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IN SITU COATING OF A NARROW-BORE GLASS CAPILLARY COLUMN WITH A HIGH TEMPERATURE NEMATIC LIQUID CRYSTAL

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SUMMARY

A method for the *in situ* coating of a narrow-bore glass capillary column with N,N'-bis(*p*-phenylbenzylidene)- α,α' -bi-*p*-toluidine (BPhBT) as stationary phase for gas chromatography is presented. The reaction components α,α' -bi-*p*-toluidine and *p*-phenylbenzaldehyde are brought together in the capillary and react with each other during the evacuation step in the static coating technique.

The gas chromatographic behaviour of five- and two-ring polycyclic aromatic hydrocarbons are compared on the two nematic liquid crystal phases BPhBT and N,N'-bis(*p*-methoxybenzylidene)- α,α' -bi-*p*-toluidine (BMBT) respectively. The quality of the columns is evaluated in terms of the effective number of theoretical plates, partition ratio (capacity factor), separation factor and Trennzahl. It is shown that a polar liquid crystal forms a coherent film on a glass surface which has been covered by a layer of barium carbonate or of carbon black. Glass capillaries pretreated in this way exhibit equal or better separation efficiencies than conventional capillary, micro- and packed columns which liquid nematic crystals as stationary phase.

INTRODUCTION

Since 1963, high temperature nematic liquid crystals have been used for difficult separations of isomers such as disubstituted benzenes^{1,2}, polycyclic aromatic hydrocarbons³⁻¹², isomers of the anti-inflammatory agent benoxaprofen¹³, polychlorinated biphenyls¹⁴ and azaheterocyclic compounds¹⁵.

The theoretical background of liquid crystal systems is discussed in many papers (refs. 16, 17 and references therein). Most of the chromatographic applications of liquid crystals have been to the separations of the above compounds on packed columns. In general, the crystal homologues and analogues of N,N'-bis(*p*-methoxybenzylidene)- α,α' -bi-*p*-toluidine (BMBT) were employed as stationary phase. Only a few papers describe the application of high temperature nematic liquid crystals as stationary phase in capillary columns¹⁸⁻²⁰.

The use of the liquid crystals BPhBT and BMBT (the *p*-phenyl and *p*-butoxy

homologues of BMBT) as wall coating substrates in wide-bore (0.75 mm I.D.) stainless-steel capillary columns was recently reported^{19,20}. The efficiencies obtained were a factor of 10–20 greater than for packed columns, but much less than those attainable on conventional (0.25 mm I.D.) capillary columns. The properties and preparation of the liquid crystal BBT and in admixture with a gum phase (SE-52) in a leached and silylated glass capillary (17.5 m × 0.2 mm I.D.) have also been reported.

In the present paper we describe the *in situ* coating of BPhBT in a narrow-bore (0.25 mm I.D.) glass capillary column and its utilization in gas chromatographic (GC) analysis. BPhBT is thermally stable in the nematic phase and also shows a high selectivity for five-ring polyaromatic hydrocarbons (PAHs). The results are compared with those obtained on a conventionally coated (OV-1) capillary column and a capillary with BMBT as stationary phase.

EXPERIMENTAL

Materials

The starting reagents, α,α' -bi-*p*-toluidine (Eastman-Kodak), *p*-phenylbenzaldehyde (Aldrich) and BMBT (Eastman-Kodak), were purified by recrystallization from water-ethanol. The purity of the reagents was checked by IR spectroscopy, solid probe mass spectrometry and thermal analysis.

Standard polycyclic aromatic hydrocarbons (Community Bureau of Reference-BCR of the European Communities, Brussels, Belgium) were used without further purification and were dissolved in glass-distilled cyclohexane. The sample bottles were wrapped in aluminium foil to prevent photolysis. The concentrations of the compounds phenanthrene, anthracene, 1,2-benzopyrene (BeP), perylene (Per), 3,4-benzopyrene (BaP) and benzo[*b*]chrysene [B(*b*)C] were 250, 250, 245, 100, 255 and 62.5 ng/ μ l respectively.

