temperature limit of 440–480 °C.

As only one SDPE phase with its exact chemical composition is commercially available (BGB-Silaren, BGB Analytik AG), it is not amazing that a detailed investigation of the chromatographic properties of this backbone stiffening unit is missing. A recent paper described the gas chromatographic properties of tetramethyl-*p*-silphenylene–dimethyl, diphenylsiloxane copolymers [12]. The aim of this work is the investigation of the similar SDPE unit. The synthesis and NMR characterization of an SDPE–dimethylsiloxane copolymer is reported. The copolymer was used as stationary phase coated on fused-silica capillary columns in GC. Several gas chromatographic properties inherent to the SDPE unit could be derived from the home-made copolymer

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as well as from a commercially available SDPE–dimethyl, diphenylsiloxane terpolymer.

2. Experimental

2.1. Polymer synthesis

A modified condensation reaction (Fig. 1) was used to prepare SDPE-33 after reference [9]. Bis(p-dimethylsilyl) diphenyl ether (from ABCR, Karlsruhe, Germany) was treated with sodium hydroxide to obtain a hydroxyl terminated oligo(tetramethyl-p,p'-sildiphenylene ether). Two grams of oligo(tetramethyl-p,p'-sildiphenylene ether) and 1.2 g of a silanol terminated polydimethylsiloxane PS340 with a molecular weight of approximately 400–700 Da (obtained from ABCR) were mixed in equimolar amounts in 100 ml toluene. The mixture was refluxed at 110 °C until all components were dissolved. After addition of 0.2 g of the catalyst 1,1,3,3-tetramethylguanidin, the solution was heated under reflux for 4 h until the water release was completed. After removal of the solvent under vacuum the pre-polymer was heated in 10°-steps from 120 to 200 °C, holding each step for 15 min. After cooling the polymer was dissolved in toluene and end-capped with trimethylchlorosilane. Finally the polymer was dissolved in toluene and precipitated with five volumes of methanol. This procedure was repeated five times to remove quantitatively the catalyst and small cyclic impurities. After evaporation of the solvent under vacuum, an opaque, white, high-viscous polymer with a yield of approximately 70% was obtained.

2.2. NMR spectroscopy

The polymer was dissolved in deuterated chloroform at concentrations of 7% (w/w). NMR spectroscopy was performed on a DRX 400 WB spectrometer (Bruker Analytische Messtechnik, Ettlingen, Germany) as previously reported [13,14]. A 5 mm broadband inverse probe was operated at 400.13 and 79.49 MHz for ^{1}H and ^{29}Si NMR spectroscopy, respectively. Typical parameters for ^{29}Si NMR spectroscopy were 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 reagent. All ^{1}H and [29]Si chemical shifts are reported relative to external tetramethylsilane, which was added after the measurement for external calibration.

2.3. Capillary preparation

The capillary columns were prepared as recently described [15]. Briefly, fused-silica tubes with a TSG high-temperature stable polyimide coating were purchased from Polymicro Technologies, Inc. (Phoenix, AZ, USA). Fifteen metres tubes (i.d. 0.32 mm) were consecutively leached with a 1 M sodium hydroxide solution and 18% hydrochloric acid at 100 °C for 12 h. After drying under a gentle stream of nitrogen at 230 °C for 1 h the capillaries were flushed with a plug of 1,3-dimethyl,-1,1,3,3-tetraphenyl-disilazane (Fluka, Buchs, Switzerland) in dichloromethane (1:3, w/w).
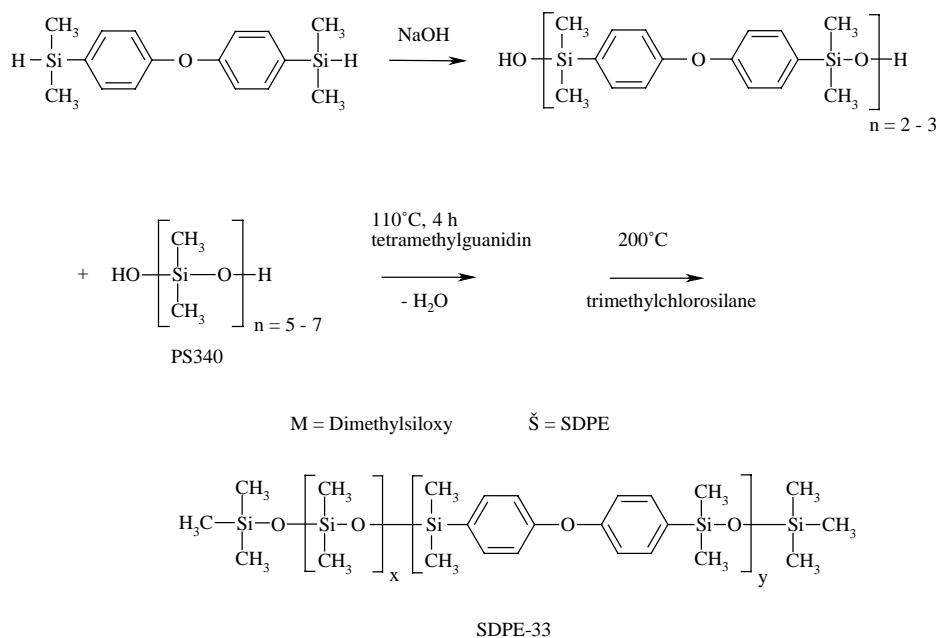

