Behaviours of siloxane polymers containing phenyl or silarylene as stationary phases for high-temperature gas chromatography

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ABSTRACT

Several kinds of mechanisms have been proposed for the thermal degradation of methylphenylsiloxane and dimethylsiloxane–silarylene copolymer in an inert atmosphere. These polymers have been used as gas chromatographic stationary phases at temperatures as high as 370°C, but there is no report on the thermal stability of the polymers during prolonged use at high temperatures, especially above 400°C. In this work, the thermal stability of these stationary phases at temperatures as high as 420°C was examined using a deactivated metal capillary column, which is much more thermally stable than the fused-silica capillary columns. It was found that these phases degraded at 380–400°C by eliminating arylene-containing moieties, which led to cross-linking, and the peak shapes therefore deteriorated. With a column treated at 420°C, elution of solutes was considerably delayed and the elution order became unusual, which could not be rationalized from the behaviours of these medium-polarity and non-polar columns. It was concluded that the medium-polarity stationary phases in these columns finally became highly cross-linked dimethylsiloxane by losing arylene-containing moieties, thus giving poor peak shapes.

INTRODUCTION

Several mechanisms have been proposed for the thermal degradation of methylphenylpolysiloxane under an inert atmosphere[1,2]. Together with the formation of benzene and cross-linking structures, the formation of methylphenyltricyclosiloxane, which results from the flexibility of the siloxane main chain as in the case of dimethylpolysiloxane, has been reported[1,2]. Arylene-containing dimethylsiloxane–

silarylene copolymer, whose main chain flexibility is restricted, showed improved thermal stability at 400–450°C in thermogravimetric analysis (TGA)[3–5]. Applications of the copolymer as a stationary phase in capillary gas chromatography (GC) have been proposed[6,7]. Above 350°C, however, scission of the main chain and the formation of branched structures are known to occur owing to the interactions between the main chains[5]. Although these degradations of the copolymer do not result in weight loss and cannot be observed by TGA, the use of the copolymer for high-temperature GC (HTGC) may not be as desirable as expected. Capillary columns of methylphenylsiloxane–silarylene copolymer and methylphenylpolysiloxane have already been characterized[8,9]. The highest temperature examined, however, was only 370°C and further study is required in order to establish the behaviour of the columns at higher temperatures such as those used in HTGC.

We have previously reported on the development of novel deactivated metal capillaries that exhibit superior characteristics for HTGC such as the maintenance of inertness, thermal stability and mechanical strength in comparison with those for fused-silica capillaries[10,11]. In this work, the high-temperature behaviours of methyl-phenylsiloxane and dimethylsiloxane–silarylene copolymer were investigated, taking advantage of the high-temperature properties of the deactivated metal capillaries.

EXPERIMENTAL

Stationary phase synthesis

Methylphenylsiloxane prepolymer. Siloxanol-type prepolymer containing 50% phenyl groups was prepared from methylphenyldichlorosilane according to the procedure of Madani and Chambaz[12].

Tetramethyldisiloxanediol (TMDSD). To a solution of ammonium carbonate (110 g) in distilled water (410 ml) was added dimethyldichlorosilane (65 ml) over 2.5 h with vigorous stirring at 0°C. The mixture was then kept standing at −5°C for 48 h. The crystals obtained were extracted with light petroleum and dried over magnesium sulphate. Concentration of the filtrate afforded crystalline TMDSD, which was further recrystallized from light petroleum before use.

Dimethylsiloxane–silarylene precopolymer. Prepolymers A and B were prepared from *p*-phenylenebis(dimethylsilanol) (PPBDMS) and TMDSD according to the reported procedure[7] under the conditions shown in Table I. Briefly, PPBDMS and TMDSD were dissolved in 150 g of toluene and tetramethylguanidine di-2-ethyl-hexanoate (TMG) was added as a catalyst. The mixture was heated to reflux and then filtered. Removal of toluene afforded a viscous product, which was dissolved in diethyl ether, washed with water five times, and dried over magnesium sulphate. Removal of the ether gave the prepolymers.

Column preparation

Methylphenylsiloxane column. Methylphenylsiloxane prepolymer was coated statically on an RAS 25 metal capillary (35 m × 0.25 mm I.D.), prepared by Nippon Chromato, which was heated at 250°C for 15 h under a flow of nitrogen at 1 ml/min and then at 300°C for 24 h under a flow of nitrogen at 0.2 ml/min. Rinsing with 5 ml of methylene chloride gave a 30-m column with a film thickness of 0.25 μm.