Apparatus and procedures

The measurements were performed on a Varian 3700 gas chromatograph equipped with a flame ionization detector. The oven temperature was measured with a mercury thermometer and a digital thermocouple (United Systems, OH, U.S.A.).

A universal capillary injection system (Chrompack, Middelburg, The Netherlands) was used in the splitless injection mode. The splitter was closed for 2 min before injecting a sample; the injection was carried out within 5–10 sec. The sample (1 μ l) was introduced using a Hamilton 701 N 10- μ l syringe (empty-needle injection).

The columns were installed via Kalrez ferrules (Carlo Erba) at the detector and with graphite ferrules at the injector. Ultra high purity hydrogen was used as carrier gas and nitrogen as make-up gas. The chromatograms were recorded on a Sigma-10 data station (Perkin-Elmer) using a electrometer setting of $8 \cdot 10^{-11}$ A full scale. Scanning electron microscopy (Jeol JSM 35) was applied to study the behaviour of the liquid crystals BPhBT and BMBT on carbon and on barium carbonate.

Preparation of the columns

Barium carbonate. The pre-treatment of borosilicate columns (0.25 mm I.D.) was studied by Grob and co-workers^{21–27} and will be commented upon only briefly.

After straightening the ends of the empty glass columns, the surface was leach-

ed with HCl in order to produce a deionized silica gel surface layer. The capillary was filled with 20% HCl solution and both ends were closed in a flame. The capillary was kept overnight at 180°C. The HCl was displaced by deionized water and then dried for 2 h at 250°C with a low helium flow. After the leaching and dehydration, the column was treated by the barium carbonate method according to Grob *et al.*^{24,27}.

Carbonization. A very thin layer of carbon was deposited on the inner surface of glass capillaries by pyrolysis of methylene chloride. Nitrogen was bubbled through methylene chloride at 0°C and directly brought into the capillary, which was held at 50°C. After 2 h, both ends were closed in a flame and the column was placed in an oven at 550°C. After 1 h the capillary was opened and a solution of 10% diethylamine in methylene chloride was sucked in, in order to remove the HCl.

Static coating. The columns were filled with a solution of *m*, *p*-toluidine and *p*-phenylbenzaldehyde in acetone–diethyl ether (50:50 v/v) at concentrations of 3.18 and 5.43 g/l respectively (molar ratio 1:2). The concentrations were based on a layer thickness of 0.5 μm and on a reaction efficiency of 100%.

With the mixture acetone–diethyl ether no visible reaction occurs, even after a week. This mixture was chosen instead of pentane or methylene chloride because of the greater solubility of water (a product of the reaction between the aldehyde and the aromatic amine). The hygroscopic solvent ethanol cannot be used because of its low vapour pressure and because of the high reaction rate of the compounds in it. In case of BMBT, methylene chloride was used as solvent.

After filling, one end of the column was closed. Four methods of closing the column were tried, namely: sodium silicate, silicone rubber, rubber of a septum and paraffin (42–44°C). The least time-consuming and most elegant method was the paraffin closing. One column end of the column was then placed in hexane and a low vacuum was applied to the other end to move the meniscus by 4–5 cm. The end with the hexane plug was then placed into the liquid paraffin (50°C) and again a low vacuum (0.1 bar) was applied to the inlet and moved the hexane–paraffin meniscus by 1–2 cm. After cooling the solid paraffin forms a good solid closure. The hexane plug is necessary to avoid reactions between the paraffin plug and the reactants during the evacuation step.

The column was immediately and completely immersed in a water-bath (10 l) at room temperature and evacuated at the open end. After 16–40 h the closed end was cut away and both ends were deactivated with an 0.1% methylene chloride solution of Carbowax (MW 400). The column was placed in the gas chromatograph for conditioning and the oven temperature was raised slowly (0.5°C min⁻¹) from room temperature to 300°C. The columns were kept at this temperature for 24 h.

