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Note

Poly(styrene–dimethylsiloxane) block copolymer as a stationary phase for capillary gas chromatography

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Poly(styrene–dimethylsiloxane) block copolymers with different ratios of the two chain segments, synthesized by anionic[1] or radical polymerization[2], have been used as surface-active agents[3] and stabilizers for non-aqueous dispersion[4]. It was reported that this kind of copolymer has good electrical properties and unexpected climatic resistance[5]. The synthesis and properties of the block copolymer have been carefully studied by many researchers in recent years. The use of this copolymer as a stationary phase for capillary gas chromatography (GC), however, has not been reported. On the other hand, polysiloxanes constitute the vast majority of stationary phases in capillary GC, and siloxane-type copolymers such as poly(silarylene–siloxane)[6] are considered to be thermally stable at high temperatures. Buijten and co-workers[7,8] prepared poly(silarylene–methylphenylsiloxane) and cyanosilicones and coated them on fused-silica capillary columns. These stationary phases exhibited high thermal stability and satisfactory chromatographic performance[9,10].

In this study, two batches of poly(styrene–dimethylsiloxane) A–B block copolymers were used as stationary phases in capillary columns and promising results were obtained. It is indicated that fused-silica capillary columns coated with these copolymers could be used routinely with temperature programming up to 290°C.

EXPERIMENTAL

Analysis of stationary phases

Poly(styrene–dimethylsiloxane) (PSDMS) block copolymers were obtained from Dow Corning and their properties are listed in Table I. Molecular weights and glass transition temperatures (T_g) were measured with a Knauer membrane osmometer (Type 01.00) and a Perkin-Elmer differential scanning calorimeter (DSC-2), respectively. The content of styrene segments was determined with a Hitachi 340 UV spectrophotometer and decomposition temperatures were evaluated with a Perkin-Elmer TGS-2 thermogravimetric analyser.

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TABLE I

PROPERTIES OF POLY(STYRENE–DIMETHYLSILOXANE) BLOCK COPOLYMERS

Copolymer	*Molecular weight ($\bar{M}_n$)*	*Content of styrene (%)*	*Glass transition temperature (°C)*	*Decomposition temperature (°C)*[a]
PSDMS-1	24 500	12	70–72	335
PSDMS-2	41 300	23	80–82	320

[a] Temperature giving a weight loss of 5%.

Coating procedure

Fused silica tubes of I.D. 0.22 mm (Yongnian Optical Fibre Factory) were purged with dry nitrogen at 250°C for 2.5 h before coating so as to remove residual nitric and hydrochloric acids, which were adsorbed on the inside wall of the capillaries. The tubes were then coated statically with the copolymers mentioned above solvated in methylene chloride, as described previously[11].

Column testing

Column testing was carried out with an SP-2305 gas chromatograph (Beijing Analytical Instrument Factory) with flame ionization detection (FID) and a GC-5A instrument (Shimadzu) with FID and a modified column system[12]. Nitrogen was used as the carrier gas in all instances. The test mixtures were (i) Grob's test mixture, (ii) a mixture of C_{10}–C_{28} *n*-alkanes and (iii) a positional isomer mixture of nitrotoluene (NT) and dinitrotoluene (DNT) and also trinitrotoluene (TNT). A Model CDMS-1B chromatographic data processor (Shanghai Institute of Computing Technology) was utilized to handle the data for the quantitative analysis of DNT isomers.

RESULTS AND DISCUSSION

Three fused-silica capillary columns were prepared with these copolymers and their properties are given in Table II. The coating experiment showed that these copolymers are easy to coat on the fused-silica tubes. Fig. 1 illustrates representative chromatograms of Grob's test mixture on these columns. From this it can be seen that these columns have acceptable inertness, although the theoretical plate number is

TABLE II

PROPERTIES OF THE FUSED-SILICA CAPILLARY COLUMNS

TPN = Theoretical plate number; *k′* = capacity factor.

