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Analysis of monomethyl- and dimethylsiloxane polymers and copolymers (functionalized or nonfunctionalized) by supercritical-fluid chromatography[1]

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Abstract

The performance of capillary supercritical-fluid chromatography (SFC) applied to the analysis of various polysiloxanes was compared with that of low mass size-exclusion chromatography (SEC). SFC gave far better results than SEC and appeared well adapted to the analysis of functionalized or nonfunctionalized polydimethylsiloxanes (PDMSs) of high degrees of polymerization (DP$\leqslant$70), the separation of linear and cyclic oligomers of polysiloxanes and the partial separation of the different oligomer series of dimethyl- and monomethylsiloxane copolymers. Moreover, the study of repeatability using either linear or integral decompression restrictors showed that, in both cases, SFC analyses were repeatable for retention times (repeatibility of 0.5 to 1%) as well as for quantitative measurements (repeatibility of 1.5 to 2%), up to high degrees of polymerization (DP of about 50). Finally, the study of the retention of PDMSs and of polymonomethylsiloxane at constant CO_2 density allowed their identification. We have demonstrated that the logarithms of the retention factors are linear functions of the degree of polymerization. Therefore, we propose a strategy that allows these complex mixtures to be identified, when spiking with pure standards is not possible. This method, based on the identification of the first oligomer of a polysiloxane using the relation $\ln k' = f(DP)$, permits the characterization of the different polysiloxanes analysed.

Keywords: Methylsiloxanes; Polymers; Polysiloxanes

1. Introduction

The analysis of silicone oils and related compounds can be realized by means of classical techniques of analysis, but it becomes very difficult in the case of series presenting high degrees of polymerization [1]. Thus gas phase chromatography has been frequently employed for the analysis of such matrices. Shatz et al. [2] listed 160 analytical methods for the separation of such compounds. However this technique is only applicable to light oligomers, as Wachholz et al. recently confirmed [3]. To achieve resolution of oligomers of higher molecular mass, some authors have proceeded either to pyrolysis of polyorganosiloxanes prior to separation, the identification being realized by pyrolysis–GC–MS [4,5], or

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direct analysis, by high-temperature gas phase chromatography (HTGC) [6,7]. In the last case, the analysis of products having boiling points of between 650 and 750°C, corresponding to polydimethylsiloxane (PDMS) oligomers with molecular masses of between 1000 and 1200 was realized [6].

Similarly the analysis of such matrices has been envisaged by high-performance liquid chromatography. These compounds have been especially separated by reversed-phase liquid chromatography and detected by atomic emission spectrometry using a plasma source (ICP–AES). Thus Biggs et al. [8] report the distribution of linear polyorganosiloxanes oligomers comprising up to 50 atoms of silicon, the time of analysis not exceeding an hour. Despite this remarkable success, it is size-exclusion chromatography that has been the most employed among HPLC techniques for the analysis of polyorganosiloxanes of high molecular mass. Thus Dodgson et al. [9] attempted to study linear and cyclic PDMSs using this technique. Heavy constituents can then be visualized but resolutions are relatively poor [10].

In such a context, supercritical-fluid chromatography (SFC) has gained acceptance [11] as a technique relatively well adapted for the analysis of polyorganosiloxanes. For oligomers of relatively high degrees of condensation, a comparable resolution to that obtained by GC, for the most volatile components, was observed [12–14]. Good results have also been obtained by time-of-flight secondary ion mass spectrometry (TOF–SIMS) [15,16]. It is interesting to note that one of these articles [15] compares the analysis of PDMSs by SFC and TOF–SIMS. The authors demonstrated that good results may be obtained with these two techniques for molecular masses higher than 3000, and that they permit an estimation of the distribution of PDMSs as a function of degree of condensation. However, although these two techniques are well adapted to the analysis of these matrices, SFC proves to be less expensive and easier to implement than the TOF–SIMS method.

With a view to the analysis of silicones oils corresponding: either to reactive or nonreactive oils (functionalized or nonfunctionalized PDMSs), to substituted PDMSs, to mixtures of linear and cyclic compounds or to copolymers, SFC has been the preferred technique. As a result, the study that we report here refers to the evaluation of the potential of capillary SFC for the analysis of such complex matrices. To estimate it objectively, we have envisaged to compare its performance with that of the size exclusion chromatography for low masses.

2. Experimental

2.1. Apparatus

2.1.1. Analyses by supercritical-fluid chromatography

SFC analyses were realized on a SFE 3000 Carlo Erba system (Thermo Quest France, Les Ulis, France) equipped with tandem pumps (maximal pressure: 40 MPa) and a flame ionization detector. To pump correctly the carbon dioxide eluent, the pump of the chromatograph was cooled to 0°C by means of a RTK Lauda cryostat (Prolabo, Paris, France) using a glycol–water mixture. The restrictors used were fused-silica capillaries supplied by Carlo Erba Instruments. The linear restrictors had an internal diameter of 10 μm, a length of 14 cm, for columns measuring 10 m, and a length of 20 cm for columns measuring 20 m. As for the integral restrictors, they allowed flow-rates of 2 or 4 ml min^{-1}. The chromatographic columns were DB5 [(5% phenyl)methylsiloxane] presenting an internal diameter of 100 μm and a film thickness of 0.4 μm, from J&W Scientific (J&W Scientific, Folsom, CA, USA). Their length was 10 or 20 m according to the analyses. Solution concentrations, temperature programming of the oven, as well as pressure or volumic mass programming during the analyses, are indicated on the different chromatograms. Finally, injector and detector temperature were 50 and 300°C, respectively.

2.1.2. Analyses by low mass size-exclusion chromatography (SEC)

Low mass SEC analyses were realized by using the following material: a 880 PU Jasco pump (Prolabo, Paris, France), an automatic injector 231 Gilson allowing 20-μl injections (Gilson, Villiers le Bel, France), a refractometric detector R401 (Waters France, Saint Quentin en Yvelines, France), 3 PL GEL columns: 600×8 mm, d_p=5 μm; average pore

diameter: 100 Å (Polymer Labs., Amherst, MA, USA).

The dichloromethane eluent was continually degassed by helium, the flow-rate of the mobile phase was set to 1.2 ml min^{-1} and the temperature of the analysis to 25°C. Finally, solutions were injected in a CH_2Cl_2 solution to a mass concentration of 1% with toluene as internal standard.

2.2. Solvents and samples

Eluents used for chromatographic analyses were carbon dioxide of SFC quality (Air Liquide, Paris la Défense, France) and dichloromethane of HPLC quality (SDS, Peypin, France). The helium used for the continuous degassing of dichloromethane, during the SEC analyses, was supplied by Air Liquide.