Fig. 1. Condensation reaction of oligo(tetramethyl-p,p'-sildiphenylene ether) with the silanol terminated oligomer PS-340 to obtain the trimethylsilyl terminated SDPE–dimethylsiloxane copolymer SDPE-33.

After removal of the solvent the capillaries were deactivated at 380 °C for 12 h and consecutively rinsed with toluene, methanol, and diethyl ether. Static coating was performed with a 0.25% (w/v) solution of the stationary phase in dichloromethane/pentane (1:1) at 30–40 °C resulting in a film thickness of 0.20 μm. Finally, the capillaries were conditioned under a flow of hydrogen at 300 °C for 5 h followed by conditioning at 350 and 380 °C for 3 h, respectively.

2.4. Capillary evaluation

All analyses were performed on a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector (Agilent Technologies, Inc., Palo Alto, CA, USA). Hydrogen with a purity of >99.9999% was used as carrier gas at a constant flow of 0.50 m/s. One microliter of aliquots of the test mixtures were introduced via cold-on-column injection. The flame ionization detector (FID) was operated 20 °C higher than the final oven temperature. The Grob test mixture for polar columns was obtained from Fluka [16,17]. The extended Donike test mixture (components obtained from Fluka) was used to evaluate the inertness of the capillary surface [18,19] and to determine the elution temperature of the n-alkane C_{34} [12]. A TAG test mixture was used to evaluate the chromatographic properties of the capillaries at high temperatures such as selectivity, polarity, separation efficiency, and inertness [20]. The components of that test mixture were purchased from Sigma (St. Louis, MO, USA). The mixture was injected at 60 °C, temperature-programmed at a rate of 25°/min to 280 °C followed by a rate of 4°/min to a final temperature of 380–400 °C. The recently introduced TAG-indices specify the carbon number (CN) at which a TAG elutes from the column [12]. For calculating the TAG-indices, a calibration curve was generated with the saturated TAGs tripalmitin (PPP, $3 \times$ C16:0), tristearin (SSS, $3 \times$ C18:0), and triarachidin (AAA, $3 \times$ C20:0). The polyunsaturated TAGs triolein (OOO, $3 \times$ C18:1), trilinolein (LLL, $3 \times$ C18:2), and trilinolenin (LnLnLn, $3 \times$ C18:3) served as probes to monitor the interaction with the stationary phase. A cholesteryl fatty acyl ester, cholesteryl dodecanoate, CE12:0 (obtained from Sigma) was used to determine its elution temperature and was analyzed under the same conditions as the TAG test mixture.

The Kováts retention indices of the first five Rohrschneider–McReynolds standards benzene, 1-butanol, 2-pentanone, 1-nitropropane, and pyridine were measured at 60 °C using split injection [21,22]. The average polarity of the stationary phase was expressed as CP-index and was calculated from the sum of the first five Rohrschneider–McReynolds constants divided by the sum of the Rohrschneider–McReynolds constants of OV-275 multiplied by 100 [23].