Column No.	*Stationary phase*	*Column length (m) × I.D. (mm)*	*Cloumn temperature (°C)*	*Test compound*	*TPN*[a] *(n/m)*	*k′*
1	PSDMS-1	9 × 0.22	120	*n*-C_{12}	1345	3.52
2	PSDMS-2	9 × 0.22	160	*n*-C_{12}	2059	1.14
3	PSDMS-2	21 × 0.22	130	*n*-C_{12}	2674	3.57

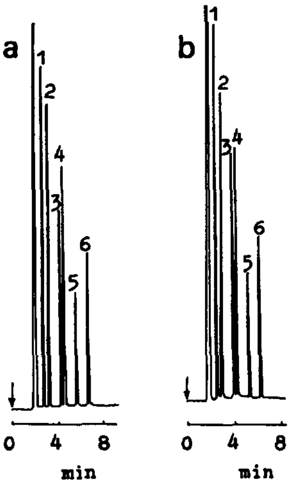

Fig. 1. Gas chromatograms of Grob's test mixture on (a) column 1 and (b) column 2 in an SP-2305 gas chromatograph. Column temperature, 140°C; injection temperature, 350°C. Peaks: 1 = *n*-octanone; 2 = *n*-octanol; 3 = 2,4-dimethylaniline; 4 = *n*-dodecane; 5 = 2,6-dimethylphenol; 6 = *n*-tridecane.

relatively poor (below 3000/m). This may be because the fused-silica tubes were not deactivated and the stationary phases were not immobilized.

According to the differential scanning calorimetric and thermogravimetric experiments (Table I), the T_g of the block copolymer is lower than that of styrene homopolymer (about 100°C). This is also shown in Fig. 2 by the linear relationship between log t'_R (adjusted retention time) and the reciprocal of column temperature (T_c) within the range 80–160°C. The height equivalent to a theoretical plate (H) as a function of carrier gas flow-rate (u) for these columns corresponds to the Van Deemter equation, as illustrated in Fig. 3. Table III gives the retention indices of several samples on these columns at 120 and 130°C. Therefore, it can be concluded that styrene–dimethylsiloxane A–B block copolymers share a common chromatographic behaviour with other polysiloxane stationary phases.

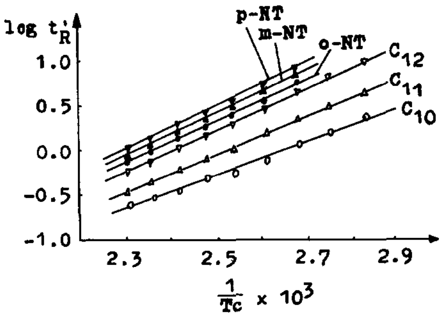

Fig. 2. Relationship between log t'_R and the reciprocal of column temperature ($1/T_c$) for isomers of NT and C_{10}–C_{12} *n*-alkanes on column 2 in an SP-2305 chromatograph. Carrier gas flow-rate, 30 cm/s; make-up gas flow-rate, 45 ml/min; injection temperature, 350°C; detector temperature, 250°C.

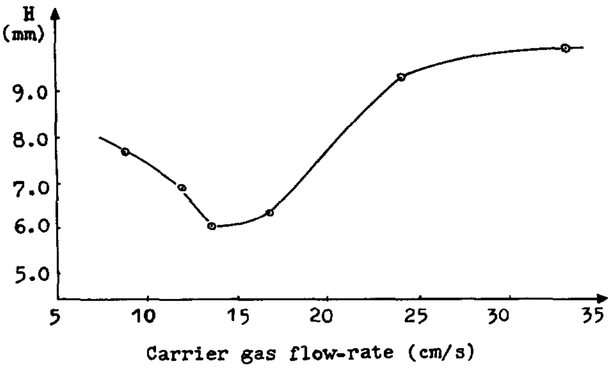

Fig. 3. Van Deemter curve for column 2 at 120°C in an SP-2305 gas chromatograph with FID.

As an example of applications, isomers of NT, DNT and TNT were separated on the above three columns, and typical chromatograms are shown in Fig. 4. Significantly, the isomers of NT and DNT can be satisfactorily separated on a column as short as 9 m within 7 min and TNT on a 21-m column within 10 min. These results are much better than those given by columns coated with SE-54 (ref. 12) and OV-101 (ref. 13), on which 2,3- and 2,4-DNT cannot be completely separated, and by a column coated with OV-225 (ref. 14), which is difficult to prepare with fused-silica tubes and has the drawback of long analytical times, although complete separation of these isomers can be obtained. These results show that the selectivity of the PSDMS block copolymer towards polar compounds is improved because of the introduction of a polystyrene chain in the polydimethylsiloxane backbone. Hence, columns coated with PSDMS block copolymers could be applied in the separation of positional isomers of compounds such as benzenes substituted with different polar groups. Table IV gives the quantitative results for a practical DNT sample on column 2. The reproducibility and accuracy are acceptable and potential applications of this type of columns are expected.