Dimethylsiloxane–silarylene columns. Toluene solutions of prepolymers A (5%)

TABLE I

PREPARATION OF DIMETHYLSILOXANE–SILARYLENE PREPOLYMERS

Prepolymer	Dope			Reaction time[a]
	PPBDMS	TMDSD	Catalyst (TMG)	
A	4.29 g 19.0 mmol (50.9 mol-%)	2.86 g 18.3 mmol (49.1 mol-%)	0.79 g	9 h
B	5.05 g 22.4 mmol (53.8 mol-%)	3.00 g 19.2 mmol (46.2 mol-%)	0.46 g	5 h

[a] At reflux temperature.

and B (7%) were coated dynamically on an RAS 25 deactivated metal capillary (12.5 m × 0.25 mm I.D.). Column A, coated with prepolymer A, was heated under a flow of hydrogen at 1 ml/min at 250°C for 50 h. Column B, coated with prepolymer B, was heated at 300°C for 20 h under a similar flow of hydrogen. Columns 10 m long were used.

Column evaluation

Methylphenylsiloxane column. The column was evaluated on a Varian 3410 gas chromatograph. Helium was used as the carrier gas and the inlet pressure was adjusted to 12.5 p.s.i. The flow-rate at ambient temperature was 1.0 ml/min and the linear velocity was 24.5 cm/s. Thermal treatment of the column and the subsequent GC measurement to evaluate the column were carried out without removing the column during the experiment, in order to minimize experimental errors. Thermal treatment of the column was carried out successively at 300°C for 15 h, at 350°C for 15 h, at 400°C for 17 h and at 420°C for 5 h, under a flow of helium at 12.5 p.s.i., the same pressure as that in the GC measurement. After each thermal treatment, the column was evaluated with a polarity test mixture (Grob and Grob's test mixture[13]). The GC conditions are given in the figure captions. Separation factors were measured for a mixture of tridecane and 1-decanol.

Dimethylsiloxane–silarylene columns. Thermal treatments of the columns were carried out in an oven under a flow of hydrogen at 1.5 ml/min. After each thermal treatment described below, GC measurement using a simplified polarity test mixture[10] was performed with an Ohkura (Tokyo, Japan) Model 701 instrument to study the changes in peak shapes and elution order. Thermal treatment for column A was at 350°C for 25 h and then at 380°C for 25 h, and for column B at 350°C for 25 h and then at 400°C for 25 h. The baseline shift was also measured for column B.

RESULTS AND DISCUSSION

Variation of methylphenylsiloxane column by thermal treatment

Separation factor (α). Separation factors were measured for a mixture of tridecane and 1-decanol using columns heated at various temperatures. As shown in

TABLE II

VARIATION OF CAPACITY FACTORS (k') AND SEPARATION FACTORS (α) WITH THERMAL TREATMENT OF METHYLPHENYLSILOXANE COLUMN[a]

Thermal treatment[b]	$k'_{(C_{13})}$[c]	$k'_{(C_{10}ol)}$[d]	$\alpha_{(C_{10}ol/C_{13})}$
300°C, 15 h	4.43	7.28	1.64
350°C, 15 h	4.32	7.03	1.63
400°C, 17 h	4.70	7.31	1.56
420°C, 5 h	—[e]	—[e]	—[e]

[a] Measured isothermally, column temperature 110°C, helium flow-rate 24.5 cm/s.
[b] Thermally treated with helium at 12.5 p.s.i., adjusted to 1 ml/min at ambient temperature.
[c] Capacity factor of tridecane.
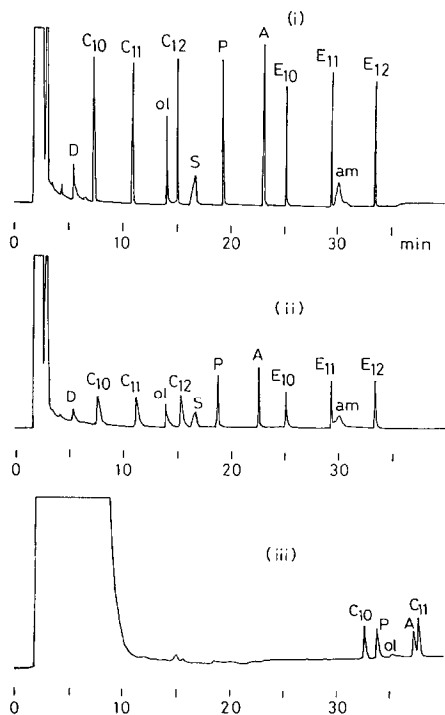[d] Capacity factor of 1-decanol.
[e] Peaks did not appear.