The minimum allowable operating temperature (MiAOT) of the capillary columns was determined by monitoring the column efficiency in the range of −20 to 160 °C with n-alkanes. The MiAOT is defined as that temperature, where the column efficiency is the half of its original value at elevated temperatures (manuscript in preparation). The upper working temperature was determined by evaluation the inertness and separation efficiency of the capillary columns with the test mixtures after conditioning up to 400 °C. Separation efficiency was expressed as separation number (Trennzahl) which were measured between the fatty acyl methyl esters E_{10}/E_{11} and E_{11}/E_{12} of the Grob test mixture at low temperature. At elevated temperatures the TZ values were determined between the n-alkanes C_{26}/C_{30} and C_{30}/C_{34} of the Donike test mixture, whereas these TZs represented a mean value of four different TZ values.

The capillary column DB-1ht, a 100% dimethyl–polysiloxane, with length 15 m, i.d. 0.32 mm, film thickness 0.1 μm was obtained from Agilent Technologies. The capillary column BGB-Silaren with a 40% SDPE–50% dimethyl, 10% diphenylsiloxane terpolymer (15 m, 0.32 mm i.d., 0.20 μm film thickness) was purchased from BGB-Analytik AG (Schlossböckelheim, Germany).

3. Results and discussion

3.1. NMR spectroscopy characterization

The ^{29}Si NMR spectrum of SDPE-33 is displayed in Fig. 2. The corresponding chemical shifts of SDPE–siloxane copolymers relevant in ^{1}H and ^{29}Si NMR spectroscopy are summarized in Fig. 3. The chemical composition of the polymer was calculated from the signal intensities of the corresponding spectra. 32.8 and 34.5% SDPE units and 67.2 and 65.5% dimethylsiloxy groups were found by ^{1}H and ^{29}Si NMR spectroscopy, respectively, which is in good agreement with the monomer feed ratio of 40:60. Additionally, ^{29}Si NMR spectroscopy provided information on the microstructure of the copolymer. However, the
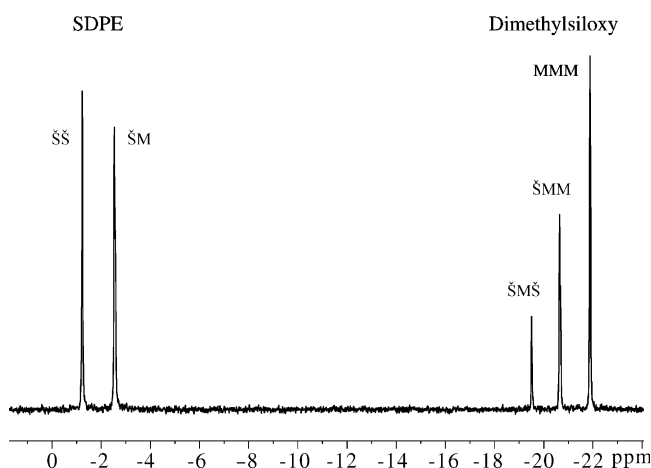

Fig. 2. ^{29}Si NMR spectrum of SDPE-33. ŠŠ and ŠM represent the SDPE diads; ŠMŠ, ŠMM and MMM represent the M-centered triads. Abbreviations: M, dimethylsiloxy; Š, tetramethyl-p,p'-sildiphenylene ether.
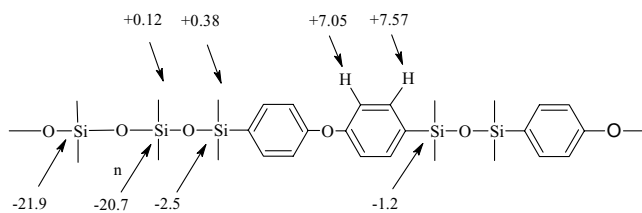
Fig. 3. Relevant chemical shifts (ppm) of SDPE–dimethylsiloxane copolymers relative to tetramethylsilane in ^{1}H and ^{29}Si NMR spectroscopy.

