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New silicon phthalocyanine-containing polysiloxanes as stationary phases for high-temperature gas chromatography analysis

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ABSTRACT

In this work a series of thermoresistant polysiloxanes containing silarylene units and macrocyclic silicon phthalocyanine (Pc) units (**PS-1** – **PS-6**) were synthesized. The Pc is linked to the polymer chain through a siloxane central group, which has two covalent bonds with two nitrogen atoms of the macrocycle and two covalent bonds with the polymer chain. The sol–gel method led to the formation of polymeric chains with a random arrangement of monomers and OH-terminated chains. Thermogravimetric analyses revealed that the polymers are stable at high temperatures exhibiting, with a weight loss of 10 % between 384 and 442 °C during heating.

Coated as stationary phases for gas chromatography, polymers **PS-1**, **PS-2** and **PS-5** showed good film-forming ability. The columns prepared with **PS-1** and **PS-5** had 3300 and 3800 plates m^{-1} , respectively, as determined using pentadecane at 130 °C for fused silica capillary columns with an internal diameter of 250 μm , a film thickness of 0.25 μm and a length of 10 m. Polarity was estimated as moderate polarity (Rohrschneider–McReynolds constants were between 841 and 916) and stationary phases can achieve very good separation of Grob's mixture, polycyclic aromatic hydrocarbons and essential oils. In addition, the columns provided excellent high temperature stability with very low bleeding (17.0 pA at 420 °C). Repeated injections of high boiling analytes revealed that **PS-1** is the most stable stationary phase at very high temperatures, as the smallest decrease of retention times (9.2 s) were observed after 50 successive injections (temperature program from 40 °C (hold 3 min) at 7 °C/min to 420 °C (hold 2 min)). Moreover, it has been demonstrated that **PS-1** is more stable than commercial high-temperature columns such as ZB-XLB-HT and ZB-35HT (35 % phenyl/65 % dimethylpolysiloxane) from Phenomenex®.

1. Introduction

One of the most important components for high-temperature gas chromatography (HT-GC) analysis is the column and the thermal stability of the stationary phase coated inside. Over the last few years, several efforts have been made to develop high-temperature stationary phases that are able to withstand temperatures above 380 °C [1,2]. Nonetheless, the availability of commercial high-temperature stationary phases is limited. This lack of GC stationary phases is due, in particular, to the difficulty of obtaining materials that are stable at high temperatures and remain as liquid stationary phases for HT-GC at the same time.

The most stable stationary phases are polysiloxane-based phases. The drawback of this polymer is that the most thermostable has a low polarity. Another weakness of these columns is the degradation of the stationary phase when heated at high temperatures. The main thermal degradation mechanism is a depolymerization initiated by a “back-biting” phenomenon in which the terminal hydroxyl group attacks the polymer backbone, releasing volatile cyclic siloxanes. Once initiated, the degradation of the polymer is stepwise and leads to shortened and nonreproducible retention times. The repeatability of the chromatographic retention time is a key parameter in gas chromatography analysis especially for HT-GC×GC [3]. Moreover, this stationary phase

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bleeding is responsible for high background signals, ghost peaks and detector contamination. To limit the depolymerization reaction, manufacturers have incorporated silarylene groups in the backbone of silicon polymers to stiffen the polymeric chain and/or cross-linking between polymer chains to create a polymeric network. In 1984 Blomberg et al. [4] prepared, for the first time, a poly(silarylene-methylphenylsiloxane) block copolymer as a thermostable stationary phase via capillary column gas chromatography and reported that high thermal stability in capillary GC can be obtained with silarylene copolymers. The poly(arylene-methylphenyl) siloxane block-copolymer was prepared by copolymerization at high temperature in the presence of a catalyst, tetramethylammonium hydroxide. When used as the stationary phase the polymers were immobilized with dicumyl peroxide or ozone, and allowed to use temperatures up to 360 °C. Furthermore, the authors focused their attention in particular on degradation mechanisms such as the backbiting and unzipping of polysiloxane [5]. These polymers have been employed as models for the preparation of similar silarylene-type stationary phases [6,7]. Moreover, the polarity of GC columns has been estimated using the Rohrschneider–McReynolds constants allowing the classification of the stationary phase from the least polar to the most polar [8,9].

More recently, several publications [10] have shown the use of dimethylpolysiloxanes containing various substituted aryl groups [11, 12], (substitution: F, CF₃, CN; condensed aromatic and pyridine) as stationary phases for GC. Owing to their unique structure and good film-forming ability, the grafted polysiloxanes showed very good selectivity for the separation of aromatic isomers, substituted benzenes, polycyclic aromatic hydrocarbons (PAHs), fatty acid esters (FAEs) and fatty alcohols. According to the authors, the tetra-aryl-dimethylpolysiloxane stationary phases exhibited greater selectivity than did the classic diphenyl-dimethylpolysiloxane phases, because of their unique polarizable characteristics in combination with other interactions, such as acceptor hydrogen bonds and dipole–dipole and dispersive interactions. When the grafted aryl group is a large conjugated heterocyclic system containing pyridine, it offers a high capacity for accepting protons. This stationary phase has better separation performance than commercial phases do toward pyridine derivatives (basic compounds), aromatic aldehydes (electron donors) and fatty alcohols (hydrogen donors and acceptors). Although this stationary phase presented interesting selectivity and acceptable thermostability, the maximum allowed operating temperature (MAOT) of 360–380 °C can be insufficient for high-temperature applications such as heavy vacuum gas oil, pyrolysis oils, and brominated -dioxins. Moreover, polar stationary phases that are stable at high temperatures were important for characterizing pollutants especially when comprehensive GC is used, such as polybrominated diphenylethers and chlorinated and brominated PAHs [13,14]. This work focused on obtaining stationary phases with increased thermal stability. Therefore, phthalocyanine macrocycle derivatives were selected because of their very high thermal stability and the possibility of incorporating these selectors in the sol-gel network to add interesting binding interactions with analytes. The sol-gel process is an interesting technology with many advantages, it combines deactivation, coating and immobilization of stationary phases into one step. Phthalocyanines are analogs of porphyrins with a highly conjugated 18 π -electron planar aromatic system and a central cavity that can accommodate various central groups or atoms. Silanediol phthalocyanine derivatives are commercially available, and thus can be readily used as starting materials for the synthesis of polysiloxane polymers containing phthalocyanine units. To the best of the author's knowledge, liquid stationary phases for GC containing porphyrins or phthalocyanine units have not been reported. However, the use of porphyrins and phthalocyanines has been successful for the preparation of HPLC stationary phases [15]. Moreover, two publications aimed at the preparation of sorbents for GC were based on modified silica gel with copper and nickel phthalocyanates [16] or with nickel porphyrinate [17]. However, initial attempts to simply mix phthalocyanines with polysiloxane led to

crystalline inclusions and thus very poor film homogeneity.

The use of silicon phthalocyanines solves this issue as phthalocyanine is now included in the polysiloxane chain. The synthesized polymers were coated in fused silica capillary columns and used as stationary phases for HT-GC [18]. The chromatographic properties and performance of the new stationary phases were evaluated in terms of efficiency and inertness by injection of the Grob test mixture. The Rohrschneider–McReynolds constants were calculated, and the separation ability of new phases was evaluated through the injection of mixtures of PAHs, and essential oils. The bleeds of the stationary phases were evaluated between 380 and 420 °C in terms of the shift in retention and the height of signal noise.