Finally, the majority of the polyorganosiloxanes were provided by Rhône Poulenc (Department Silicones, Saint Fons, France), except the following compounds: hexamethyldisiloxane (Sigma France, La Verpillère, France), 1,1,3,3-tetramethyldisiloxane, purity: 97% (Aldrich France, L'Isle d'Abau, France) and the octamethyltrisiloxane, purity: 98% (Aldrich France).

3. Results and discussion

The different polyorganosiloxane families which were analyzed as well as their structures and their global characteristics are gathered in Table 1.

These samples have all been studied by SFC on an apolar capillary column [(5%-phenyl) methylpolysiloxane], the supercritical fluid used was carbon dioxide, without additive.

3.1. Chromatographic separation

3.1.1. Analysis of nonfunctionalized polydimethylsiloxanes (PDMS)

The majority of manufactured polyorganosiloxanes are of the PDMS type. Those considered in this paper present different degrees of polymerization, increasing from sample A1 to sample A5 (cf. Table 1). The chromatograms obtained by SFC for the A1 and A2 samples, which are the less-condensed PDMSs, are presented in Fig. 1. As shown in this figure, an excellent resolution is obtained for the A2 sample, allowing a complete visualization of its distribution as a function of the degree of condensation. However, in these operating conditions, if the resolution proves to be satisfactory for the most condensed oligomers of the A1 sample, only a partial separation of the first oligomers can be obtained. One can nevertheless note, by comparing these two chromatograms, that the oligomers characterized by a low degree of condensation are totally absent in the A2 sample.

In the case of PDMSs with higher degrees of polymerization (samples: A3, A4 and A5), a 20-m column was used so as to obtain an efficiency gain allowing a correct visualization of these more complex mixtures. Moreover, more eluting analysis conditions were necessary to show the heaviest constituents. Consequently, the solvating power of CO_2 at the end of analysis was increased, the pressure programming final value varied from 24

Table 1
Structure and characteristics of the analyzed polyorganosiloxanes

	Name	Composition	Estimated polymerization degree[a]
Nonfunctionalized PDMSs	A 1–5	$(CH_3)_3SiO[(CH_3)_2SiO]_nSi(CH_3)_3$	A1: $n\sim4$ A2–A5: $n>4$
Functionalized	B 1,2	$HO(CH_3)_2SiO[CH_3)_2SiO]_nSi(CH_3)_2OH$	B1: $n<100$ B2: –
PDMSs	C	$H(CH_3)_2SiO[(CH_3)_2SiO]_nSi(CH_3)_2H$	–
Substituted PDMSs	D	$(CH_3)_3SiO[H(CH_3)SiO]_pSi(CH_3)_3$	–
Copolymers	E 1,2	$(CH_3)_3SiO[(CH_3)_2SiO]_n[H(CH_3)SiO]_pSi(CH_3)_3$	E1: $n\sim13$; $p\sim2,5$ E2: $n\sim10$; $p\sim4$
Cyclic compounds	F	$[(CH_3)_2SiO]_3$	–
	G	$[(CH_3)_2SiO]_4$	–

[a] Polymerization degree indicated by the manufacturer.

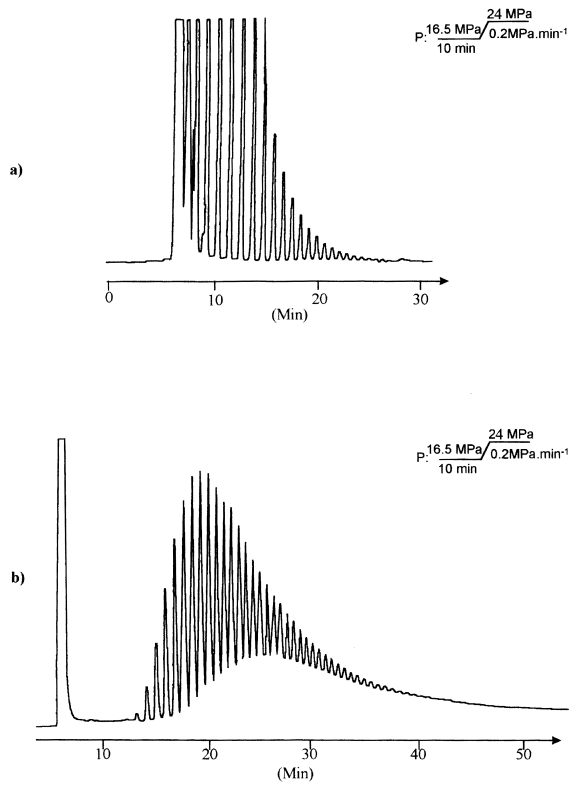

Fig. 1. SFC analysis of PDMSs presenting different polymerization degrees on a capillary column (length: 10 m). Operating conditions: capillary column: DB5 (10 m×100 μm); eluent: CO_2; temperature: 110°C; integral restrictor: 1 ml min^{-1}; linear pressure programming (see chromatograms); solution in CH_2Cl_2: 15% (v/v). (a) Sample A1; (b) sample A2.

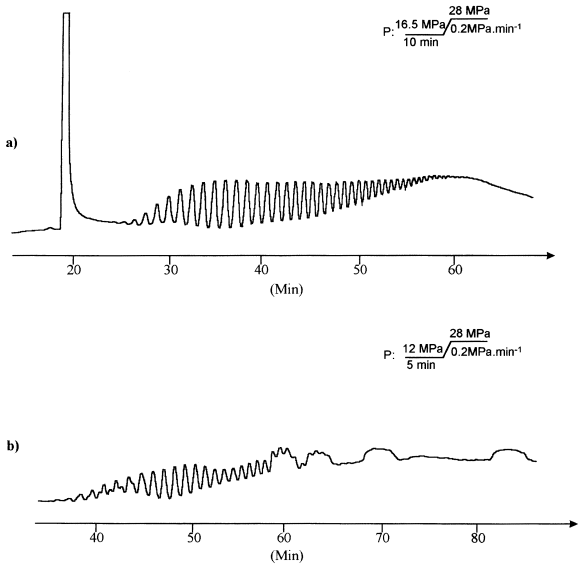

Fig. 2. SFC analysis of PDMSs presenting different polymerization degrees on a capillary column (length: 20 m). Operating conditions: as in Fig. 1. (a) Sample A4; (b) sample A5.

MPa to 28 MPa, the temperature was constant during the analysis. The chromatograms of samples A4 and A5 are reported in Fig. 2.