Fig. 4. Grob test chromatogram of SDPE-33 after thermal treatment at 380 °C. Capillary length 16 m, film thickness 0.20 μm, i.d. 0.32 mm. Temperature program: 40–160 °C at 4°/min. 0.5 m/s hydrogen linear velocity. Grob test mixture: D: 2,3-butanediol, C_{10}: decane, C_{11}: undecane, ol: octanol, al: nonanal, S: 2-ethylhexanoic acid, P: 2,6-dimethylphenol, A: 2,6-dimethylaniline, am: dicyclohexylamine, E_{10}–E_{12}: methyl ester of decanoic, undecanoic, and dodecanoic acid.

information derived from the spectrum is limited, as it is not possible to determine both neighboring groups of an SDPE unit. Only one neighbor can be determined, as the second neighbor is 12 bonds apart. Therefore, only diads are assigned for the SDPE unit in Fig. 2. This is analogous to tetramethyl-*p*-silphenylene–siloxane copolymers, where also only one neighboring group of the silphenylene unit can be determined [14]. Nevertheless, the microstructure parameters can be determined for the dimethylsiloxy group, where triad assignment is readily possible. The run number for the dimethylsiloxy group is 43.1, which is very close to the theoretical run number of 45.2 for a random distribution. Some additional information can be derived from the ^{29}Si NMR spectrum: As no signals were observed for the trimethylsiloxy or silanol end group (expected at +9 and −11 ppm, respectively), a molecular weight higher than approximately 50000 must be assumed. Furthermore, no additional signals could be detected which were caused by small cyclic impurities. Therefore, the precipitation procedure succeeded in removing those reaction byproducts. To sum up, SDPE-33 is a linear 35% tetramethyl-*p,p′*-sildiphenylene ether–65% dimethylsiloxane copolymer with random microstructure, rather high molecular weight and free of small cyclic impurities.

Unfortunately, ^{29}Si NMR spectroscopy is not able to distinguish between an SDPE and a tetramethyl-*p*-silphenylene unit on the basis of their chemical shifts. Exactly the same chemical shifts as for SDPE–siloxane copolymers were reported for silphenylene–siloxane copolymers [14]. This is plausible as the differences in the backbone stiffing units are five bonds apart from the silicon atom and are too small to be detected. However, a distinction between SDPE and silphenylene units is somehow possible by ^{1}H NMR spectroscopy: The protons of the SDPE unit give rise to duplets at 7.57 and 7.05 ppm, whereas the silphenylene protons give rise to a singlett at 7.55 ppm [6]. Unfortunately, the methyl protons of the SDPE and the silphenylene unit can also not be distinguished as their chemical shifts are very similar, i.e. 0.38 and 0.35 ppm, respectively.

3.2. Selectivity

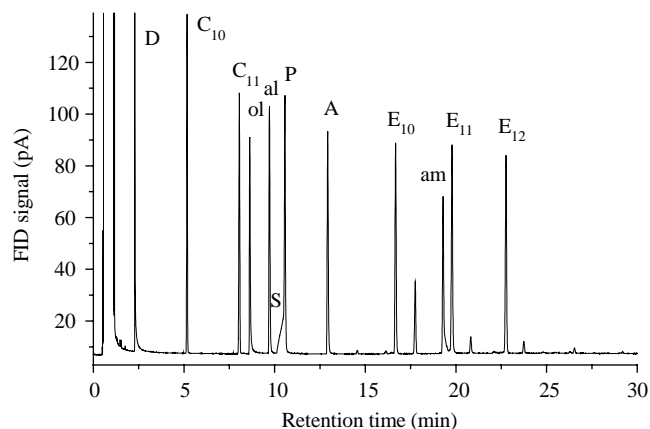To facilitate comparison with other stationary phases, the Grob test chromatogram of SDPE-33 is given in Fig. 4. The elution pattern of the test compounds closely resembles the one reported by Blum and Aichholz [9]. Less tailing and improved peak shapes could be obtained for SDPE-33 in comparison to SDPE-0 coated glass capillary columns which were reported in ref. [9]. However, the commercially available capillary column BGB-Silaren exhibits less tailing than SDPE-33.