Fig. 1. Gas chromatograms of polarity test mixture on a deactivated metal capillary coated with methylphenylsiloxane prepolymer having terminal OH groups (50% phenyl) (30 m × 0.25 mm I.D.). Thermal treatment: (i) 300°C, 15 h + 350°C, 15 h; (ii) as (i) + 400°C, 17 h; (iii) as (ii) + 420°C, 5 h. Conditions: carrier gas, helium at 12.5 p.s.i. constant pressure; temperature programme, start 60°C, increased at 3°C/min. Peaks: D = 2,3-butanediol; C_{10} = n-decane; C_{11} = n-undecane; ol = 1-octanol; C_{12} = n-dodecane; S = 2-ethylhexanoic acid; P = 2,6-dimethylphenol; A = 2,6-dimethylaniline; E_{10} = methyl decanoate; E_{11} = methyl undecanoate; am = dicyclohexylamine; E_{12} = methyl dodecanoate.

Table II, only slight changes were observed for both the capacity factors (k') and separation factors (α) of the solutes up to 350°C, but with thermal treatment at 400°C an increase in $k'_{(C_{13})}$ and a decrease in α, that is, a decrease of polarity, were observed. The decrease in α is not due to the decrease in the number of terminal OH groups of the stationary phases, as the $k'_{(C_{13})}$ values after treatment at 300 and 350°C are almost the same. The decrease in α is considered to be due to the elimination of arylene-containing moieties. This assumption is supported by the observation that the pak shapes of tridecane and 1-decanol after thermal treatment at 400°C became triangular with a vertical section in front and some tailing. This indicates elimination of arylene-containing moieties and solidification of the remaining phases by cross-linking[8]. An increase in $k'_{(C_{13})}$ after the thermal treatment at 400°C is a sign that the elution time became so long that the solute was not eluted in the normal time after thermal treatment at 420°C.

   Variation of peak shapes and elution order of solutes. The chromatograms for the polarity test mixture are shown in Fig. 1. There was little difference up to 350°C. After thermal treatment at 400°C, however, it is clearly seen from the comparison of Fig. 1(i) and (ii) that the peak shape for each hydrocarbon became triangular with a vertical section in front and tailing, and that, although the elution order was same, the elution time became longer, as was observed in Table II.

   After thermal treatment at 420°C, the elution time became very long, as shown in Fig. 1(iii), and the elution order changed dramatically. This column was fitted to a Shimadz GC 8A instrument and a gas chromatogram was measured under the same conditions. As shown in Fig. 2, a very long elution time and dramatically changed elution order, similar to those in Fig. 1(iii), were observed. The same phenomenon was confirmed with another methylphenylsiloxane column after treatment at 420°C. With the change in elution order, 2,6-dimethylaniline (A) was eluted earlier than *n*-undecane (C_{11}) in Figs. 1(iii) and 2, which cannot be understood from the behaviours of the original column shown in Fig. 1(i) or the dimethylsiloxane column shown in Fig. 3.

   The ratio of the elution times for each solute after and before thermal treatment of the column is shown in Table III as the retardation factor. Table III shows that, with
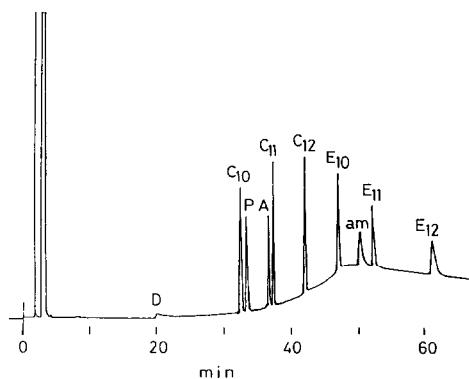

Fig. 2. Gas chromatogram of polarity test mixture on a deactivated metal capillary coated with methylphenylsiloxane prepolymer having terminal OH groups (50% phenyl) (30 m × 0.32 mm I.D.). Thermal treatment: 300°C, 15 h + 350°C, 15 h + 400°C, 17 h + 420°C, 5 h. Conditions: carrier gas, nitrogen at 1.0 ml/min constant flow-rate; other condition and peaks as in Fig. 1.
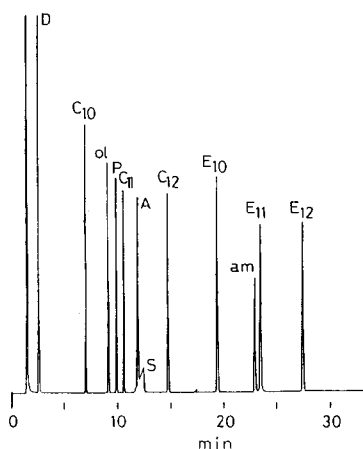
Fig. 3. Gas chromatogram of polarity test mixture on a deactivated metal capillary coated with dimethylsiloxane prepolymer having terminal OH groups and thermally treated (30 m × 0.25 mm I.D.). Conditions and peaks as in Fig. 2.