2. Experimental

2.1. Reagents and apparatus

All solvents and reagents were purchased from VWR International (West Chester, USA), Sigma-Aldrich (St Louis, MO, USA), Acros Organics (Morris Plains, NJ, USA), Carlo Erba (Milan, Italy) and Alfa Aesar (Schiltigheim, France). The solvents used were HPLC or GC grade. The PAH mixture was purchased as custom-made solution from Restek (Lisses, France). Fused-silica tubing capillary columns (0.25 mm inner diameter) were purchased from MicroQuartz (Munich, Germany) or Molex (Milano, Italy).

The synthesized copolymers were characterized via UV–Vis and FT–IR spectroscopic methods. The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) and quantitative bleed measurements. TGA was performed using a Netzsch TG 209 apparatus. The baseline was calibrated from 30 to 550 °C with a heating rate of 10 °C min⁻¹. Approximately 10 mg of polymer was placed into a ceramic crucible. A nitrogen flow of 15 mL min⁻¹ was applied during the measurements. Data processing was performed with Netzsch-TA Proteus® software (version 4.8.4). Quantitative bleed measurements were performed on a Hewlett-Packard 6890 N. The injector temperature was set at 300 °C, the FID detector temperature was set at 350 °C and the carrier flow rate was 0.8 mL/min (Helium).

2.2. Synthesis

The preparation of the new phthalocyanine-polysiloxane polymers is depicted in Fig. 1 and the structural composition is detailed in Table 1.

Moreover, some authors [19] reported that silicon phthalocyanines have been distinguished from structurally related porphyrin analogues by their intense far-red absorption and emission characteristics. Unlike most other silicon phthalocyanines have two additional axial bonds that reduce aggregation in solution.

2.2.1. General procedure for the preparation of polymers PS-1 – PS-7

Into a headspace vial were placed **1a** or **1b**, silicon phthalocyanine dihydroxide **PC-a** or **PC-b** and dichloromethane. The mixture was shaken and then placed in an ultrasonic bath for a minimum of 5 min to obtain a dark blue solution. Separately, **2a** or **2b** were dissolved in tetrahydrofuran and added to the above mixture. Then, trifluoroacetic acid containing 5 % water was added. The vial was sealed and the reaction mixture was stirred for 24 h at 25 °C. After that, the majority of the solvent (approximately 50 % by volume) was slowly evaporated and the mixture was left without agitation for another 24 h at room temperature. Finally, the solvent was removed by evaporation under vacuum and the material obtained was dried under vacuum until all traces of acid and water were removed. To obtain the end-capped polymer **PS-3** trimethylchlorosilane dissolved in dichloromethane was added to a **PS-1** solution before the final step and the mixture was stirred for an additional 30 min. Furthermore, the obtained polymers were dissolved in 15 mL of a dichloromethane-pentane 1:1 mixture, vigorously stirred to homogenize the solution and then, filtered through a 0.2 μ m PTFE

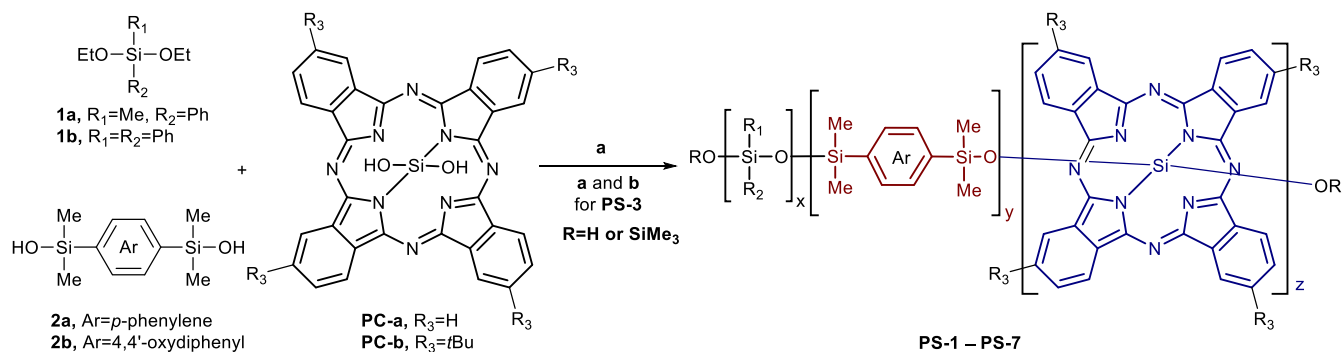


Fig. 1. General reaction scheme for the preparation of phthalocyanine-polysiloxane polymers. *Reagents and conditions:* a) CF₃COOH containing 5 % H₂O, CH₂Cl₂, tetrahydrofuran, rt, 24 h, then partial evaporation followed by 24 h at rt, no stirring; b) (CH₃)₃SiCl, rt, 0.5 h.

Table 1

Composition of the new phthalocyanine-polysiloxane polymers PS-1–PS-7.

	x	y	z	R	R ₁	R ₂	Ar	R ₃
PS-1	75.0	24.75	0.25	H	Me	Ph	p-phenylene	H
PS-2	75.0	24.5	0.5	H	Me	Ph	p-phenylene	H
PS-3	75.0	24.75	0.25	SiMe ₃	Me	Ph	p-phenylene	H
PS-4	75.0	24.75	0.25	H	Ph	Ph	p-phenylene	H
PS-5	75.0	24.5	0.5	H	Me	Ph	p-phenylene	tBu
PS-6	75.0	24.0	1.0	H	Me	Ph	4,4'-oxydiphenyl	H
PS-7	99.35	0	0.65	H	Me	Ph	—	H

x, y and z are expressed as percentage of mass and R₃ is the substituent of the phthalocyanine macrocycle (Fig. 1).

syringe filter to eliminate insoluble particles. The solvent is fully evaporated to obtain the desired polymers as blue gels.

2.2.1.1. For polymer PS-1. Reagents: 0.555 g (2.64 mmol) methylphenyl(diethoxy)silane **1a**, 5.05 mg (8.79 μmol) silicon phthalocyanine dihydroxide **PC-a** and 3 mL dichloromethane; 0.200 g (0.879 mmol) of 1,4-bis(hydroxydimethylsilyl)benzene and 1 mL tetrahydrofuran; 100 μL trifluoroacetic acid and 5 μL water. The yield was 0.56 g of polymer. UV–Vis λ_{max} (nm, CH₂Cl₂) (%): 672 (19), 605 (3), 355 (40), 270 (11), 264 (12), 230 (100). IR (cm⁻¹, neat): 3069.7 (CH_{aromatic}), 3048.6 (CH_{aromatic}), 2957.7 (CH_{aliphatic}), 1591.7, 1428.4, 1380.2, 1256.8 (CH₃-Si-CH₃), 1136.7 (Si-C₆H₄-Si), 1122.4, 1014.3, 996.4, 820.4, 773.1, 726.2 (CH₃-Si(O)-C₆H₅), 695.76 (CH₃-Si(O)-C₆H₅), 504.2, 475.8, 425.0.

2.2.1.2. For polymer PS-2. Reagents: 0.55 g (2.61 mmol) methylphenyl(diethoxy)silane **1a**, 10 mg (17.4 μmol) silicon phthalocyanine dihydroxide **PC-a** and 3 mL dichloromethane; 0.193 g (0.853 mmol) of 1,4-bis(hydroxydimethylsilyl)benzene and 1 mL tetrahydrofuran; 100 μL trifluoroacetic acid and 5 μL water. The yield was 0.54 g of polymer. UV–Vis λ_{max} (nm, CH₂Cl₂) (%): 672 (36), 605 (5), 355 (8), 264 (12), 230 (100). IR (cm⁻¹, neat): 3069.6 (CH_{aromatic}), 3048.5 (CH_{aromatic}), 2957.5 (CH_{aliphatic}), 1591.7, 1428.4, 1380.2, 1256.8 (CH₃-Si-CH₃), 1136.7 (Si-C₆H₄-Si), 1122.3, 1014.9, 996.6, 820.2, 773.2, 726.2 (CH₃-Si(O)-C₆H₅), 695.8 (CH₃-Si(O)-C₆H₅), 504.2, 476.4, 420.8.