In order to investigate the influence of the SDPE unit on the selectivity in general, the only commercially available capillary column with an SDPE containing stationary phase, BGB-Silaren with a 40% SDPE–50% dimethyl, 10% diphenylsiloxane terpolymer, was tested and compared to the results of SDPE-33. The selectivity of stationary phases is quantitatively described by the concept of Rohrschneider and McReynolds [21,22]. The Rohrschneider–McReynolds constants of SDPE-33 and BGB-Silaren and their overall polarity expressed as CP-index are listed in Table 1.

It can be easily seen from the overall polarity of both SDPE–siloxane copolymers, that the SDPE unit has a serious impact on the selectivity. For example, the CP-index of 13.0 reveals, that SDPE-33 has an overall polarity similar to 20% diphenyl, 80% dimethyl–polysiloxane. For simplification, the selectivity of SDPE–siloxane copolymers was compared to that of dimethyl, diphenyl–polysiloxanes. In Fig. 5 the diphenyl content of dimethyl, diphenyl–polysiloxanes was plotted versus their overall polarity, resulting in an almost linear relationship at low polarity of the stationary phase. This graph can be used to evaluate the influence of the SDPE unit on the selectivity. A recently introduced model assumes that a silarylene unit is equivalent to dimethylsiloxy and diphenylsiloxy units [12]. Model C is based on the assumption that a silarylene unit is equivalent to two dimethylsiloxy and one diphenylsiloxy group, whereas model D assumes that a silarylene unit is equivalent to two dimethylsiloxy and one-half of a diphenylsiloxy group. In the case of SDPE

Table 1
Rohrschneider–McReynolds constants and overall polarity of SDPE-33 and BGB-Silaren

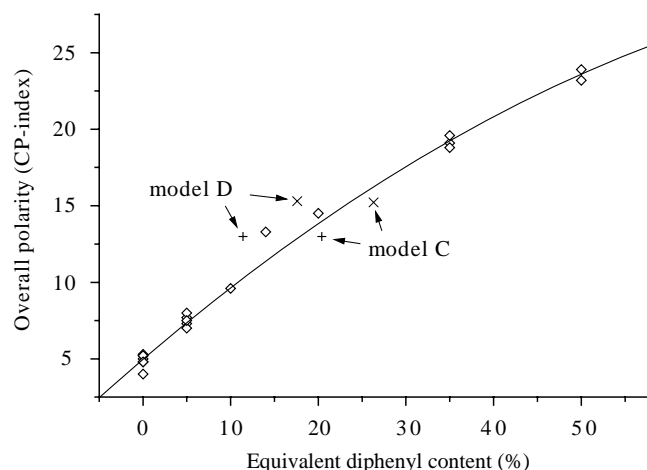|	Benzene	n-Butanol	2-Pentanone	Nitropropane	Pyridine	CP-index
SDPE-33	57.4	117.4	107.9	152.2	109.1	13.0
BGB-Silaren	72.6	130.1	126.0	177.1	133.2	15.3

Fig. 5. Overall polarity versus equivalent diphenyl content of (◇) dimethyl, diphenyl–polysiloxanes, (+) SDPE-33, and (×) BGB-Silaren. The theoretical equivalent diphenyl contents of the SDPE-phases were calculated according model C or D.
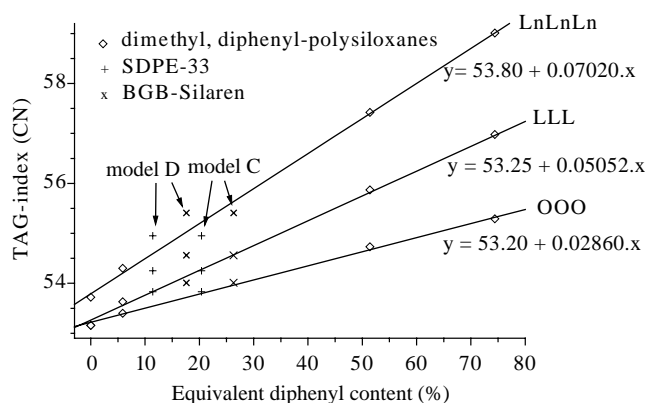

Fig. 6. Equivalent diphenyl content versus TAG-indices of (+) SDPE-33 and (×) BGB-Silaren. The theoretical equivalent diphenyl contents of the SDPE-phases were calculated according to model C or D.

units, Fig. 5 reveals that the theoretical data calculated after model D are in better agreement with the experimental data. The equivalent diphenyl contents calculated after the equivalence models and derived from the overall polarity are summarized in Table 2.