RESULTS AND DISCUSSION

The coating technique

During work on packed and micro-packed glass columns with BPhBT as stationary phase⁵ we observed a yellow film on the silanized glass surface after emptying the column. The origin of this film can be ascribed to column-bleed and/or to diffusion of the pure liquid crystal from the Chromosorb support to the glass wall. So there are intermolecular attraction forces between functional groups on the surface and the stationary phase BPhBT, and/or bleeding.

TABLE I
CAPILLARY COLUMNS USED
Phen = phenanthrene; anth = anthracene.

No.	Length (m)	T (°K)	Pre-reat- ment*	Liquid phase	Film thickness** (μm)	TZ*** BaP/BeP	N [†] BaP	TZ Phen/Anth	N Phen	Flow (cm sec ⁻¹)	
										Measured ^{†††}	Methane ^{††††}
1	18.5	538.8	BaCO ₃	DPhBT	0.5	2.85	712	—	—	303.7	38.5
2	17.0	451.5	C	BMBT	0.5	—	—	7.60	818	67.9	34.5
3	32.0	479.5	BaCO ₃	BMBT	0.5	—	—	7.85	526	67.8	25.2

* See Experimental section.

** In the case of BPhBT, this was calculated on the basis of 100% yield of the reaction α,α' -bi-*p*-toluidine and *p*-phenylbenzaldehyde.

*** Maximum attainable values of TZ, calculated from

$$\text{TZ} = \frac{f_{R,\text{BaP}} - f_{R,\text{BeP}}}{w_{0.5,\text{BaP}} + w_{0.5,\text{BeP}}} - 1$$

where $w_{0.5}$ is the peak width at half-height.

† Effective theoretical plate number per metre, $5.54 (V_R/w_{0.5})^2$.

†† The flow measured with a soap-film meter, divided by the cross-sectional area.

††† The flow calculated from the retention of methane.

Therefore, in order to study the wettability of the silica framework we had to treat the support surface. This treatment is based on the principles of the so-called geometrical and chemical film stabilization²⁶.

There are two pre-requisites in making glass capillary columns. First there should be an uninterrupted coherent "liquid crystal" film on the glass surface in order to achieve maximum separation efficiency. Secondly, there should be no active sites on the surface in order to avoid adsorption of sample and catalytic effects on sample and stationary phase degradation. Untreated and HCl-leached/dehydrated glass surfaces are highly reactive, because of the dipole moment of the functional group Si-OH. Such surfaces form good substrates for the semipolar phase BPhBT. However, some active sites remain on the surface which can result in adsorption of polycyclic aromatic hydrocarbons and/or increased retention of some aromatic hydrocarbons, and also give rise to severe peak distortions.

The use of persilylated surfaces²² is not possible in our case, because of the medium polarity of the liquid crystals. So we applied the barium carbonate deactivation method and carbonization of the glass surface. The barium carbonate layer is less active than the leached surface itself and it roughens the glass wall²⁸. Carbonized glass is also suitable for the coating of glass capillaries with polar liquid crystals. Our attempts to spread the BPhBT on the glass surface with the static coating technique did not succeed. The solubility of BPhBT in various solvents is too low to yield a suitable film on the glass wall. Moreover, BPhBT crystallizes during the evacuation step in the static coating technique when working with slurries of BPhBT in methylene chloride. The crystals can move freely through the column after the coating.