If the analysis of the PDMSs A4 appears very satisfactory, only a part of the constituents of the sample A5, which corresponds to the low mass oligomers, can be visualized. The partial analysis of this last PDMS reveals the limitation of the chosen configuration: a capillary column [(5% phenyl) methylpolysiloxane], supercritical CO_2 as eluent and flame ionization detector.

Indeed, in these conditions, an increase in the eluting power of the mobile phase proves necessary to obtain the elution of the heaviest oligomers. In the case of capillary SFC, this requires the addition of a noticeable amount of an organic cosolvent to the supercritical CO_2, totally incompatible with the flame ionization detector. However, with this configuration, SFC allows the visualization of approximately 45 peaks during the analysis of the nonfunctionalized PDMS A4. As the less-retained oligomer of this PDMS presents a relatively high degree of polymerization in comparison with the nonfunctionalized PDMSs, we estimate that, in these analysis conditions, the molecular mass upper limit is about 3600.

On the basis of these results, we decided to study the potential of capillary SFC for the characterization of functionalized PDMSs.

3.1.2. Analysis of functionalized and substituted PDMS

Thus we have studied some functionalized PDMSs by capillary SFC, i.e., PDMSs either with SiOH end groups (samples B1 and B2, in Table 1) or with SiH end groups (sample C equally recorded in Table 1). A polymethylsiloxane (sample D of Table 1) was also analyzed.

The two chromatograms obtained for the B1 and B2 samples are represented in Fig. 3a and b, respectively. Whatever the studied sample, the resolution is very satisfactory: baseline separation of the

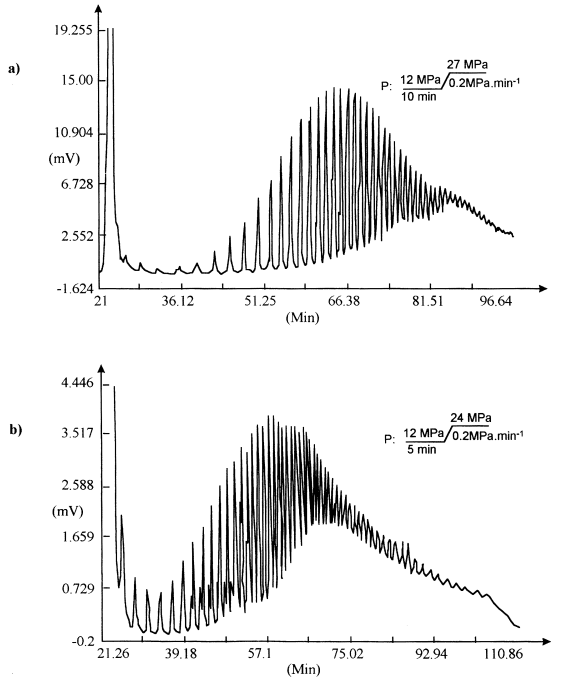

Fig. 3. SFC analysis of PDMSs functionalized by SiOH bonds. Operating conditions as in Fig. 2, except for the restrictor (linear restrictor, I.D. 10 μm). (a) Sample B1 in solution (CH_2Cl_2, 15%, v/v); (b) crude sample B2.

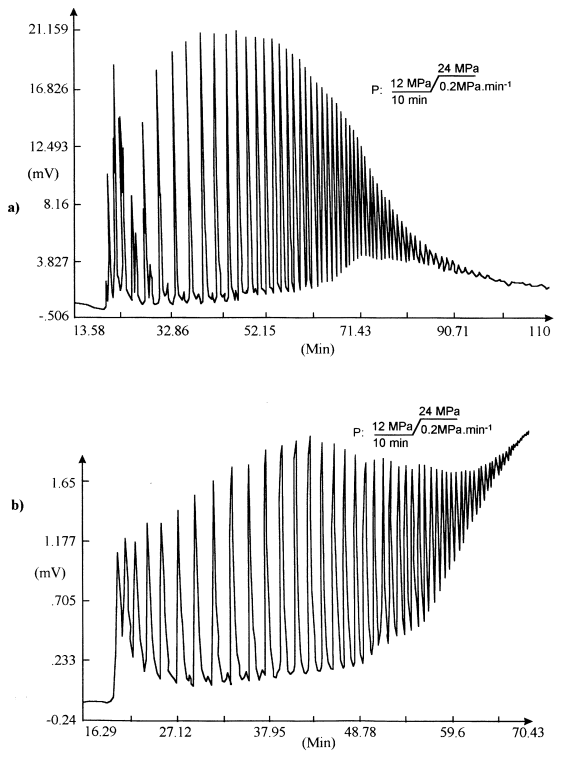

Fig. 4. SFC analysis of PDMSs functionalized by SiH bonds (sample C, chromatogram a) or substituted (sample D, chromatogram b). Operating conditions: as in Fig. 3.

oligomers was obtained for these two PDMSs. Concerning the sample B1, up to 45 peaks were separated, with an analysis time not exceeding 95 min. Thus, the last oligomers visualized have molecular masses close to 3500. As for sample B2, the analysis time was approximately 110 min and up to 60 peaks were resolved at the baseline, the last oligomers reached molecular masses of approximately 4600. Moreover, whichever sample was studied, a secondary distribution was observed and can probably be attributed to the cyclic oligomers.

The chromatograms corresponding to the PDMS C and to the substituted PDMS D are represented in Fig. 4. We still observe a baseline separation of the different oligomers, whichever PDMS was studied. Thus, the analysis of sample C allows the baseline separation of 60 peaks in approximately 110 min, the molecular mass of the last eluted oligomers may reach about 4600. We can equally note for this PDMS, a secondary distribution that could correspond to the cyclic oligomers. Concerning sample D, analysed under the same conditions as sample C, approximately 50 oligomers were separated in 70 min. Thus, the last eluted oligomers present maximal molecular masses close to 3200.

The totality of these results being very encouraging, we attempted to analyze the dimethyl-hydromethylsiloxane copolymers.

3.1.3. Copolymers analysis

Fig. 5a and b show the chromatograms obtained for E1 and E2 samples, presenting the number *n* of $[H(CH_3)SiO]$ groups and the number *p* of $[(CH_3)_2SiO]$ groups (cf. Table 1).