TABLE III

VARIATIONS OF ELUTION TIME AND ORDER OF SOLUTES ON THERMAL TREATMENT OF METHYLPHENYLSILOXANE

Solute[a]	Methylphenylsiloxane column				Retardation factor[e]	Non-polar column[f]: elution order
	Thermal treatment					
	$300 \rightarrow 350°C$[b]		$300 \rightarrow 420°C$[c]			
	Elution order	Elution time (min)	Elution order	Elution time (min)[d]		
D	1	5.5	1	20.0	3.6	1
C_{10}	2	7.3	2	32.9	4.5	2
C_{11}	3	10.8	6	37.7	3.5	5
ol	4	14.0	4	35.0[g]	2.5	3
C_{12}	5	14.9	7	42.5	2.9	8
S	6	16.7	7[h]			7
P	7	19.1	3	33.6	1.8	4
A	8	22.9	5	36.8	1.6	6
E_{10}	9	25.1	9	47.4	1.9	9
E_{11}	10	29.4	11	52.5	1.8	11
am	11	30.0	10	50.6	1.7	10
E_{12}	12	33.4	12	61.5	1.8	12

[a] For abbreviations, see Fig. 1.
[b] 300°C, 15 h + 350°C, 15 h.
[c] 300°C, 15 h + 350°C, 15 h + 400°C, 17 h + 420°C, 5 h.
[d] Calculated value corresponding the elution time in Fig. 1(iii), corrected by multiplying the elution time in Fig. 2 by 1.0086 using the elution time of C_{11} as standard.
[e] Ratio of elution times between the two columns.
[f] See Fig. 3.
[g] Measured value from Fig. 1(iii).
[h] Estimated elution order. Peak did not appear in Fig. 2.

treatment at 420°C, early-eluted solutes are retarded much more than the late-eluted solutes. The retardation factor is relatively small for the solutes which have a cyclic structure in the molecule, such as P, A and am (see Fig. 1 for abbreviations). Basic solutes such as am eluted from the column which was adsorptive-active after treatment at 420°C for 5 h. This indicates that the adsorptive activity is not due to the acidity usually seen with active columns.

Thermal treatment of the column was carried out under helium at a pressure of 12.5 p.s.i., which was the same as that in the GC measurement. Hence it was expected that, on thermal treatment of the column, the front part of the column would lose phenyl groups and become highly cross-linked and non-polar, thus giving triangular peak shapes. The latter part of the column was expected to contain more arylene-containing moieties that have migrated from the front part. Hence the peak shapes with the latter part of the column were expected to be more normal and the elution order should be different from that with the front part of the column.

To confirm the above expectations, the following experiments were carried out. After the measurements in Fig. 2, the column that had been treated at 420°C was divided into four parts to give short columns, (i)–(iv). Every peak that eluted prior to n-dodecane (C_{12}) was assigned by measuring each solute by isothermal GC at 100°C. Fig. 4(i) shows a chromatogram using the front 7.5 m of the 30-m column. As expected, the peak shapes were triangular with a vertical section in front. The elution time was short and the elution order was C_{10}, ol, P, C_{11} and A, if ol eluted, the same order as was