2.2.1.3. For polymer PS-3. Reagents: 0.545 g (2.59 mmol) methylphenyl(diethoxy)silane **1a**, 13.8 mg (17.3 μmol) silicon phthalocyanine dihydroxide **PC-a** and 3 mL dichloromethane; 0.193 g (0.846 mmol) of 1,4-bis(hydroxydimethylsilyl)benzene and 1 mL tetrahydrofuran; 100 μL trifluoroacetic acid and 5 μL water; 150 μL trimethylchlorosilane dissolved in 1.0 mL dichloromethane. The yield was 0.54 g of polymer.

IR (cm⁻¹, neat): 3069.7 (CH_{aromatic}), 3048.8 (CH_{aromatic}), 3002.6 (CH_{aliphatic}), 2957.5 (CH_{aliphatic}), 2900.1 (CH_{aliphatic}), 1591.7, 1488.5, 1428.4, 1407.2, 1380.1, 1334.3, 1256.8 (CH₃-Si-CH₃), 1136.6 (Si-C₆H₄-Si), 1122.4, 1027.0, 1014.5, 912.3, 996.6, 820.5, 773.2, 725.8 (CH₃-Si(O)-C₆H₅), 695.6 (CH₃-Si(O)-C₆H₅), 618.7, 555.4, 504.2, 476.5, 424.4, 416.7.

2.2.1.4. For polymer PS-4. Reagents: 0.729 g (2.68 mmol) diphenyl(diethoxy)silane **1a**, 5.2 mg (8.93 μmol) silicon phthalocyanine dihydroxide **PC-a** and 3 mL dichloromethane; 0.200 g (0.883 mmol) of 1,4-bis(hydroxydimethylsilyl)benzene and 1 mL tetrahydrofuran; 100 μL trifluoroacetic acid and 5 μL water. The yield was 0.55 g of polymer.

2.2.1.5. For polymer PS-5. Reagents: 0.545 g (2.59 mmol) methylphenyl(diethoxy)silane **1a**, 13.8 mg (17.3 μmol) silicon 2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine dihydroxide **PC-b** and 3 mL dichloromethane; 0.193 g (0.846 mmol) of 1,4-bis(hydroxydimethylsilyl)benzene and 1 mL tetrahydrofuran; 100 μL trifluoroacetic acid and 5 μL water. The yield was 0.52 g of polymer. IR (cm⁻¹, neat): 3069.6 (CH_{aromatic}), 3048.6 (CH_{aromatic}), 2957.4 (CH_{aliphatic}), 1591.6, 1428.3, 1380.2, 1256.9 (CH₃-Si-CH₃), 1136.5 (Si-C₆H₄-Si), 1122.4, 1014.1, 996.5, 820.4, 773.2, 725.9 (CH₃-Si(O)-C₆H₅), 695.6 (CH₃-Si(O)-C₆H₅), 504.2, 476.2, 431.6, 416.7.

2.2.1.6. For polymer PS-6. Reagents: 0.283 g (1.31 mmol) methylphenyl(diethoxy)silane **1a**, 10.4 mg (17.4 μmol) silicon phthalocyanine dihydroxide **PC-a** and 2 mL dichloromethane; 0.135 g (0.418 mmol) of (oxybis(4,1-phenylene))bis(dimethylsilyl)anol **3** and 2 mL tetrahydrofuran; 50 μL trifluoroacetic acid and 5 μL water. The yield was 0.315 g of polymer. IR (cm⁻¹, neat) : 3069.6 (CH_{aromatic}), 3049.1 (CH_{aromatic}), 3022.9, 2957.5, 1581.3, 1493.0, 1428.4, 1394.2, 1303.2, 1258.4 (CH₃-

Si-CH₃), 1238.9, 1174.6 (Si-C₆H₄-Si), 1112.5, 1024.5, 997.6, 869.6, 823.6, 776.2, 726.7 (CH₃-Si(O)-C₆H₅), 696.1 (CH₃-Si(O)-C₆H₅), 619.3, 596.3, 549.6, 515.0, 477.8, 420.9, 416.7, 405.4, 401.8.

2.2.1.7. For polymer PS-7. Reagents: 0.793 g (3.77 mmol) methylphenyl(diethoxy)silane **1a**, 15.3 mg (26.6 μmol) silicon phthalocyanine dihydroxide **PC-a** and 3 mL dichloromethane; 200 μL trifluoroacetic acid and 10 μL water. The yield was 0.45 g of polymer.

2.3. Preparation of the capillary column

The polymers were coated via the conventional static method [20, 21] mainly on an untreated fused silica capillary column. Prior to coating, the untreated fused silica capillary was rinsed with 1 mL of methanol and then with 1 mL of dichloromethane, and finally dried with nitrogen gas for at least 2 h. In some cases, deactivated fused silica capillaries were used to coat of polymers and they were prepared as follows. The fused silica capillaries were treated with 2 % HCl solution at 220 °C for 6 h. Then, they were subsequently rinsed with a 2 % HCl solution and 1 mL of methanol and then purged with helium at 250 °C for 2 h. Next, the capillary was 50 % filled with DPTMDS or HMDS and heated at 330 °C for 6 h with both ends sealed. Afterward, the tube was subsequently rinsed with 1 mL of methanol and 1 mL of diethyl ether, and purged with dry nitrogen for at least 2 h.

The columns were then statically coated with the new polymers. The phthalocyanine–polysiloxane polymer was dissolved in a mixture of solvents (dichloromethane/pentane ratio of 1/1) at a concentration of 0.4 % (w/v) to obtain a theoretical film thickness of approximately 0.25 μm. The theoretical film thickness (d_f) was calculated using the Eq. (1).

$$d_f = (d_c \times C) / (4 \times \rho) \quad (1)$$

where d_c is the inner diameter of the capillary tubing (expressed in millimeters), ρ is the polymer density (which is supposed to be equal to 1000 g.L⁻¹) and C is the concentration of the coating solution expressed in g.L⁻¹.

Prior to filling the capillary, the polymer solution was filtered through a 0.2 μm PTFE syringe filter. The capillary was filled with the polymer solution and after sealing one side, the solvent was evaporated at 25–30 °C by connecting the other end to a vacuum pump system. Afterward, the capillary columns coated with the polymer were purged with nitrogen gas to remove traces of residual solvent. Finally, the capillary columns were held at 280 and 390 °C under helium a constant flow of 0.4 ml/min. For this, the temperature was increased at a rate of 1° min⁻¹ from 40 °C to 280 °C, maintained for 6 h, then increased to 390 °C and maintained for 12 h. A column with a 0.1 μm film thickness was prepared in a similar manner using a solution with a concentration of 0.16 % (w/v).