An excellent resolution of these two samples is observed for the oligomers of low condensation degree as well as for the oligomers showing higher molecular masses. Moreover, one can visualize the multiple distributions of these mixtures that seem to correspond to relative variations of the number of groups $[H(CH_3)SiO]$ versus that of $[(CH_3)_2SiO]$

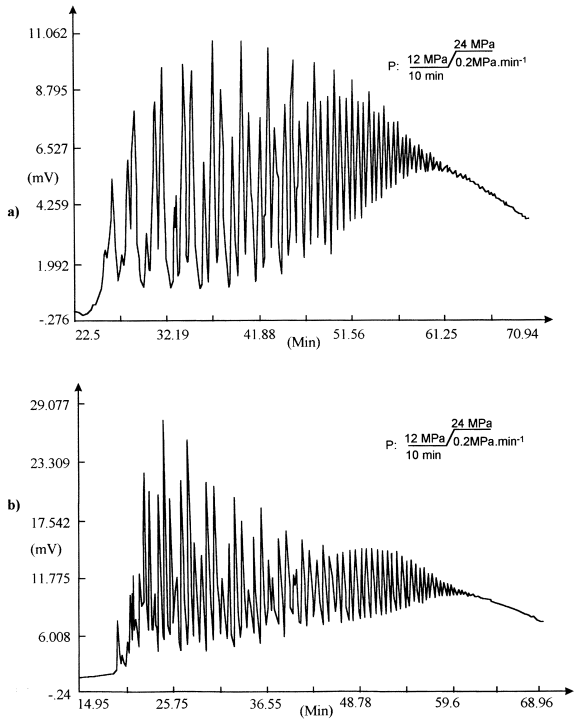

Fig. 5. SFC analysis of copolymers. Operating conditions: as in Fig. 3. (a) Sample E1; (b) sample E2.

moieties. Thus, for sample E1, we can notice that a triple distribution exists. Such a characteristic perfectly corroborates the degrees of polymerization reported in Table 1 and established by the manufacturer. Sample E2 clearly appears more complex, the number of overlapping distributions being probably superior to that obtained for the precedent copolymer.

Thus, from this study, it is clear that capillary SFC is a chromatographic technique well adapted to the resolution of silicones, whatever their complexity, and that it allows: the analysis of functionalized or nonfunctionalized PDMSs with high degrees of polymerization; the likely differentiation of linear and cyclic compounds and the partial resolution of multiple distributions in the copolymers.

To confirm these potentialities, we have subsequently compared the results of the SFC analyses to those obtained by SEC, which is the technique commonly used to analyze polyorganosiloxanes.

3.2. Comparison between capillary supercritical-fluid chromatography and the size-exclusion chromatography for low masses

The chromatograms obtained by SEC of some products analyzed previously by SFC are presented in Figs. 6 and 7. The average pore diameter of the gel was 100 Å.

By comparing these chromatograms to those previously realized by SFC, it can be observed that SEC allows a good separation only for the less condensed PDMSs, i.e., the sample A1. The separation is no longer satisfactory for the PDMS A3, while in SFC, this sample and sample A4 are very well resolved (cf. Fig. 2). Concerning functionalized PDMSs (B2 and C samples) SEC provides acceptable resolutions only for the first oligomers, contrary to SFC (comparison of Fig. 7 with Figs. 3 and 4). The minoritary distributions, that we have previously attributed to the cyclic compounds, do not appear. Finally, in the case of the copolymer E2, SEC does not provide

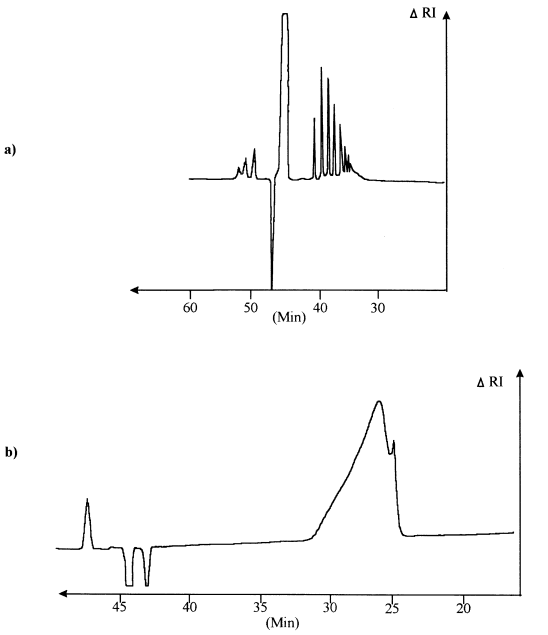

Fig. 6. SEC analysis of PDMSs presenting different polymerization degrees. Operating conditions: 3 columns: PL GEL (5 μm, 100 Å, $L=60$ cm); eluent: CH_2Cl_2; flow-rate: 1.2 ml min^{-1}; refractometric detection. (a) Sample A1; (b) sample A3.

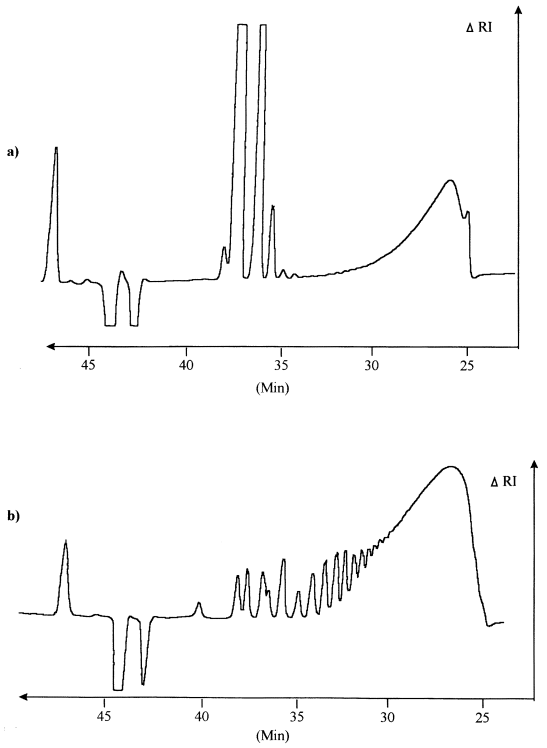

Fig. 7. SEC analysis of functionalized PDMSs. Operating conditions: as Fig. 6. (a) Sample B2; (b) sample C.

evidence of the multiple distributions characterizing this complex mixture.

In summary, if SEC is effectively a technique adapted for the analysis of the oligomers of low molecular masses, it does not allow, contrary to SFC, discrimination of cyclic and linear compounds. Furthermore it does not allow the satisfactory analysis of very complex matrices such as the copolymers.

As these results validated capillary SFC as a choice technique for the characterization of polyorganosiloxanes, we then set out to determine its reproducibility.

3.3. Study of reproducibility

This study concerned the reproducibility of analyses according to the geometry of the restrictor. This element still remains a problem in capillary SFC. Sample B2 was chosen for this study because of its complexity (cf. Table 1). It consists of cyclic and functionalized PDMSs presenting a high degree of polymerization and is a representative sample of the totality of the susceptible polyorganosiloxanes to be met.