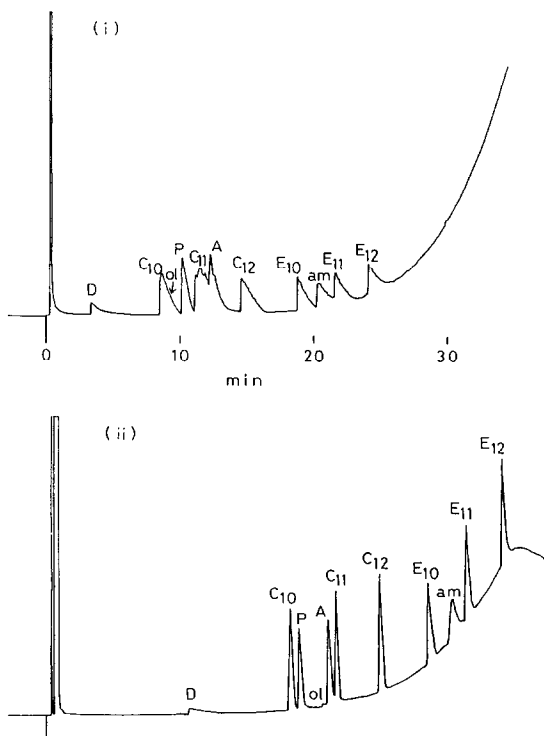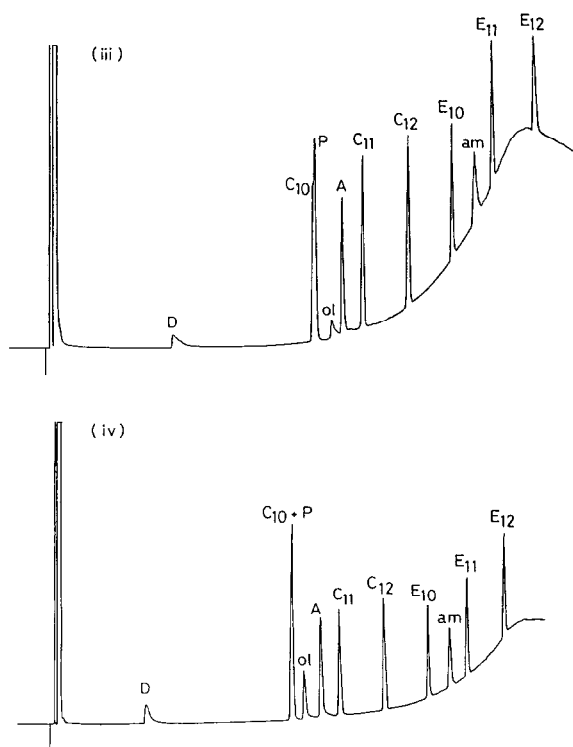Fig. 4.   (*Continued on p. 266*)

Fig. 4. Gas chromatograms of polarity test mixture on sectioned columns after thermal treatment. Columns coated with methylphenylsiloxane (7.5 m × 0.25 mm I.D.). Thermal treatment: 300°C, 15 h + 350°C, 15 h + 400°C, 17 h + 420°C, 5 h, under a flow of helium at 12.5 p.s.i. Carrier gas nitrogen at 1 ml/min; other test conditions and peaks as in Fig. 1. (i)–(iv): numbered as quartered columns cut from the top of the 30 m column.

seen in Fig. 3 with the non-polar dimethylsiloxane column. As shown in Fig. 4(ii)–(iv), the elution time became large with columns (ii)–(iv) compared with column (i), but P and A were retarded comparably less. P and A shifted forward between C_{10} and C_{11} with the latter column, as shown in Fig. 4(ii)–(iv), the chromatograms of which cannot be understood from the results with the ordinary polymethylphenylsiloxane column [Fig. 1(i)] and polymethylsiloxane column (Fig. 3).

Based on the chromatograms obtained, we interpreted the mechanism of the thermal degradation of the polymethylphenylsiloxan column as follows. At *ca*. 370°C, the column begins to lose polarity by eliminating benzene and forming branched structures[8]. With treatment at 400°C for 17 h, cross-linking proceeds and the stationary phase solidifies[8]. With treatment at 420°C for 5 h, scission of the solidified phase occurs and siloxane oligomers migrate back to the latter part of the column. Hence relatively large holes remain in the solidified phase as a result of the loss of the oligomers. With column (i), the holes are too large to retain solutes, which elute in order to their boiling points without significant retardation. With column (ii), however, the solidified phase with large holes captures siloxane oligomers and swells,

thus making the holes smaller. The smaller holes in column (ii) can retain linear hydrocarbons such as C_{10} and C_{11}, and their retention times become longer. However, aromatic solutes such as P and A are difficult to retain in the smaller holes, and the increases in retention time for the aromatic solutes are smaller than those for the linear solutes, resulting in the order of elution C_{10}, P, A and C_{11}. The peak shapes are greatly improved with column (ii) [Fig. 4(ii)] compared with column (i). Siloxane oligomers may also be acting as tailing reducers. Larger amounts of siloxane oligomers should have migrated into columns (iii) and (iv), making the holes in the solidified phase smaller. P and A are more difficult to retain in the smaller holes of columns (iii) and (iv), thus leading to a shorter elution time for P and A. P eluted at the same time as C_{10} in Fig. 4(iii) and (iv).