2.4. Capillary column evaluation

All gas chromatographic analyses were carried out on a Thermo Fisher Scientific Trace GC Ultra gas chromatograph equipped with an FID, a split/splitless injector and helium as the carrier gas at a linear velocity of 25 cm s⁻¹. The split ratio was set at 1:30. Methane was injected to measure the dead time. The chromatograms were processed and stored with Thermo Chrom-Card software (version 2.4.1). Efficiency was expressed as the number of theoretical plates per meter for the peaks of *n*-tetradecane or *n*-pentadecane analyzed at 130 °C. The polarity was evaluated by measuring the Rohrschneider–McReynolds [8,9] constants at 40 °C as the sum of the retention index differences of the 5 probes (benzene, 2-pentanone, 1-nitropropane, 1-butanol, and pyridine) calculated for each of the given liquid phases and the squalane (Eq. (2)).

$$\Delta I = I_{\text{liquid phase}} - I_{\text{Squalane}} \quad (2)$$

It is important to notice that the Rohrschneider–McReynolds

constants were not calculated as 120 °C which could affect the polarity evaluation. The conventional polarity P is given as the sum of the five ΔI values of each probe. Moreover, the polarity number (PN) of the stationary phase [22] is calculated via Eq. (3):

$$PN = (P_{\text{liquid phase}} / P_{\text{SLB-IL-100}}) \times 100 \quad (3)$$

where $P_{\text{liquid phase}}$ represents the sum of the five Rohrschneider–McReynolds constants (benzene, 2-pentanone, 1-nitropropane, 1-butanol, and pyridine) on the given liquid stationary phase, whereas $P_{\text{SLB-IL100}}$ is the sum of the five Rohrschneider–McReynolds constants calculated on the SLB-IL100 column.

The coating efficiency (E%) was estimated by using the Eq. (4):

$$E \% = \frac{H_{\text{theoretical}}}{H_{\text{min}}} \times 100 \quad (4)$$

With H_{min} was deduced from Golay's plot [23] and $H_{\text{theoretical}}$ was estimated using the Eq. (5):

$$H_{\text{theoretical}} = r_c \sqrt{\frac{1 + 6k + 11k^2}{3 \times (1 + k)^2}} \quad (5)$$

Where r_c is the column radius.

3. Results and discussion

3.1. Synthesis and thermal stability of the polymers

The target polymers **PS-1** – **PS-7** were prepared using the sol–gel method catalyzed by acid as previously described [24–26]. For this purpose, the corresponding siloxane (**1a,b**) and the corresponding phthalocyanine macrocycle (**PC-a,b**) were dissolved in dichloromethane and the corresponding silarylene (**2a,b**) was dissolved in tetrahydrofuran to increase the solubility of the reagents. The acid and water catalysts were subsequently added to the combined solutions and then stirred at room temperature for 24 h. To promote further chain growth, the solvent was partially evaporated, and the mixture was left to rest at room temperature for another 24 h. After full evaporation under vacuum, the polymers were obtained as blue gels. The synthesized polymers exhibit a random distribution of monomer units and are OH-terminated. For purposes of scope, a SiMe₃-terminated polymer (**PS-3**) was also prepared. For the latter, the terminating agent trimethylchlorosilane, dissolved in dichloromethane, was added at the end of the polymerization reaction, and allowed to react for 30 min at room temperature.

All the polymers obtained were deep blue transparent gels, which is an indication of the presence of phthalocyanine macrocycles in the polymeric structure as they were blue dyes. The obtained polymers were characterized by FT–IR and UV–Vis analyses. FT–IR spectra of the phthalocyanine polymers showed the expected features (Fig. 2), such as, an intense and broad band between 990 and 1100 cm⁻¹ corresponding to Si–O–Si bonds, a sharp band at 1122 cm⁻¹ corresponding to *p*-substituted silphenylene or two sharp bands at 696 and 726 cm⁻¹ corresponding to Me–Si(O)–Ph groups. Notably, the presence of a band related to the eventual hydrogen bonding of terminal OH groups was not observed.

According to UV–Vis absorption spectra of the polymers two specific regions characteristic of phthalocyanines are expected. These bands are the Soret (or B) band, which is usually observed in the range of 300–400 nm and the band in the region of 620–750 nm named the Q band. Even though phthalocyanine is present in a small ratio, both specific regions are observed for the studied polymers. Broad absorption at 354 nm, corresponding to the B band and an intense absorption at 672 nm corresponding to the Q band were visible for the investigated polymers in dichloromethane solution. Additionally, satellite peaks are observed at 605 and 639 nm.

The final properties of the stationary phase depend upon the

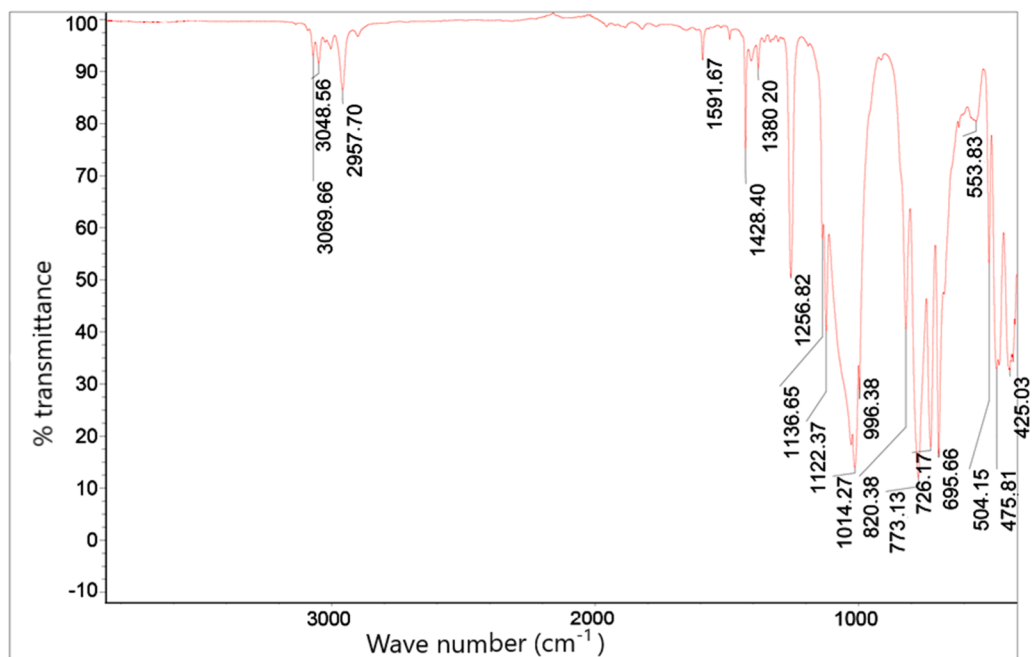


Fig. 2. FTIR spectrum of the polymer PS-1.

composition ratio of the soft siloxane segments and the rigid silarylene and phthalocyanine blocks. To preserve the high diffusion coefficients of the solutes in the polymers, the average molar ratio between soft and rigid units should be approximately 75:25. The percentage of phthalocyanine added ranged from 0.25 to 1 %-mol. This limitation is due to the extremely poor solubility of the phthalocyanines.

The thermal stability of the new polymers was evaluated by thermogravimetric analysis. The analyses were performed under a nitrogen atmosphere and heated with a ramp rate of 10 °C/min from room temperature to 550 °C. The TGA thermograms are presented in Fig. 3a and b and the individual decomposition temperatures measured at 5 % and 10 % weight loss, are shown in Table 2. Overall, the polymers start to decompose slightly above 350 °C and significantly above 500 °C, except for the polymer PS-7 which presents significant weight loss after 250 °C. It is well known that silarylene units increase the thermal stability of a siloxane polymer by increasing the rigidity of the chain. A more rigid polymer chain is very beneficial because it restricts the formation of cyclic oligomers. In our case, the polymers containing approximately 25 mol-% silarylene units exhibited high thermal

Table 2

Temperatures measured at 5 % and 10 % weight loss for each stationary phase.