During this study, we have compared the decompression restrictors of integral and of linear types. However, it is necessary to underline that, according to Pinkston and Hentschel [17], the fritted restrictors give a better resolution than the other types of restrictors for PDMSs of molecular masses lower than 10 000. The integral restrictors used for this study allow two flow-rates (2 and 4 ml min^{-1}). This type of restrictor, characterized by an important orifice, avoids the relatively rapid and unfortunately unavoidable, progressive-filling phenomena which is observed with the 2 ml min^{-1} integral restrictors. Obviously, with this type of restrictor and considering the pressures used in the course of these analyses, the linear velocity of the mobile phase can no longer be maintained at the optimal value, thus leading to a reduction in analysis times. In these new operating conditions, the linear velocity of the mobile phase corresponds to approximately 5 times the optimal velocity. Nevertheless, this unavoidable loss of efficiency does not necessary imply a loss of resolution. Indeed, analyses being faster and times of analysis being maintained constant, it then becomes possible to elute the most retained products with greater retention factors, i.e., to operate under less eluting conditions and therefore, in the case of supercritical carbon dioxide, with a lower volumic mass. The temperature of analysis being the same, whatever the type of restrictor used, the operating pressures and therefore the differences of pressure between the entrance and exit ($\Delta P = P_{entr} - P_{exit}$) are lower. The loss of selectivity in a SFC system being more important when the difference ΔP is greater, a lowering of the operating pressure, accompanying the utilization of an integral restrictor of 4 ml min^{-1} type, will result in a gain of selectivity. Thus the substitution of a 2 ml min^{-1} decompression restrictor of integral type, by a 4 ml min^{-1} integral restrictor, results in a decrease of the system efficiency and in the increase of its selectivity, leading to a globally constant resolution. It is effectively what we observed experimentally.

Therefore to compare similar conditions, it would

have been necessary, in the case of the decompression restrictors of linear type, to use a diameter of 12 to 15 μm in order to obtain, under the same pressure drop, a linear velocity of the mobile phase identical to that obtained with the 4 ml min^{-1} integral restrictor. Unable to obtain such capillaries, we used linear restrictors of 10 μm. With this last type of restrictor, it would be necessary to use a shorter capillary (10 cm), in order to obtain, under the same pressure drop, a linear velocity truly identical to that obtained with the integral restrictor. As a result of the geometry of the SFC system, the linear restrictor cannot present a length smaller than 14 cm. In such conditions, the study of the reproducibility of the analytical technique, with the linear as well as the integral restrictors, has not been rigorously obtained under the same linear velocity of the mobile phase. This point being established, we have studied successively, the reproducibility of retention times and of relative peaks areas (simulating thus an internal calibration), using decompression restrictors of both integral and linear types. Whatever is the geometry of the restrictor used, this reproducibility study was systematically based on five independent analyses, the variation coefficient corresponding to the ratio of the standard deviation (σ_{n-1}) to the average value of the studied parameter (expressed in %).

3.3.1. Case of an integral type decompression restrictor (4 ml min^{-1})

The results obtained with this restrictor geometry are indicated in Table 2a and b concerning elution times and relative peak areas, respectively. This study has focused on some oligomers covering the retention range. These tables reveal that, with this restrictor geometry, the developed analytical technique results in relatively reproducible and reliable times of retention, a quite acceptable coefficient of variation being obtained whatever the oligomer considered.

Concerning relative peak areas, a satisfactory variation coefficient is obtained in these conditions, varying from 1 to 5% for the first 40 oligomers of sample B2, the relative standard deviation being 10% for the most retained compounds. Considering these values as relatively reasonable, a quantification using internal calibration seems realistic. However, perfect reproducibility from an integral restrictor to an other integral restrictor being extremely difficult to obtain, we have subsequently studied the reproducibility of

Table 2
Study of the reproducibility for some selected chromatographic peaks of the sample B2 analyzed by SFC with an integral restrictor (4 ml min^{-1}).

(a) *Retention time*

Oligomer corresponding to the peak no.	Analysis number Retention time (t_r, min)					t_r (min)	R.S.D. (%)
	1	2	3	4	5		
10	18.6	18.3	18.7	18.8	18.6	19	1
20	31.6	31.9	31.9	31.8	31.7	31.8	0.4
30	43.2	43.5	43.5	43.2	43.4	43.4	0.3
40	54.8	55.3	55.3	54.8	55.0	55.0	0.4
50	68.3	68.9	68.9	68.1	68.5	68.6	0.5

(b) *Relative peak area*

Oligomer corresponding to the peak no.	Analysis number Peak area/max. peak area (%)					Averaged relative area (%)	R.S.D. (%)
	1	2	3	4	5		
10	29.9	32.3	30.4	31.7	30.2	31	3
20	94.4	96.2	94.8	96.4	94.6	95	1
30	96.6	94.8	94.3	92.2	93.7	94	2
40	72.5	71.2	66.8	69.0	76.6	71	5
50	41.3	37.5	31.7	35.5	40.6	37	10

the technique when the decompression restrictor used is a linear capillary.

3.3.2. Case of a decompression restrictor of linear type (10 μm)

The results obtained with this restrictor geometry are given in Table 3a and b reporting elution times and relative peaks areas, respectively. As previously, the studies of reproducibility have been obtained from five independent analyses and have focused on different oligomers covering the retention range.

Some information of interest can be deduced from these tables as well as from their comparison with homologous tables obtained with an integral restrictor (Table 2 a and b). Thus, it appears that the utilization of a linear restrictor leads to a reproducibility of retention times slightly less satisfactory than in the case of a decompression restrictor of integral type. Indeed, the coefficient of variation now reaches 2% against 1% in the case of the integral restrictor. This precision appears nevertheless acceptable. On the other hand, the reproducibility of relative peak areas proves identical, whatever the geometry of the decompression capillary, and is comprised of between 2 and 5% for the oligomers containing up to 40 monomer groups.

In summary, the chromatographic technique proposed is relatively reproducible from a qualitative viewpoint (retention times) and from a quantitative viewpoint (relative peak areas) for the polyorganosiloxanes presenting less than 40 monomer groups, whatever the decompression mode used.

On the basis of this observation, we then studied the retention of the polyorganosiloxanes as a function of the polymerization degree in order to identify the different oligomers. Nevertheless, to validate such a strategy, we have, for the first time, limited this approach to the case of nonfunctionalized and substituted PDMSs that apparently do not contain components other than the expected linear oligomers and to series where monodispersed standards are easily available.