As shown in Fig. 4, the columns coated with PSDMS block copolymers can be used up to 268°C, indicating that these new stationary phases are thermostable. To investigate further the stability of these columns, a mixture of *n*-alkanes was injected after column conditioning at 270°C for 30 h and a representative chromatogram is shown in Fig. 5. It is found that these columns could be used with temperature

TABLE III

RETENTION INDICES OF DIFFERENT COMPOUNDS ON PSDMS

DMA = Dimethylaniline; DMP = dimethylphenol.

Column No.	T_c *(°C)*	*n-Octanone*	*n-Octanol*	*2,4-DMA*	*2,6-DMP*
1	120	1017	1094	1177	1256
2	120	1018	1085	1179	1256
3	130	1026	1100	1168	1263

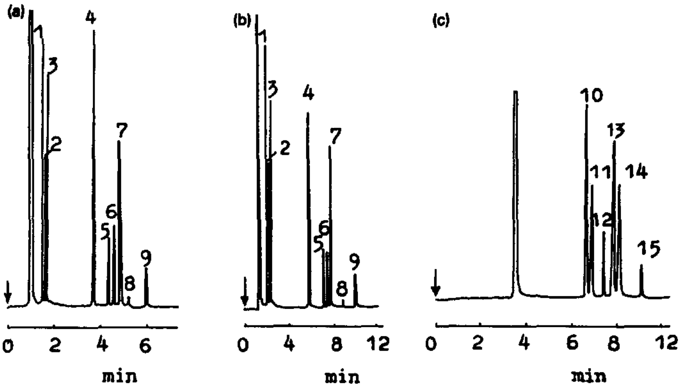

Fig. 4. Gas chromatograms of (a) NT and DNT on column 1 at 180°C with a carrier gas flow-rate of 17.0 cm/s; (b) NT and DNT on column 2 at 166°C with a carrier gas flow-rate of 17.0 cm/s; and (c) TNT on column 3 at 268°C with a carrier gas flow-rate of 12.0 cm/s. Peaks: 1 = *o*-NT; 2 = *m*-NT; 3 = *p*-NT; 4 = 2,6-DNT; 5 = 2,5-DNT; 6 = 2,3-DNT; 7 = 2,4-DNT; 8 = 3,5-DNT; 9 = 3,4-DNT; 10 = 2,4,6-TNT; 11 = 2,3,6-TNT; 12 = 2,3,5-TNT; 13 = 2,4,5-TNT; 14 = 2,3,4-TNT; 15 = 3,4,5-TNT.

TABLE IV

QUANTITATIVE ANALYSIS OF A PRACTICAL DNT SAMPLE

The results are means of six runs, calculated by peak-area normalization. Column temperature, 172°C; injection temperature, 350°C; detector temperature, 250°C; carrier gas flow-rate, 16.0 cm/s.

Isomer	*2,6-DNT*	*2,5-DNT*	*2,4-DNT*	*3,5-DNT*	*3,4-DNT*
Content (%)	12.38	0.65	78.15	3.41	4.40
Standard deviation (%)	0.2791	0.0227	0.1973	0.1775	0.1473
Relative standard deviation (%)	2.086	3.492	0.252	5.206	3.348

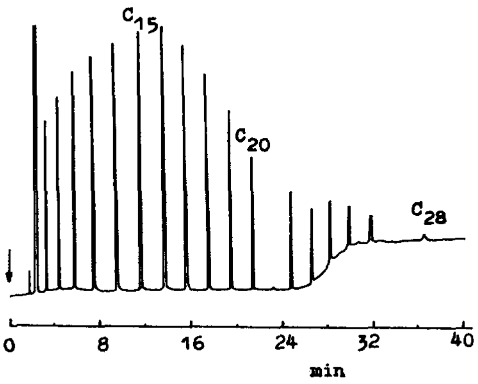

Fig. 5. Gas chromatogram of *n*-alkanes. Column temperature, programmed from 120 to 290°C at 6°C/min; injection temperature, 350°C; carrier gas flow-rate, 18.8 cm/s.

programming up to 290°C and the baseline drift is very slight. The thermal stability would be further improved by cross-linking or immobilization of the stationary phase on the column. Further studies are in progress.

CONCLUSIONS

PSDMS A–B block copolymers can be used as stationary phases for capillary GC. The columns, which are easily coated with these copolymers, are thermally stable at elevated temperature up to 280°C. For the separation of different polar substances, they may serve as potential stationary phases in capillary column GC for laboratory and industrial analysis.

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