To overcome the problems of solubility and film formation from slurries, BPhBT was synthesized directly in the column during the evacuation step of the static coating method. One problem that should not be overlooked is the rôle of water which is generated as a by-product of the reaction between the amine and the aldehyde. The water can destroy or at least influence the barium carbonate layer in a negative sense. The water has to be removed because the reaction



has to be displaced to the right. We, therefore, chose an acetone-diethyl ether mixture in which water is reasonably soluble. However, we could not find any influence of water on the barium carbonate layer. This could support the fact that the divalent cation (Ba^{2+}) has a considerable crystal lattice energy at the silicate surface and thus resistance to hydrolysis, as pointed out by Pretorius *et al.*²⁸.

Gas chromatography

Table I lists the columns used. We started this study with mixed phases such as a gum phase OV-1 or a phase like OV-101. In both cases severe bleeding was observed. So we discarded the idea of an "epitactic" layer between the liquid crystal and the glass wall itself. After coating the columns there are small white crystals on the column wall. These crystals disappear after heating in the gas chromatograph to leave a yellow film on the glass surface.

From Table II it can be seen that the surface modification and pre-treatment has a small influence on the molar enthalpy of solutions. The surface area is probably

TABLE II

PARTIAL MOLAR ENTHALPIES OF SOLUTION OF THREE-RING PAHs ON BMBT (COLUMNS 2 AND 3)

Compound	Carbonized surface			Barium carbonate surface		
	ΔH^* (kJ mol ⁻¹)	C**	r ^{2***}	ΔH (kJ mol ⁻¹)	C	r ²
Phenanthrene	-56.84	-8.33	0.95	-50.20	-5.37	0.98
Anthracene	-57.09	-8.14	0.99	-55.50	-6.42	0.98

* Calculated from plots of $\log_e(t_R - t_0)$ vs. $1/T$.

** C is the constant (entropy term) of the equation:

$$\log_e(t_R - t_0) = -\Delta H/RT + C$$

*** r² is the coefficient of determination:

$$r^2 = \frac{[\sum xy - (\sum x \sum y/n)]^2}{[\sum x^2 - (\sum x)^2/n][\sum y^2 - (\sum y)^2/n]}$$

greater in the case of the carbonized surface so the heat evolved increases when a solute is transferred from the gas phase to the solution. Table III summarizes the partial molar enthalpies of solution of five-ring PAHs. Also in this case, the enthalpies are greater on a carbonized surface than on a barium carbonate treated surface²⁹.

TABLE III

PARTIAL MOLAR ENTHALPIES OF SOLUTION OF FIVE-RING PAHs ON BPhBT (COLUMN 1, BARIUM CARBONATE SURFACE)

For definitions see Table II.

Compound	ΔH (kJ mol ⁻¹)	C	r ²
1,2-Benzopyrene	-63.64	-8.70	0.99
Perylene	-61.72	-8.11	0.99
3,4-Benzopyrene	-61.84	-8.09	0.99
Benzo[b]chrysene	-76.53	-10.15	0.99

As the temperature decreases, α , k , TZ and N increase as is seen in Tables IV-VI. So the best separation efficiency and resolution of the liquid crystal can be obtained in the vicinity of the solid nematic transition temperature. Plots of TZ vs. $1/T$ in the temperature range 265-282°C for BPhBT and 185-225°C for BMBT are linear with a coefficient of determination of 0.98 and 0.97 respectively (Figs. 1 and 2). The plots of $\log_e t_R'$ vs. $1/T$ in Fig. 3 show clearly the solid-nematic transition point of BPhBT. This transition point is sharper than in the case of a micro-packed column as has been shown previously⁵.