3.4. Study of the retention of nonfunctionalized and substituted PDMSs according to their degree of polymerization

For different series of homologous compounds: alkanes, ketones, aromatic hydrocarbons, it has been demonstrated that in SFC [18,19], for a given value of the volumic mass, there exists a relationship of the type:

Table 3
Study of the reproducibility for some selected chromatographic peaks of the sample B2 anlayzed by SFC with a linear restrictor (10 μm)

(a) *Retention time*

Oligomer corresponding to the peak no.	Analysis number Retention time (t_r, min)					t_r (min)	R.S.D. (%)
	1	2	3	4	5		
10	27.9	28.0	29.3	29.3	28.9	29	2
20	45.6	45.9	47.4	47.4	46.9	47	2
30	61.8	62.0	63.9	63.8	63.8	63	2
40	78.5	78.6	81.1	80.9	80.4	80	2
50	97.4	97.7	100.9	100.7	100.3	99	2

(b) *Relative peak area*

Oligomer corresponding to the peak no.	Analysis number Peak area/max. peak area (%)					Averaged relative area (%)	R.S.D. (%)
	1	2	3	4	5		
10	30.4	29.2	28.9	30.5	28.5	29	3
20	95.8	94.2	97.2	97.1	92.6	95	2
30	95.8	96.1	94.4	94.1	96.3	95	1
40	72.9	76.9	66.7	70.6	74.1	72	5
50	18.8	26.9	19.4	18.2	28.5	22	22

$$\ln k' = a + bn \quad (1)$$

where n is the number of carbon atoms of the considered compound, and a and b are constants that are functions of the nature of the studied compound as well as of the operating conditions.

Having a technique clearly adapted for the separation of the homologous oligomers constituting the PDMSs, we have considered whether such a relationship could be generalized to a skeleton presenting a structure totally different to the hydrocarbon chains studied until now. So, we have retained, as test sample, the nonfunctionalized sample of PDMS A1, of general formula: $(CH_3)_3SiO[(CH_3)_2SiO]_n$-$Si(CH_3)_3$ (cf. Table 1). The analysis of this sample, using constant volumic mass, i.e. under given pressure and temperature, between the final and initial conditions indicated in Fig. 1, allows visualisation of the first 11 oligomers. So in order to know the correspondence between the number of chromatographic peaks and the number n of $[(CH_3)_2SiO]$ groups constituting the oligomers of this PDMS, we have injected, under the same conditions: the hexamethyldisiloxane or HMDS (corresponding to $n=0$) and the octamethyltrisiloxane or OMTS ($n=1$).

From these analyses, and by taking as reference the retention time of the methanol for the calculation of the different retention factors of the visualized oligomers, we have been able to obtain the evolution of these retention factors as a function of the group number n (cf. Fig. 8a). The methanol can be, as a first approximation, assimilated to an unretained compound (inert compound) since among the totality of studied solvents (chloroform, dichloromethane, methanol, ethanol, acetone and acetonitrile), it proves to be the least retained.

Fig. 8a shows that the octamethyltrisiloxane has a chromatographic behavior identical to that of peak 1. This allows us to assert that the corresponding compound comprises only one group $[(CH_3)_2SiO]$. In such conditions, we can attribute to each chromatographic peak, a number of $[(CH_3)_2SiO]$. Moreover, a quasilinear curve obeying the following relationship is obtained:

$$\ln [(t_r - t_{methanol})/t_{methanol}] = -3.14 + 0.45n \quad (2)$$

n now being the number of $[(CH_3)_2SiO]$ groups constituting the oligomers of the studied PDMSs.

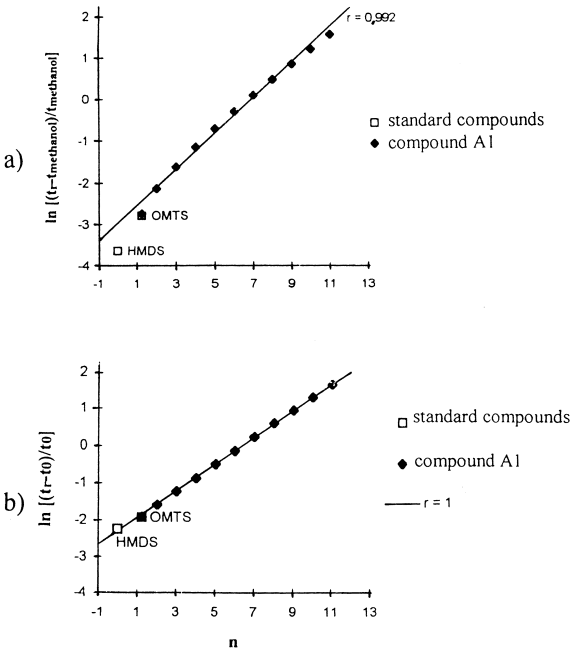

Fig. 8. Evolution of retention factors as a function of the number n of $[(CH_3)_2SiO]$ groups for sample A1, HMDS and OMTS. Operating conditions: capillary column: DB5 (20 m×100 μm); linear restrictor: I.D. 10 μm; eluent: CO_2; temperature: 110°C; pressure: 14 MPa.

The good correlation coefficient ($r=0.992$) clearly demonstrates that the previously established relationship for homologous series based on the same hydrocarbonated skeleton (Eq. (1)) can be generalized to homologous series presenting different structures, i.e. in the present case, dimethylsiloxanes chains. The light curvature noticed on Fig. 8a can probably find its origin in a slight imprecision in the time-of-purge (t_0) of the column. Indeed, at this stage of the experimentation, nothing allows invalidation or confirmation that the methanol behaves as an inert compound. The configuration of the equipment did not allow rigorous access to the purge time, therefore, we have tried to determine a t_0 value from the evolution of retention times according to the number n of $[(CH_3)_2SiO]$ groups for a given homologous series. Indeed, if this linear relationship is verified, namely:

$$\ln [(t_r - t_0)/t_0] = An + B \quad (3)$$

it can equally be written under the form:

$$t_r = t_0[1 + \exp(An + B)] \quad (4)$$

Thus, experimental retention times obey such a law if:

$t_0 = 16.12$; $A = 0.36$ and $B = -2.27$

The comparison of the value thus found for t_0 with that of the elution time of methanol ($t_{MeOH} = 17.39$ min) shows that this latter cannot be considered as an unretained compound and that it presents in reality a slight interaction with the stationary phase, its retention factor being equal to 0.078. This extremely important point being established, we have represented the real evolution of retention factors for the different oligomers constituting the studied PDMSs as a function of the number n of $[(CH_3)_2SiO]$ groups. This evolution is described in Fig. 8b, reporting the chromatographic behavior of our reference compounds (HMDS and OMTS). Thus, we can observe the excellent correlation between $\ln k'$ and n ($r = 1$) when one correctly evaluates t_0. Moreover, we can notice on the one hand, the identical chromatographic behaviors of the octamethyltrisiloxane and of the oligomer corresponding to peak 1 and on the other hand, the perfect adjustment of $\ln k'$ (HMDS) on the straight line for a number of $[(CH_3)_2SiO]$ null groups.