The behaviours of ol, S and am, which often cause problems due to adsorption, were examined with the short columns (i)–(iv). As shown in Fig. 4(i)–(iv), the columns show adsorptive activity towards ol and S. The deactivated metal capillary column coated with dimethylsiloxane prepolymer did not show adsorptive activity[10] even after treatment at 450°C, and columns coated with dimethylsiloxane–silarylene precopolymer that had been treated above 420°C did not show adsorptive activity towards ol. There is little possibility of catalytic degradation of the stationary phase by the metal column, as exemplified by the result that no appreciable difference was observed with methylphenylsiloxane between the experiments using the RAS 25 deactivated metal capillary reported here and preliminary experiments using a leached glass capillary column. Hence the adsorptive activity of the columns coated with methylphenyl-siloxane prepolymer after high-temperature treatment is due to some kind of
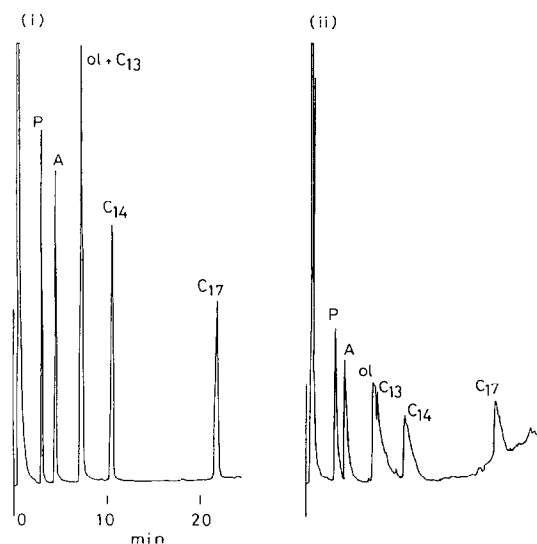

Fig. 5. Gas chromatograms of simplified polarity test mixture on a deactivated metal capillary coated with dimethylsiloxane–silarylene coprepolymer (A) having terminal OH groups (10 m × 0.25 mm I.D.). Thermal treatment under hydrogen at 1.5 ml/min: (i) 350°C, 25 h; (ii) as (i) + 380°C, 25 h. Conditions: carrier gas, nitrogen at 1.5 ml/min constant volume; temperature programme, start 60°C, increased at 3°C/min. Peaks: P = 2,6-dimethylphenol; A = 2,6-dimethylaniline; ol = 1-decanol; C_{13} = n-tridecane; C_{14} = n-tetra-decane; C_{17} = n-heptadecane.

degradation of the stationary phase and not to the activation of the deactivated metal capillaries.

Variation of dimethylsiloxane–silarylene column by thermal treatment

Variation in peak shapes and elution order of solutes. Column A, coated with prepolymer A shown in Table I, was heated at 350°C for 25 h and a chromatogram was then obtained with the simplified polarity test mixture. The chromatogram obtained, shown in Fig. 5(i), is similar to that obtained before the thermal treatment. After further heating at 380°C for 25 h, however, the peak shapes, as shown in Fig. 5(ii), became triangular and ol and C_{13} became resolved. This indicates that silarylene-containing moieties began to be eliminated, and at the same time the stationary phase became non-polar accompanied by cross-linking and solidification.

With column B, the chromatograms before and after thermal treatment at 350°C for 25 h were same as that in Fig. 5(i). A baseline shift with column B after thermal treatment at 350°C for 25 h, as shown in Fig. 6, was observed at temperatures from 325°C and degradation of the stationary phase appeared vigorous above 370°C. After an additional thermal treatment at 400°C for 25 h, the peak shapes, as shown in Fig. 7, became triangular, the elution time became long and non-polar solutes were retarded relatively longer, as was described with the methylphenylsiloxane columns.

There appears to be little difference between columns A and B. Fig. 5(ii) with column A can be regarded as the pre-stage of Fig. 7 with column B, and at this stage solutes were retarded only slightly, although the peak shapes were not good. Columns A and B began to eliminate silarylene-containing moieties and cross-link on treatment at 380°C for 25 h, thus becoming less polar. This resulted in a chromatogram as in Fig. 5(ii), in which ol eluted earlier and the peak shapes became triangular. The longer retention time and relatively earlier elution of P and A after treatment at 400°C for 25 h, as shown in Fig. 7, is due to the same reason as suggested for Fig. 4(i). The same chromatogram as shown in Fig. 7 was obtained after rinsing column B that had been thermally treated at 400°C for 25 h, which indicates that considerable cross-linking of the stationary phase occurred.
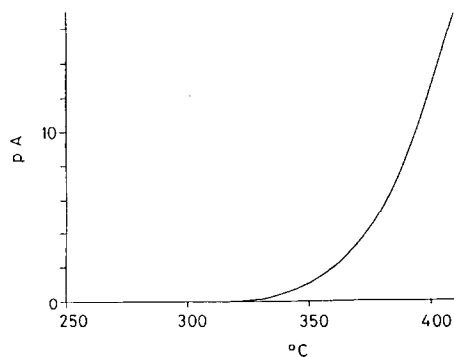