Polymer	PS-1	PS-2	PS-3	PS-4	PS-5	PS-6	PS-7
T ₅ %	344 °C	337 °C	365 °C	Nd	366 °C	321 °C	255 °C
T ₁₀ %	410 °C	404 °C	424 °C	Nd	442 °C	384 °C	281 °C

nd = not determined.

stability (Table 2), whereas a test polymer that was deprived of silarylene units (PS-7) had very low thermal stability. Although phthalocyanine units are present in a small ratio in the polymer chain, we assume that they contribute to the rigidity of the polymer chain. The planar and bulky phthalocyanine macrocycle is positioned perpendicular to the polymer chain creating a shape resembling dumbbells. It is possible that the chain geometry created by the presence of the macrocycle contributes to the reduction in the “backbiting” phenomenon, and hinders intermolecular rearrangement at high temperatures which is accompanied by the formation of smaller and volatile fragments (unzipping).

TGA is just a first method for determining polymer stability because

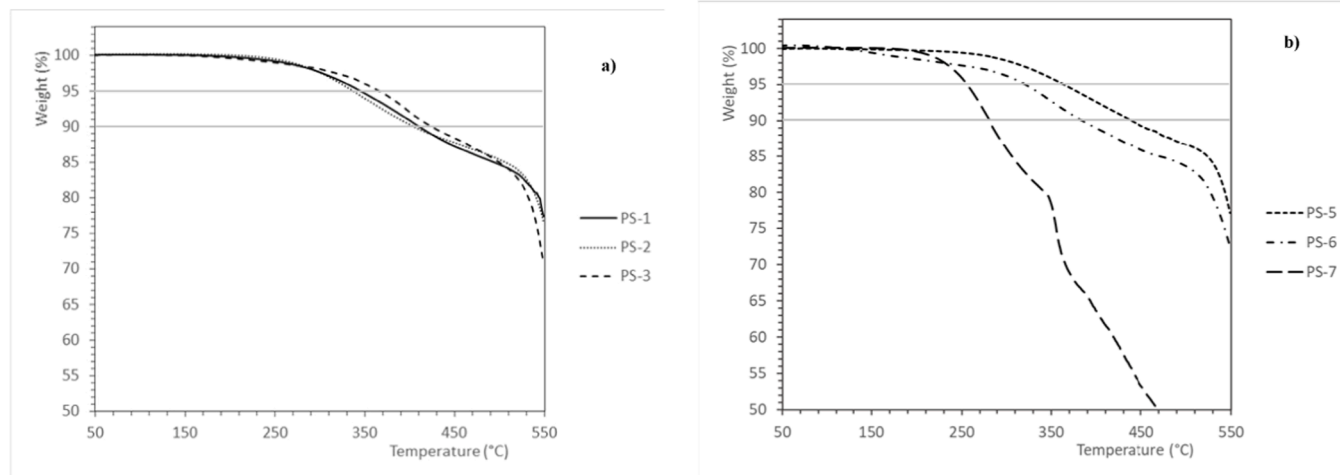


Fig. 3. a) TGA plots for PS-1 - PS-3 (left); b) TGA plots for PS-5 - PS-7 (right).

GC is so sensitive that stationary phase bleeding could be undetected via TGA.

3.2. Column efficiency

The polymers **PS-1–6** were used to coat the inner walls of the capillary silica columns. Column efficiencies were measured at 130 °C via the injection of *n*-tetradecane (*n*-C14) or *n*-pentadecane (*n*-C15). All the stationary phases presented good efficiency (see Table 3), but only **PS-1**, **PS-2** and **PS-5** had very good peak shapes after conditioning at 390 °C, whereas the other stationary phases presented some peak tailings. The peak tailing could be attributed to a lack of capillary wall deactivation or the presence of an adsorption surface on the stationary phase.

Thus, the new stationary phases **PS-1** and **PS-5** exhibited good film formation and coating ability on an untreated capillary (3300 and 3800 plates m^{-1} respectively). These results corresponded to coating efficiency values *E* (%) of 70 % and 80.0 % respectively, indicating good film coatings. Attempts to coat **PS-1** on HDMS or DPTMDS-deactivated capillaries led to a very poor film quality. The stationary phase **PS-2** gave the best results when coated on a DPTMDS deactivated capillary.

3.3. Polarity

The Rohrschneider–McReynolds constants [8,9] are commonly used to characterize the polarity of GC stationary phases. Each probe molecule interacts with the stationary phase in a particular way: *via* dispersive interactions in the case of benzene, X; *via* proton donor and acceptor capabilities and dipolar interactions in the case of *n*-butanol, Y; *via* dipolar interactions and weak proton acceptor interactions in the case of 2-pentanone, Z; *via* dipolar interactions in the case of 1-nitropropane, U; and *via* strong proton acceptor capabilities in the case of pyridine, S. The Rohrschneider–McReynolds constants were calculated at 40 °C, and the sums were calculated as 859, 916 and 841, respectively (Table 4). The columns were conditioned for 2 h at 420 °C prior to analysis. The three columns could be considered intermediate polar phases compared with the ZB-35 column, which was the closest commercial phase in terms of polarity (PN = 18).

3.4. Grob test mixture

The inertness of the chromatographic system, including the column, was assessed using the Grob test mixture [27,28]. The chromatogram obtained from the stationary phase of **PS-2** is presented in Fig. 4. The order of the elution corresponds to a stationary phase with an intermediate polarity. All the peaks were baseline resolved, except for those of dicyclohexylamine and methyl undecanoate which coeluted. It should be mentioned that dicyclohexylamine was eluted when this basic compound was injected separately at high concentration. D(-)-2,3-butane-diol, 1-octanol and 2-ethylhexanoic acid presented significant peak tailing, indicating the existence of weakly acidic adsorption sites. Stationary phases **PS-1** and **PS-5** provided nearly identical chromatograms.

Table 3
Efficiencies and retention of *n*-C14 and *n*-C15 on PS-1–PS-6 columns.

Stationary phase	Capillary deactivation	Efficiency (plates. m^{-1}) for <i>n</i> -C14	Retention factor k	<i>E</i> (%)	Efficiency (plates. m^{-1}) for <i>n</i> -C15	Retention factor k	<i>E</i> (%)
PS-1	untreated	2700	3.7	55	3300	6.4	70
PS-2	DPTMDS	2100	2.4	48	nd	nd	–
PS-3	untreated	2700*	1.9	49*	3150*	4.2	65*
PS-4	untreated	3500*	1.3	58*	2100*	3.9	42*
PS-5	untreated	2800	2.8	54	3800	5.1	80
PS-6	untreated	2100*	2.2	39*	3100*	3.8	63*

nd = not determined;

* = peak tailing, efficiency is given as an indication.

3.5. Column bleed

The column bleed was evaluated in two ways. First, the column bleed was investigated by measuring the loss in retention time for a heavy boiling analyte such as *n*-C40 after repeated injections at high temperature. For this purpose, a mixture of 14 *n*-alkanes selected from the range of *n*-C14 to *n*-C40 was injected 10 times. Two series of 10 repetitions were performed with the oven cycling up to 390 °C (hold 5 min) and 420 °C (hold 5 min). The retention time for *n*-C40 corresponding to the tenth injection was subtracted from the retention time of the first injection (Δt_{1-10}) to calculate the retention time drift, expressed in seconds. A thermally stable stationary phase was the one with the least loss of retention time. The stationary phases **PS-1**, **PS-2** and **PS-5** (10 *m* × 0.25 mm id × 0.25 μ m film thickness) were compared with the commercial column ZB-XLB-HT from Phenomenex (10 *m* × 0.25 mm id × 0.1 μ m film thickness). All three stationary phases outperformed the commercial column. **PS-1** gave the best results with a minimal loss of retention time of 2.3 s when the oven was heated to 390 °C and 4.02 s when the oven was heated to 420 °C (Fig. 5).