Contrary to the Rohrschneider–McReynolds constant, the recently introduced TAG-indices describe the selectivity of stationary phases at elevated temperatures [12]. The unsaturated TAGs OOO, LLL, and LnLnLn served as analytes, whereas a homologous series of saturated TAGs PPP, SSS, and AAA was used as reference material. A plot of TAG-indices versus diphenyl content reveals that a linear relationship is obtained for dimethyl, diphenyl–polysiloxanes, see Fig. 6. This relationship can be used to evaluate the influence of the SDPE unit on the selectivity. The TAG-indices of SDPE-33 and BGB-Silaren are 53.83 and 54.01 for OOO, 54.25 and 54.56 for LLL, 54.95 and 55.41 for LnLnLn, respectively. From these TAG-indices the equivalent diphenyl content of the stationary phases can be calculated with the corresponding regression curve (Table 2).

The best correlation between theoretically calculated and experimentally determined equivalent diphenyl contents was found with model C for both SDPE–siloxane copolymers. This model assumes that an SDPE unit is equivalent to two dimethylsiloxy and one diphenylsiloxy group, therefore, the two aromatic rings of the diphenylene ether unit acts like a diphenylsiloxy group. That means that all individual building blocks contribute to the overall selectivity of the SDPE unit. Model D which described best the influence of the phenylene ring of silphenylene–siloxane copolymers [12] underestimates the influence of the SDPE unit, as the SDPE unit has a distinctly higher impact on the selectivity than the silphenylene unit.

3.3. Column bleed

Thermal gravimetric analysis data demonstrate that SDPE–siloxane copolymers are more stable in an inert atmosphere than silphenylene–siloxane copolymers [3,8]. On the other side, SDPE–siloxane copolymers are less stable than silphenylene–siloxane copolymers under thermo-oxidative conditions [8]. Consequently, it is not easy to predict the thermal stability of SDPE–siloxane copolymers as stationary

Table 2
Equivalent diphenyl content of SDPE–siloxane copolymers calculated after two theoretical models and experimental data

	Calculated after		Derived from overall polarity	Derived from TAG-index		
	Model C	Model D		OOO	LLL	LnLnLn
SDPE-33	20.4	11.4	18.0	22.0	19.8	16.4
BGB-Silaren	26.3	17.6	23.8	28.3	25.9	22.9

Table 3
Column bleed of SDPE-33, BGB-Silaren and four stationary phases with similar polarity at 360 and 380 °C

Stationary phase	Relative bleed (pA) at	
	360 °C	380 °C
SDPE-33[a]	2.8	5.7
BGB-Silaren	4.2	10.1
SM-30[b]	6.3	16.1
SM-50[b]	11.4	23.9
DB-1ht[b,c]	4.6	10.3
OV-1[b]	13.4	29.2
Blank fused silica tube	0.4	0.6

Relative bleed is bleed at elevated temperature minus bleed at 60 °C. Capillary columns after thermal treatment at 380 °C, capillary dimensions: length 15 m, i.d. 0.32 mm, film thickness 0.20 μm.
[a] Mean value from two different capillary columns.
[b] Data taken from reference [12].
[c] Film thickness 0.1 μm.

phases in GC. Therefore, the bleeding level of several capillary columns was determined at 360 and 380 °C under standardized conditions, see Table 3. It came apparent that SDPE-33 offers lower bleeding rates than SM-30 and SM-50, which are silphenylene–dimethylsiloxane copolymers and which were coated with the same procedure. The bleeding level of SDPE-33 was almost only the half of that of BGB-Silaren and DB-1ht, a 100% dimethyl–polysiloxane dedicated for high-temperature analysis. To enable comparison all capillary columns were conditioned at 380 °C. That means, lower bleeding levels of BGB-Silaren may be possible, if the capillary column is thermally treated at its maximum allowable operating temperature of 450 °C.