Fig. 6. Baseline shift for dimethylsiloxane–silarylene copolymer (B) after thermal treatment at 350°C, 25 h. Column, 10 m × 0.25 mm I.D.; carrier gas, nitrogen at 1.5 ml/min constant volume; temperature, programmed at 3°C/min.
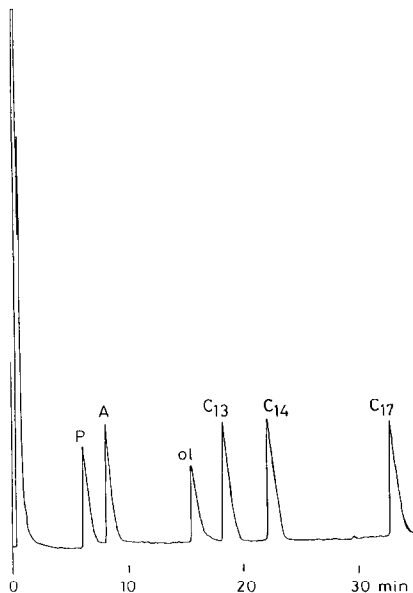
Fig. 7. Gas chromatogram of simplified polarity test mixture on a deactivated metal capillary coated with dimethylsiloxane–silarylene copolymer (B) having terminal OH groups (10 m × 0.25 mm I.D.). Thermal treatment: 350°C, 25 h + 400°C, 25 h. Conditions and peaks as in Fig. 5.

Volatile products obtained by thermal treatment of the precopolymer. Precopolymer was placed in a glass tube and heated gradually from 350 to 420°C under a stream of nitrogen at 2 ml/min and maintained at 420°C for 3 h. Volatile compounds were collected as an oil in a trap cooled with liquid nitrogen. GC–mass spectrometric (GC–MS) measurements were made on the gas phase and methylene chloride solution of the liquid phase from the trap. Using a fused-silica column coated with OV-1, the gas phase was analysed at ambient temperature and the liquid phase with temperature programming from 100 to 300°C at 10°C/min and a hold at 300°C. Benzene was not detected in the gas phase. GC of the liquid phase is shown in Fig. 8. MS measurements were made on the peaks with the underlined scan numbers. As a result, parent peaks or peaks from which hydrogen atoms were abstracted were observed at m/z 281 (observed in scan number 27), 341 (scan number 53), 343 (114), 355 (56), 415 (142), 429 (88), 461 (221), 475 (204) and 489 (161).

Among these peaks, that of m/z 341 was identified as coming from abstraction of a hydrogen atom from the structure 1 with $n = 2$, which was formed by adding two hydrogen atoms to a corresponding radical. The peaks of m/z 415 and 489 were identified as structure 1 with $n = 3$ and 4, respectively. The peak of m/z 475 is considered to come from the random copolymer segment 2. A peak observed at m/z 281 can be assigned to a hydrogen atom-abstracted product from the cyclic structure of a radical 3, which, however, is hardly possible because of the strain of such a small molecule having a silarylene unit. The peaks of m/z 355 and 429, both of which have one more $Si(CH_3)_2$–O unit compared with structure 3, also cannot be assigned either, together with the peaks of m/z 343, 461 and 475. This experiment also confirmed that
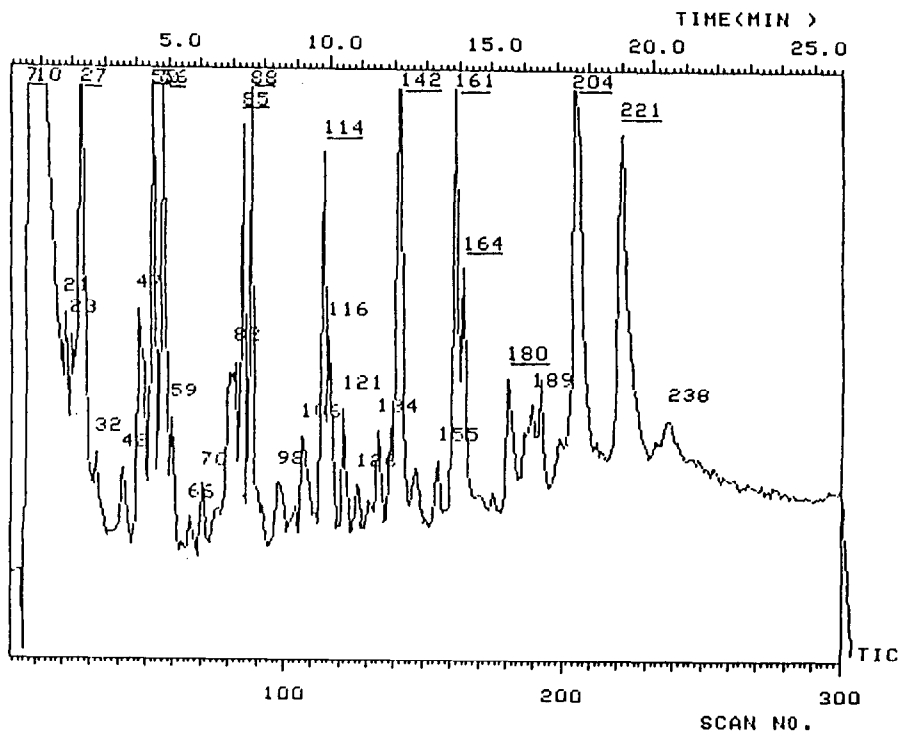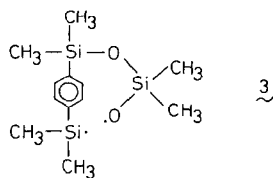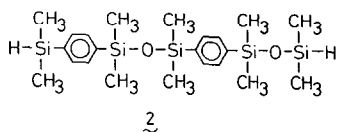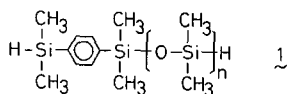
Fig. 8. Gas chromatogram of volatile liquid products obtained by thermally treating dimethylsiloxane–silarylene precopolymer.