In a similar way, we have drawn $\ln k' = f(n)$ for this same compound at different pressures, the temperature being maintained constant and equal at 110°C (Fig. 9).

Whatever the volumic mass, Eq. (3) is always verified, the coefficient of correlation being very satisfactory. However, as one would expect, the slope and the ordinate origin vary, according to the analytical conditions used. Consequently, a comparison can be realized only if one operates under identical analytical conditions. Thus, in the case of nonfunctionalized PDMSs presenting curtailed distributions, it becomes then possible to attribute, step by step, a number of dimethylsiloxanes to each of the constituents.

Thus, Fig. 10a shows the evolution of retention

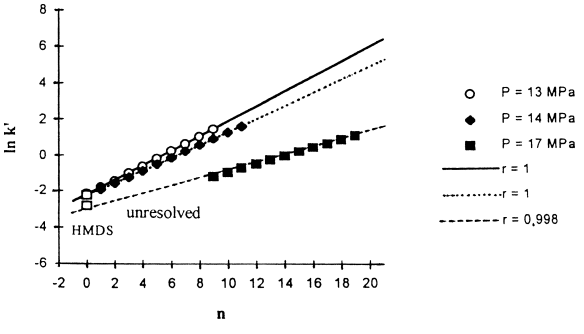

Fig. 9. Evolution of retention factors as a function of the number n of $[(CH_3)_2SiO]$ groups in the case of the sample A1, for different volumic masses. Operating conditions: as Fig. 8, the pressure excepted.

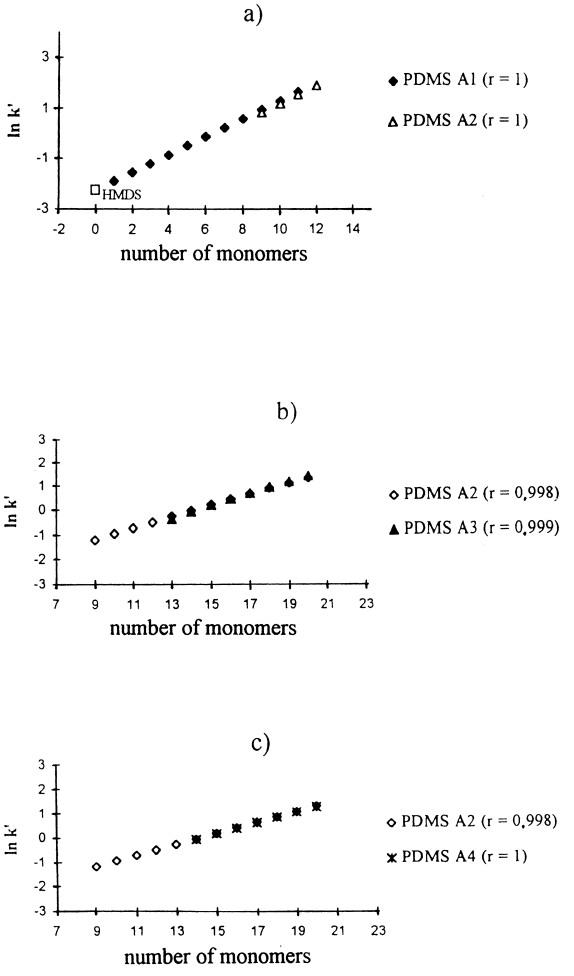

Fig. 10. Comparison of retention factors as a function of the number of $[(CH_3)_2SiO]$ groups for different PDMS: (a) A1 and A2 samples (pressure: 14 MPa). (b) A2 and A3 samples (pressure: 17 MPa). (c) A2 and A4 samples (pressure: 17 MPa). Other operating conditions: as Fig. 8.

factors as a function of the number of [$(CH_3)_2SiO$] groups of A1 and A2 samples, to a pressure of 14 MPa and to a temperature of 110°C. These linear relations allow the number of groups of the first oligomer present in the PDMS A2 to be determined (i.e. $n=9$). In the same way, we have been able to determine the number of groups of the first oligomer contained in each of the nonfunctionalized studied PDMSs (Fig. 10 b and c). Thus, the first oligomer of the sample A3 is composed of 13 [$(CH_3)_2SiO$] groups and that of sample A4 of 14 groups. From these results and from the chromatograms obtained by SFC and by programming volumic mass, we have been able to establish the distribution of the oligomers of each nonfuntionalized PDMS. We have supposed that the response coefficient of each oligomer is identical. It was then possible to draw the combined histograms (area and cumulated area) of these different PDMSs and average polymerization degrees (DPs) can be proposed for each of the studied PDMSs. Thus, the sample A1 would present an average number of 3.7 groups, in agreement with values given by the manufacturer ($n\sim4$). Similarly, the average DPs of the A2 and A3 PDMSs would be 20.1 and 24.8, respectively. Finally, concerning sample A4, the presence of two distributions, respectively centered on 21 and 28 [$(CH_3)_2SiO$] groups is likely. In fact, if one looks at the group number corresponding to 50% of the cumulated area, we then obtain $n=27.4$ groups.

Thus, at the end of this study on the evolution of the retention of nonfunctionalized PDMSs, it appears that SFC allows, by comparison of their chromatographic behaviors, the identification of the nature of their various constituents and thus to establish their essential characteristics, i.e.: the minimal number of [$(CH_3)_2SiO$] groups, the maximal number of [$(CH_3)_2SiO$] groups, and the average polymerization degree.

The precise identification that we obtained allows us to establish without ambiguity that one cannot visualize, under these operating conditions, nonfunctionalized PDMS oligomers containing more than 60 dimethylsiloxane groups, i.e. an oligomer presenting a maximal molecular mass close to 4600. We have then attempted to generalize this experimentation to other PDMSs. However, before undertaking this study, it has been necessary to define a strategy of identification. Indeed, for nonfunctionalized PDMSs, the identification is relatively easy because one of our two standard compounds, OMTS, is present in one of the studied series (corresponding to the PDMS A1). Consequently, the attribution can be realized by spiking or by studying the evolution of the retention factors as a function of the polymerization degree. So as to validate this second method, we have drawn, in the case of nonfunctionalized PDMS (for which the identification has been perfectly established) the evolution of the coefficient of correlation corresponding to Eq. (3) as a function of the number of groups attributed to the first eluted oligomer ($n1$). If one consider a 0.998 value of the correlation coefficient as acceptable, the uncertainty on the number of dimethylsiloxane groups (n_1) attributed to the first eluted oligomer is relatively small (Table 4).