These encouraging results prompted us to carry out a more in-depth evaluation of the stationary phase **PS-1**. As such, three series of 50 consecutive injections were performed by injecting a mixture of 34 *n*-alkanes (*n*-C7–*n*-C40). The behavior of a column coated with **PS-1** (10 *m* × 0.25 mm i.d. × 0.25 μ m) was compared to that of Column ZB-35HT Phenomenex® (10 *m* × 0.25 mm i.d. × 0.1 μ m) and Column ZB-XLB-HT Phenomenex® (10 *m* × 0.25 mm i.d. × 0.1 μ m). All the columns were new and had not been used before this testing. The operating conditions for the first series of repeatability were as follows: 10 *m* × 0.25 mm i.d. fused silica capillary column, temperature program from 40 °C (hold 3 min) at 7 °C min^{-1} to 390 °C and hold for 2 min, helium carrier gas, FID, and split injection (1:50). The loss of retention time was calculated after 50 injections for the *n*-C40 peak as the difference between the retention time of the first injection and the retention time of the last injection. The loss of retention time was also calculated in the same manner when the samples were heated to 400 °C (hold 2 min) and 420 °C (hold 2 min) respectively. The 150 analyses of the three series were all consecutive.

For all three series of samples, the column coated with **PS-1** presented the lowest loss of the retention time. Thus, the retention time of the column coated with **PS-1** decreased by 4.2 s after 50 injections when it was heated to 390 °C, 5.9 s when it was heated to 400 °C and 9.2 s when it was heated to 420 °C. The ZB-35HT and ZB-XLB-HT columns have a MAOT of 400 °C as recommended by the manufacturer. Column ZB-35HT exhibited high stability when heated to 390 °C and 400 °C, but when it was heated over the MAOT at 420 °C the retention time was significantly greater (27.2 s). The ZB-XLB-HT column presented the greatest loss of retention time at all three temperatures (Fig. 6).

The second method used to evaluate column bleed consists of measuring the baseline drift of the FID signal of the stationary phases and was compared to the ultralow bleed commercial column ZB-35HT from Phenomenex®. The columns were new and never used, prior to this testing. The commercial column was purchased directly from the original manufacturer and was conditioned as recommended by the manufacturer before testing. The operating conditions were as follows:

Table 4

The Rohrschneider–McReynolds constants and polarity number for stationary phases calculated for PS-1, PS-2 and PS-5.

Stationary phase	benzene (x')	butanol (y')	2-pentanone (z')	nitropropane (u')	pyridine (s')	Sum	PN
PS-1	84	147	230	219	178	859	19
PS-2	98	158	235	233	192	916	21
PS-5	82	137	233	215	174	841	19

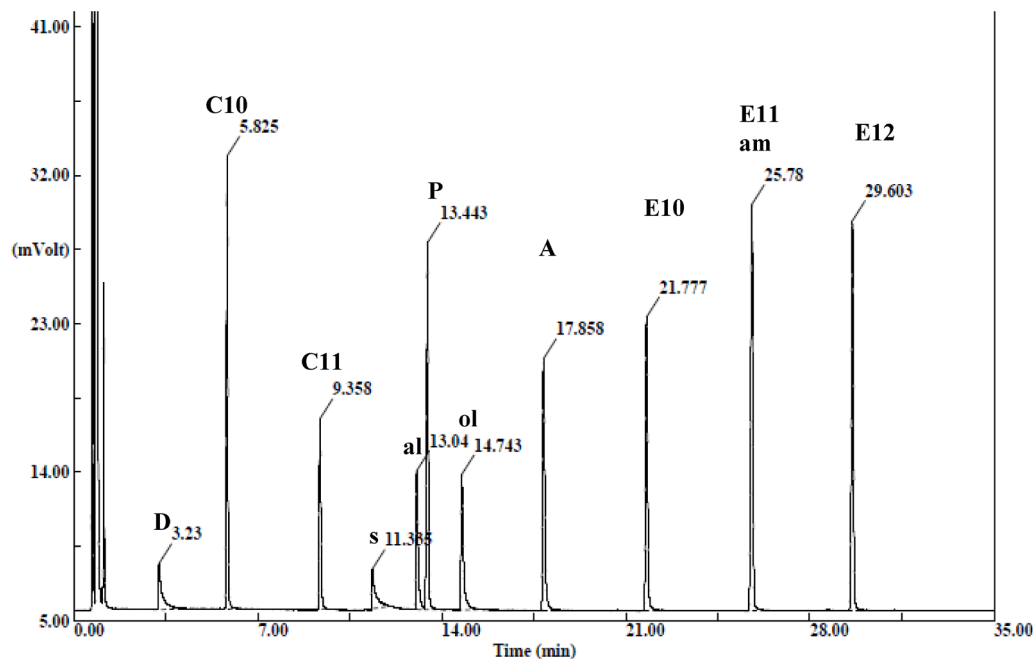


Fig. 4. Separation of the Grob mixture on PS-2. GC conditions: 10 m x 0.25 mm i.d. fused silica, temperature program from 40 °C to 200 °C at 3 °C min⁻¹, helium carrier gas flow rate 0.8 ml min⁻¹, FID, injection volume 0.1 µl, split injection (1:30), concentration of each compound in the text mixture was between 0.5 and 0.6 mg.mL⁻¹. Peak identification: (D) D(-)-2,3-butanediol; (10) decane; (11) undecane; (ol) 1-octanol; (al) nonanal; (E10) methyl decanoate; (S) 2-ethylhexanoic acid; (P) 2,6-dimethylphenol; (A) 2,6-dimethylaniline; (E11) methyl undecanoate, (am) dicyclohexylamine; (E12) methyl dodecanoate.

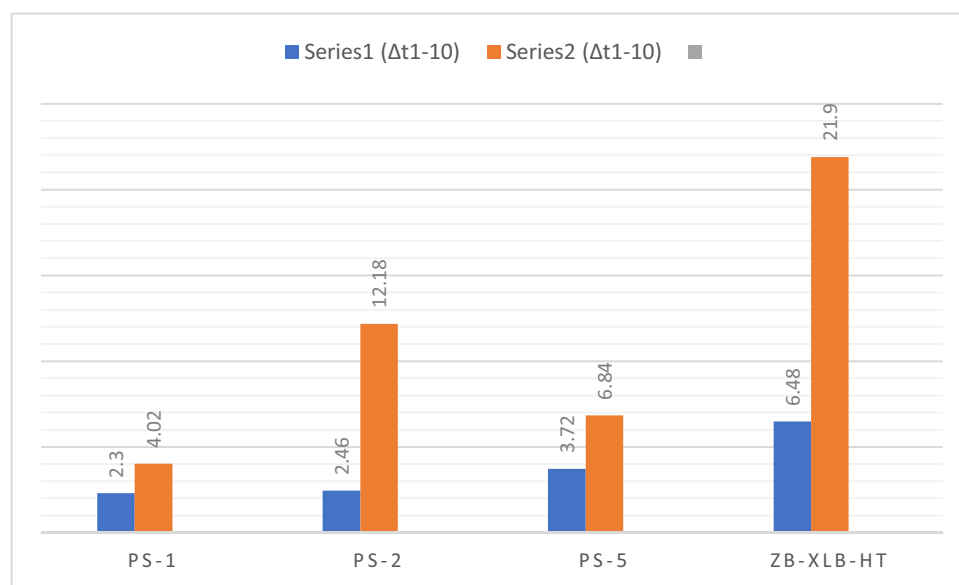


Fig. 5. Retention time stability (Δt , sec) calculated for two different oven programming (series 1 and 2) after 10 repeated injections for PS-1,2,5 and commercial column ZB-XLB-HT: a) Series 1: Oven temperature was set at 40 °C and ramped up to 390 °C (hold 5 min) by rate of 5 °C/min; b) Series 2: Oven temperature was set at 40 °C and ramped up to 420 °C (hold 5 min) by rate of 5 °C/min.