columns coated with precopolymer decompose easily by eliminating silarylene-containing moieties.

CONCLUSIONS

The thermal stabilities of arylene-containing polymers, methylphenylsiloxane polymer and dimethylsiloxane–silarylene precopolymer as stationary phases for HTGC were examined using a deactivated metal capillary column. The thermal stabilities of the stationary phases were evaluated from the variations in peak shapes and elution orders of solutes of a polarity test mixture after prolonged thermal treatment at 300–420°C.

All the phases examined start to lose arylene-containing moieties and to cross-link on prolonged use at 380°C, and the peak shapes became triangular with a vertical section in front.

Although the retention time was expected to become short owing to decomposition and migration of stationary phases after prolonged use at 400–420°C, the retention time became very long for every solute. It was proposed that siloxane oligomers migrated from the solidified stationary phase and holes that were too large to retain solutes remained, thus making the solidified phase porous. Migrating siloxane oligomers were then trapped by the solidified porous stationary phase of the latter part of the column, thus making the phase swell. The smaller holes so obtained can trap solutes, leading to longer retention times. As relatively large cyclic solutes cannot be easily trapped in the smaller holes, the increase in retention time is small compared with that of linear solutes. Consequently, the elution order varied dramatically and became completely different from that of the non-degraded column or non-polar column.

These stationary phases are not suitable for HTGC above 400°C. Their maximum operating temperature is limited to 350–360°C and to 380–400°C for brief periods with temperature programming. Repeated use, however, will result in degradation of the column. The column should not be used further when the peak shapes of hydrocarbon become triangular, otherwise great changes in elution time and elution order will occur.

REFERENCES

1 N. Grassie, I. G. Macfarlene and K. F. Francey, *Eur. Polym. J.*, 15 (1979) 415.
2 T. H. Thomas and T. C. Kendrick, *J. Polym. Sci., Part A-2*, 8 (1970) 1823.
3 R. W. Lenz and P. R. Dvornic, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, 21, No. 2 (1980) 142.
4 N. Koide and R. W. Lenz, *J. Polym. Sci., Polym. Symp.*, 70 (1983) 91.
5 N. Grassie and S. R. Beattie, *Polym. Degrad. Stabil.*, 7 (1984) 109.
6 I. P. Yudina, K. I. Sakodynskii, V. P. Mipeshkevich, S. B. Dolgoplosk, G. N. Semina and L. I. Ananeba, *Russ. Pat.*, SU 105650 (1983).
7 J. Buijten, L. Blomberg, S. Hoffmann, K. Markides and T. Wännman, *J. Chromatogr.*, 301 (1984) 265.
8 A. Bemgård, L. Blomberg, M. Lymann, S. Claude and R. Tabacchi, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 881.
9 A. Bemgård, L. Blomberg, M. Lymann, S. Claude and R. Tabacchi, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 302.

10 Y. Takayama, T. Takeichi and S. Kawai, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 732.
11 Y. Takayama, *M&E Japan*, Dec. (1988) 138.
12 C. Madani and E. M. Chambaz, *Chromatographia*, 11 (1978) 725.
13 K. Grob and G. Grob, *J. Chromatogr.*, 219 (1981) 13.