Moreover, as evidenced in the Table 4, we observe a relatively satisfactory agreement between the real value and the value thus estimated for n_1. Nevertheless, this agreement is better if the degree of polymerization of the first oligomer is small, i.e. close to the compound of reference one, in our case, the HMDS. Under such conditions and when the coelution cannot be envisaged, as a result of the absence of monodispersed and polydispersed standards, we can propose, for any series, the following strategy of identification:

1. analyze the unknown sample under isocratic conditions and, if possible, analyze a known oligomer of the same structure (for instance the head compound, $n=0$);
2. use Eq. (4) to estimate the purge time under the same conditions; this estimation is done from the

Table 4
Comparison of true and estimated values of the condensation degree for the first eluted peak of different nonfunctionalized PDMSs

Nonfunctionalized PDMS	Number n_1 of group corresponding to the first eluted oligomer	
	True	Estimated ($r\leq0.998$)
A1	$n_1=1$	$1\leq n_1\leq2$
A2	$n_1=9$	$6\leq n_1\leq9$
A3	$n_1=13$	$9\leq n_1\leq13$
A4	$n_1=14$	$10\leq n_1\leq18$

retention times of the different oligomers of a known sample;

3. search the values of n_1 (polymerization degree of the first oligomer eluted during the analysis of the unknown sample) resulting in correlation coefficients greater than 0.998 for the equation $\ln k' = f(n)$ (this correlation including the head compound);
4. analyze this sample with density programming and estimate its characteristics: minimum, maximum and average degrees of polymerizaton.

It is this strategy that we have applied to the substituted PDMS D that seems to contain the expected linear oligomers, and for which there is no commercially available standard. Moreover, the head compound of this PDMS series ($n=0$) corresponds to the HMDS that is also a reference compound for nonfunctionalized PDMSs. Fig. 11 shows the evolution of the correlation coefficient according to n_1. For the PDMS D, this coefficient being superior or equal to 0.998 for n_1 inferior or equal to 3, one can reasonably suppose that the number of monomers of the first eluted compound is one, two or three. As the best coefficient of correlation is obtained for $n_1=2$, it is this last value that we will retain. In this case, if one draws $\ln k'$ as a function of the polymerization degree for the A1 and D samples in the same operating conditions, one obtains two straight lines, of which the intersection point corresponds, as expected, to the reference compound, namely in the present case, the HMDS (cf. Fig. 12). This verification validates a posteriori, the value retained for the condensation degree of the first oligomer constituting the PDMS D.

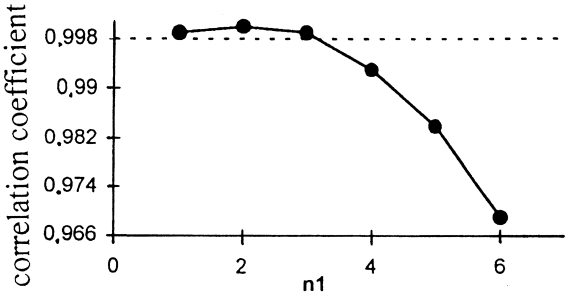

Fig. 11. Evolution of the correlation coefficient corresponding to Eq. (3) as a function of the number n_1 of monomer groups attributed to the first oligomer present in the PDMS D.

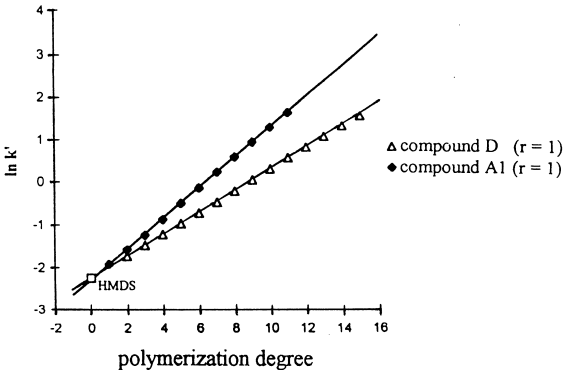

Fig. 12. Evolution of retention factors for the A1 and D samples as a function of the condensation degree. Operating conditions: as Fig. 8.

We can equally notice from these graphs that the time of retention, at an identical degree of condensation, is shorter for the oligomers of D than for A1. In other words, the substitution of a hydrogen of the monomers by a methyl group results, in the case of an apolar stationary phase [(5% phenyl)methylpolysiloxane], in a longer elution time of these last compounds. This observation leads to the attribution of a more polar character to the SiH bond as compared to the $SiCH_3$ bond. This is in perfect agreement with a study reported by Voronkov et al. [20], using infrared spectroscopy, that attributes the shift to the high frequencies of stretching vibration for Si-O-Si, when one substitutes CH_3 by H in the HDMS, to the more electronegative character of the H substituent relative to the CH_3 group.

The condensation degree of the oligomer presenting the lower molecular mass in the PDMS D, being established, we can attribute a precise condensation degree to each of the oligomers constituting this polyorganosiloxane. Then from the histogram giving areas and cumulated areas, deduced from the chromatographic analysis of this mixture, it becomes possible to determine an approximate value of the average polymerization degree, i.e. $n=17.3$ for this substituted PDMS. It would be equally interesting to proceed to such a study in the case of the other polyorganosiloxanes. Unfortunately, these formulations prove far more complex than nonfunctionalized and substituted PDMSs because of the presence of constituents still unidentified at this stage.

4. Conclusion

Capillary SFC is proposed as an analytical technique perfectly adapted for the analysis of matrices containing a great number of structurally close products and presenting a medium polarity, such as silicones oils. It appears very complementary to liquid chromatography and gas chromatography, by allowing: the analysis of PDMSs, functionalized or nonfunctionalized, and presenting high condensation degrees; the differentiation of linear and cyclic chains; finally, the partial visualization of multiple distributions of the dimethylhydromethylsiloxanes copolymers. If a study of the chromatographic behavior and the establishment of a relationship between the logarithm of the retention factor and the number of monomer units allows a precise identification of constituents in the case of nonfunctionalized or substituted PDMSs, such an approach proves impossible in the case of functionalized PMDSs or copolymers. In the case of the copolymers, the complexity is too great, with multiple overlapped distributions, and this approach will fail. Consequently, in order to proceed to an equally precise identification of these extremely complex mixtures, we decided to study the potentiality of the coupling between capillary supercritical fluid chromatography and Fourier transform infrared spectroscopy to overcome this problem.

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