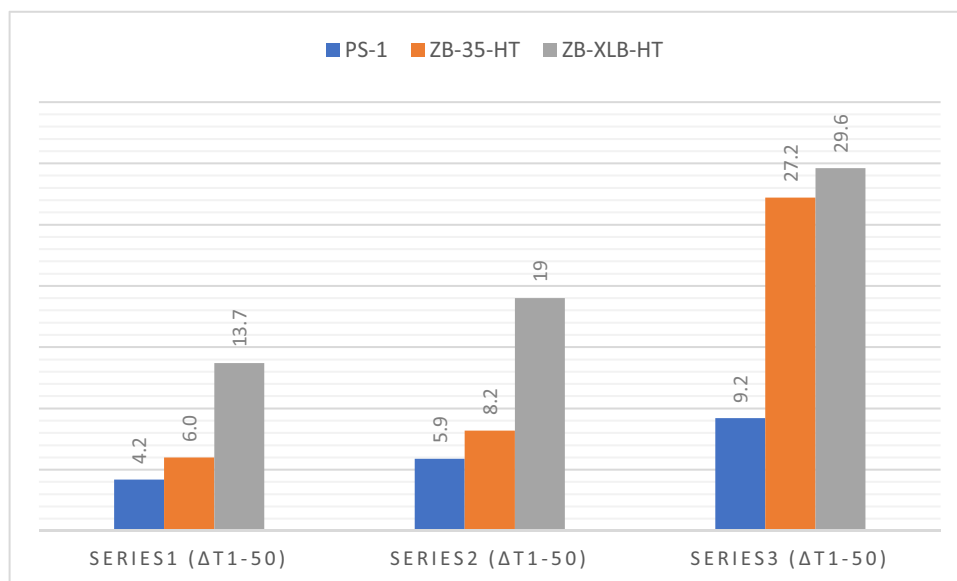


Fig. 6. Retention time stability Δt (sec) after 50 consecutive injections: **Series 1** - GC conditions: 10 m \times 0.25 mm i.d. fused silica, temperature program from 40 °C (hold 3 min) at 7°/min to 390 °C (hold 2 min); helium carrier gas flow rate 0.8 ml min⁻¹, FID 350 °C, split injection (1:50). **Series 2** - GC conditions: temperature program from 40 °C (hold 3 min) at 7°/min to 400 °C (hold 2 min); helium carrier gas flow rate 0.8 ml min⁻¹, FID 350 °C, split injection (1:50). **Series 3** - GC conditions: 10 m \times 0.25 mm i.d. fused silica, temperature program from 40 °C (hold 3 min) at 7°/min to 420 °C (hold 2 min); helium carrier gas flow rate 0.8 ml min⁻¹, FID 350 °C, split injection (1:50).

column dimensions were 10 m \times 0.25 mm i.d. capillary column coated with a 0.1 μ m polymer film, temperature program from 40 °C (hold 60 min) at 1 °C min⁻¹ to 380 °C (hold 3 h), 400 °C (hold 3 h), and 420 °C (hold 1 h); helium carrier gas flow rate 0.8 ml min⁻¹ and FID 350 °C. Both columns presented very low bleeding with a rise in the baseline value of <20 pA. The thermal stability diagram is represented in Fig. 7. The phthalocyanine-polysiloxane stationary phase (PS-1) exhibited a baseline drift profile at 420 °C that tended to stabilize and was therefore more stable and less prone to increase.

3.6. Applications

PAHs are a class of aromatic compounds with at least two condensed

benzene rings. They are labeled priority pollutants with marked carcinogenicity, teratogenicity, and mutagenicity. Fig. 8 illustrates the application of PS-5 to the analysis of PAHs. PS-1 and PS-2 produces very similar results. A total of 20 PAHs were separated with well-shaped peaks within 20 min on a short column of 10 m. The new phthalocyanine-polysiloxane stationary phases showed good shape/size selectivity for PAHs. Most of the PAHs were baseline separated except for the pair of isomers [benzo(b)fluoranthene and benzo(k)fluoranthene] and [benzo(e)pyrene and benzo(a)pyrene] which display only partial resolution, whereas dibenz(a,h)anthracene and indeno[1,2,3-c,d]pyrene were coeluted.

Fig. 9a and b illustrate the application of PS-2 to the analysis of two essential oils. Although, the elution of essential oils does not require very

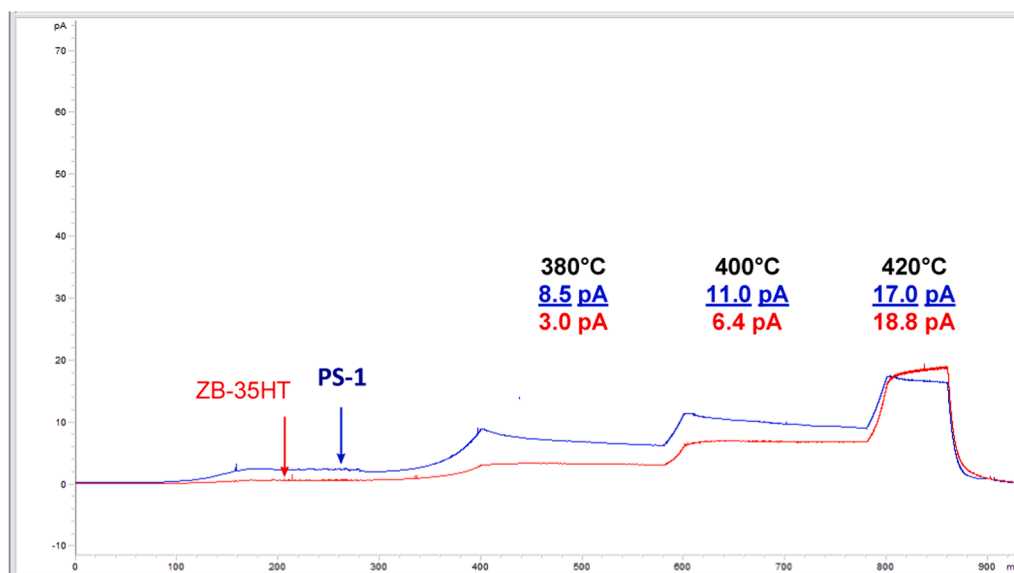


Fig. 7. Thermal stability diagrams of PS-1 (blue) and ZB-35HT® (red) columns coated with 0.1 μ m film thickness. GC conditions: 40 °C (hold 60 min) at 1 °C min⁻¹ to 380 °C (hold 3 h), to 400 °C (hold 3 h), to 420 °C (hold 1 h), helium carrier gas, flow rate 0.8 ml min⁻¹, FID at 350 °C.