For comparison purposes, a blank fused silica tube without any stationary phase film was added to Table 3. The extremely low bleeding rates of the blank tube indicate, that the contribution of the external polyimide coating, injector, septa, detector, etc. to column bleed is very low and can usually be neglected. Due to the low bleeding rate of SDPE-33, this extra-column contribution may be subtracted resulting in a net column bleed of 2.4 and 5.1 pA at 360 and 380 °C, respectively.

3.4. Working range

The applied high-temperature silylation with dimethyl-tetraphenyldisilazane resulted in an inert capillary surface. Even after thermal treatment at 400 °C, the excellent inertness of the capillary surface persists. The Donike test chromatogram of SDPE-33 after thermal treatment at 380 °C is displayed in Fig. 7. The high inertness of the phase film is indicated by both the relatively high recovery of trimethylsilyl esters of the fatty acids and the symmetrical peak shapes of the analytes. Since no higher temperatures were applied, an upper working temperature limit of 400 °C must be specified. The MiAOT was determined by monitoring the column efficiency at temperatures between −20 and 160 °C. MiAOTs of 16 and 32 °C were found for SDPE-33 and BGB-Silaren,
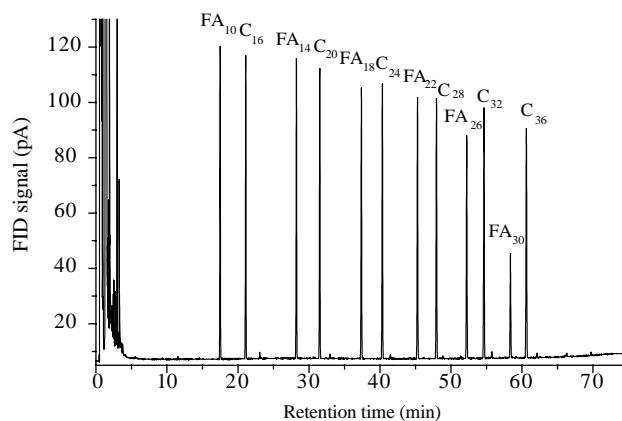

Fig. 7. Donike test chromatogram of SDPE-33 after thermal treatment at 380 °C. Capillary length 16 m, film thickness 0.20 μm, i.d. 0.32 mm. Extended Donike test mixture for apolar stationary phases: FA_{10}–FA_{30} are trimethylsilyl esters of the corresponding fatty acids; C_{16}–C_{36} are *n*-alkanes with corresponding carbon atoms. Temperature program: 50 to 320 °C at 4°/min, 0.5 m/s hydrogen linear velocity.

respectively. These rather high MiAOTs are plausible as the bulky SDPE unit increases the glass transition temperature of the polymers compared to 100% dimethyl–polysiloxanes. For example, a glass transition temperature of −37 °C was reported for a 33% SDPE–67% dimethylsiloxane copolymer [3,6], which closely resembles SDPE-33. For BGB-Silaren, a higher glass transition temperature is expected as it contains more SDPE and diphenyl units than SDPE-33. That means that the backbone stiffening SDPE unit increases both the glass transition temperature and the MiAOT. A similar effect was reported for the tetramethyl-*p*-silphenylene unit [12].