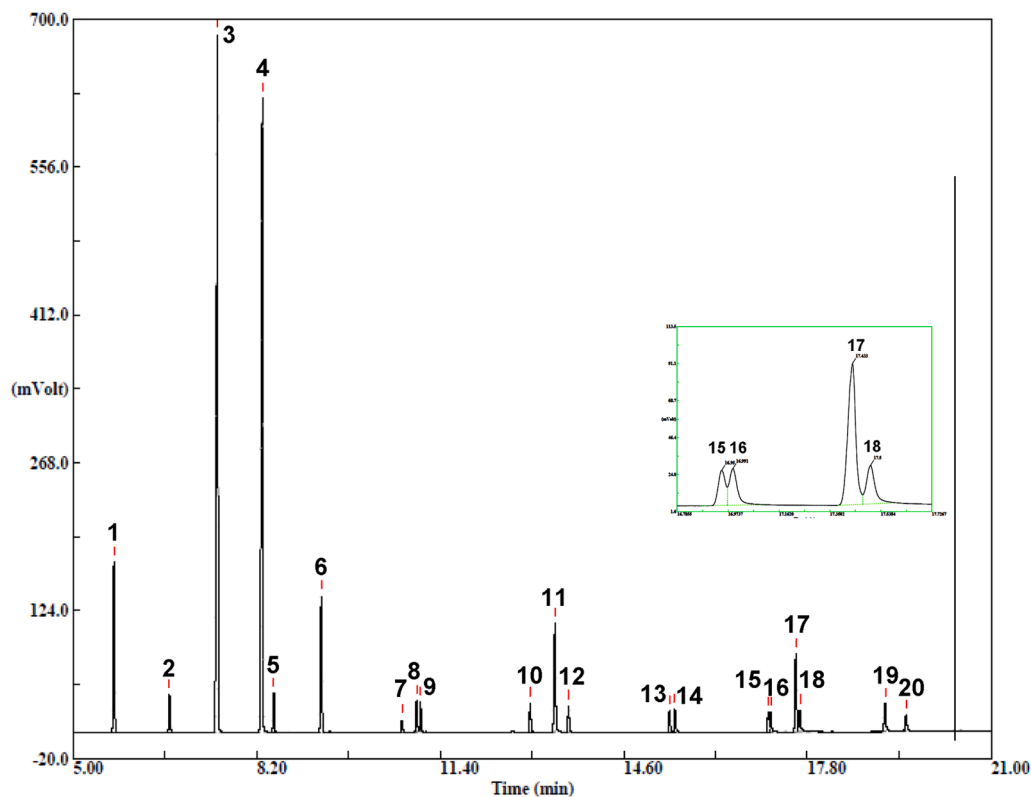


Fig. 8. Chromatograms of the separation of 20 PAHs on the PS-5 column. GC conditions: 10 m x 0.25 mm i.d. fused silica, temperature program from 100 °C at 15 °C min⁻¹ to 390 °C and hold for 2 min, helium carrier gas, flow rate 0.8 ml min⁻¹, FID, split injection (1:30). Peak identification: (1) naphthalene, (2) 2-methylnaphthalene, (3) biphenyl, (4) acenaphthene, (5) acenaphthylene, (6) fluorene, (8) phenanthrene, (9) anthracene, (10) fluoranthene, (11) pyrene, (12) benz(a)anthracene, (13) chrysene, (14) 2-methylfluoranthene, (15) benzo(b)fluoranthene, (16) benzo(k)fluoranthene, (17) benzo(e)pyrene, (18) benzo(a)pyrene, (19) dibenz(a,h)anthracene and indeno[1,2,3-c,d]pyrene, (20) benzo(ghi)pyrene.

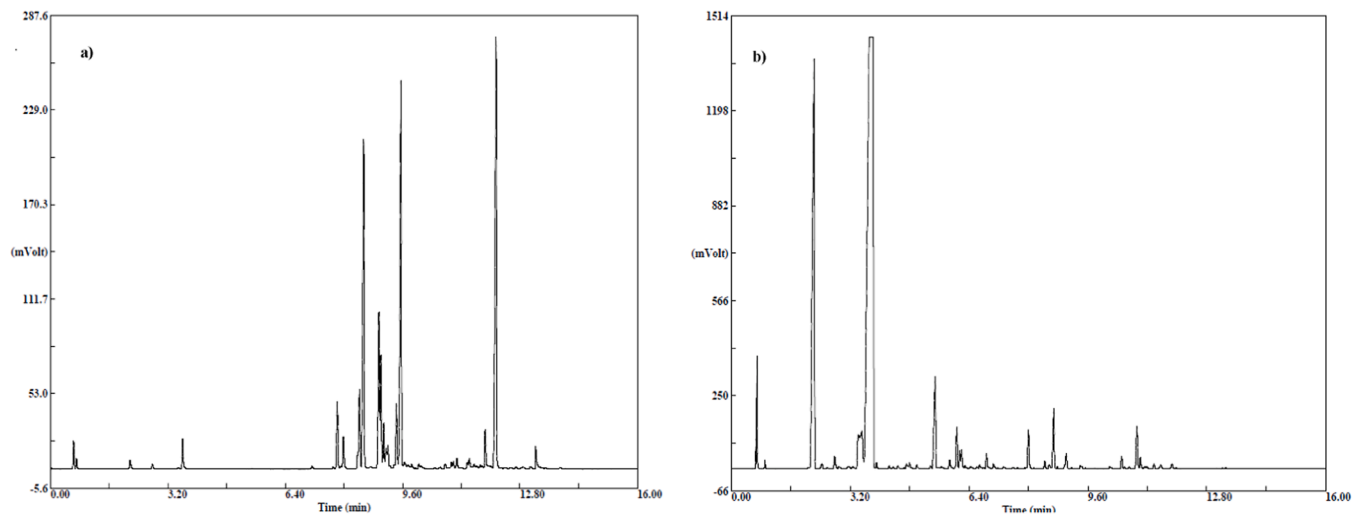


Fig. 9. (a). Separation chromatogram of pure patchouli essential oil (*Pogostemon cablin*); (b). Separation chromatogram of pure eucalyptus essential oil (*Eucalyptus globulus*). GC conditions: 10 m x 0.25 mm i.d. fused silica, temperature program from 50 °C at 10 °C min⁻¹ to 200 °C, helium carrier gas, flow rate 0.8 ml min⁻¹, FID, split injection (1:100).

high temperature analysis, PS-2 effectively separates for patchouli and eucalyptus essential oils.

4. Conclusions

This work proposed a method for the synthesis of siloxane–silarylene polymers containing Pc units. When PS-1, PS-2 and PS-5 were used as a

stationary phase to prepare the capillary column for GC, they showed good coating ability and excellent thermal stability. Evaluation at very high temperatures proved that the new stationary phases were more stable than the commercial high-temperature columns were. Additionally, they exhibited very good selectivity for analytes with a wide range of polarities, including *n*-alkanes, PAHs and essential oils, suggesting that the Pc based stationary phase has great potential for HT-GC

applications. Moreover, these stationary phases can also open new doors to analyze the polar parts of bio-oils obtained from the pyrolysis of plant or plastic samples.

CRedit authorship contribution statement

Mihaela-Liliana Țîntaş: Writing – original draft, Visualization, Formal analysis. **Valérie Peulon-Agasse:** Writing – review & editing, Methodology, Data curation. **Marco Piparo:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition. **Pierre Giusti:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition. **Jean-Maurice Mallet:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Conceptualization. **Pascal Cardinael:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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