3.5. Increase of elution temperature

The elution temperatures of four test analytes (methyl dodecanoate, E_{12}; *n*-tetratriacontane, C_{34}; cholesteryl dodecanoate, CE12:0; and tripalmitin, PPP) were determined on capillary columns with standardized dimensions (15 m, i.d. 0.32 mm, film thickness 0.20 μm) under standardized conditions [12]. In Fig. 8, the elution temperatures of the four test analytes are plotted versus the overall polarity of the stationary phases. It can be seen, that the elution temperatures of all four test analytes are increased on the SDPE phases in comparison to dimethyl, diphenyl–polysiloxanes. Interestingly, the increase of the elution temperature rises with increasing temperature, e.g., the difference for SDPE-33 is 22 °C for E_{12}, 31 °C for C_{34}, 32 °C for CE12:0, and 39 °C for PPP. Increased elution temperatures were also reported for silphenylene–dimethyl, diphenylsiloxane copolymers [12] and for an SDPE–dimethyl siloxane copolymer [9]. However, the elution temperatures are more increased by SDPE than by silphenylene polymers, see Fig. 8. Obviously, the elution temperatures increase in the following way: polysiloxanes < silphenylene–siloxane copolymers <
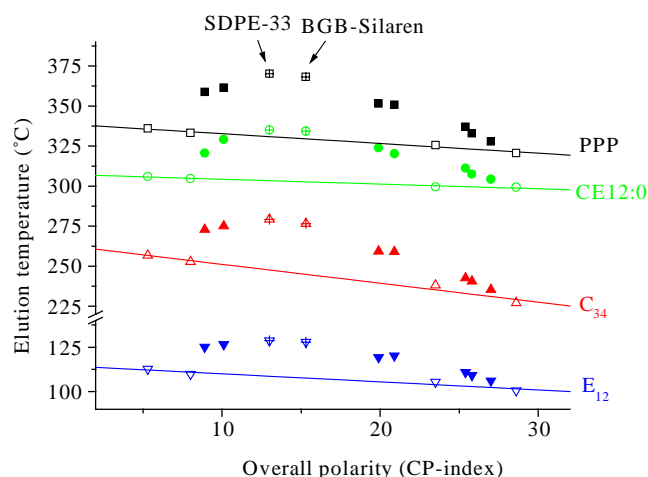
Fig. 8. Elution temperatures of four test analytes versus overall polarity of stationary phases: dimethyl, diphenyl–polysiloxanes (open symbols), silphenylene–siloxane copolymers (solid symbols), and SDPE–siloxane copolymers (+-centered symbols).

SDPE–siloxane copolymers. This is inconsistent to reference [11] where higher elution temperatures were reported for a silphenylene–siloxane than for an SDPE–siloxane copolymer. On the other side, such high elution temperatures of SDPE phases are comprehensible since increased elution temperatures of about 90 °C were reported for a polyphenyl ether sulfon, which also contained diphenyl ether units [25]. This increase is not proportional to the polarity of the backbone stiffing unit, but must be attributed to other interactions with analytes, e.g., steric interactions of the SDPE unit or dipole interactions of the ether oxygen. As an important consequence, the advantageously low column bleed of SDPE–siloxane copolymers get partly lost due to increased elution temperatures.

3.6. Separation efficiency

The fused-silica capillary columns exhibited high separation efficiency, which was expressed in terms of separation number (Trennzahl, TZ). The TZ values of E_{10}/E_{11} and E_{11}/E_{12} from the Grob test mixture were approximately 20 and 19 for SDPE-33 (mean values from two capillary columns), whereas slightly higher TZs were found for BGB-Silaren, i.e. 22 and 20. On the other side, the TZs of C_{26}/C_{30} and C_{30}/C_{34} were similar for both capillary columns, approximately 40 and 33. These TZ values are in the same range than those of similar prepared capillary columns coated with seven silphenylene–dimethyl, diphenylsiloxane copolymers [12] and an octylmethyl, diphenyl–polysiloxane [24].

3.7. Application of the capillary column

Although the capillary columns exhibit exceptionally low bleeding rates, they are not or only with reservations suit-

able for high-temperature analyses, such as TAG separation. This is caused by seriously increased elution temperatures of approximately 40 °C, which results in a dramatically enhanced thermal degradation of the analytes despite highly deactivated capillary surfaces. SDPE phases can be proposed for the separation of volatile organic compounds, as the analytes are more retarded due to increased interactions with the stationary phase. Their unique selectivity recommends SDPE phases for the separation of isomers, e.g., of polynuclear aromatic hydrocarbons or polychlorinated biphenyls, which can not or only hardly be separated on conventional stationary phases.

4. Conclusion

Several chromatographic properties are inherent to SDPE containing stationary phases: (i) The influence of the SDPE unit on the selectivity can be described by the model: an SDPE unit is equivalent to two dimethylsiloxy and one diphenylsiloxy group. (ii) The thermal stability is improved by incorporating SDPE units into the polysiloxane backbone leading to low bleed stationary phases. The column bleed decreases in the following order of the backbone stiffing units: polysiloxanes > silphenylene > SDPE. (iii) The elution temperatures are seriously increased on SDPE containing stationary phases. The elution temperatures increase in the following order: polysiloxanes < silphenylene < SDPE.

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