Fig. 4 combines two chromatograms of five-ring PAHs on a BPhBT and a OV-

TABLE IV

RETENTION, TRENNZAHL, EFFECTIVE NUMBER OF THEORETICAL PLATES, PARTITION RATIO AND SEPARATION OF PHENANTHRENE AND ANTHRACENE AS A FUNCTION OF TEMPERATURE WITH BMBT ON A CARBON SUPPORT AND A BARIUM CARBONATE LAYER (COLUMNS 2 AND 3 RESPECTIVELY)

T (°K)	Retention (sec)*		TZ	N		k**		α^{***} Anth/Phen
	Phen	Anth		Phen	Anth	Phen	Anth	
<i>Carbonized column</i>			<i>Nematic phase</i>					
499.5	213	247 [‡]	3.49	6380	9597	4.33	5.56	1.285
490.0	273	355	4.69	9500	11,490	5.56	7.22	1.300
481.0	346	463	5.08	9625	11,425	7.04	9.42	1.339
471.0	462	620	5.95	10,125	14,795	9.39	12.60	1.343
461.5	623	852	6.74	12,920	17,440	12.65	17.32	1.365
			<i>Solid phase</i>					
451.5	842	1171	7.60	13,900	16,295	17.10	23.81	1.393
<i>Barium carbonate column</i>								
496.0	880	1120	5.78	14,619	21,730	6.92	8.80	1.272
489.5	1088	1411	6.18	14,893	19,147	8.55	11.1	1.294
479.5	1354	1803	7.50	16,826	22,636	10.67	14.1	1.331

* Adjusted retention (t'_R) = retention time minus retention time of methane.

** Partition ratio (capacity factor) = t'_R/t_{methane} .

*** The separation factor, i.e., the ratio of the corrected retentions of anthracene and phenanthrene.

[‡] Mean from two measurements.

TABLE V

RETENTION, TRENNZAHL, EFFECTIVE NUMBER OF THEORETICAL PLATES AND PARTITION RATIO AS A FUNCTION OF TEMPERATURE

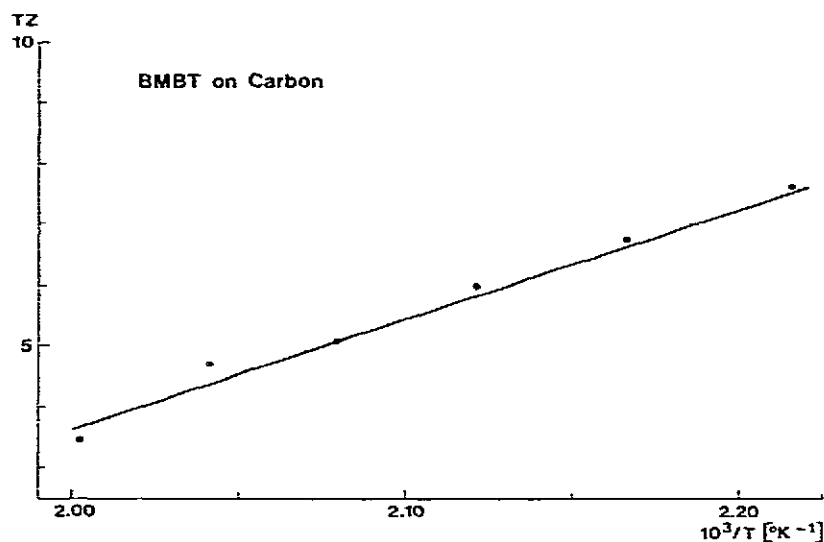
BPhBT as stationary phase on BaCO₃ (column 1, Table I). For definitions see Tables I and IV.

T (°K)	Retention (sec)				k				N		TZ BeP/ BaP
	BeP	Per	BaP	B(b)C	BeP	Per	BaP	B(b)C	BeP	BaP	
<i>Nematic phase</i>											
557.2	153	184	188	581	3.19	3.83	3.92	12.1	—	—	—
555.5	161	191	204	—	3.35	3.98	4.25	—	2462	2713	1.04
552.6	174	204	215	699	3.63	4.25	4.48	14.56	4806	6351	1.60
547.0	200	235	247	804	4.17	4.90	5.15	16.76	—	—	—
543.3	219	257	270	898	4.57	5.36	5.63	18.71	7628	7969	2.31
538.8	245	290	302	1022	5.09	6.04	6.29	21.30	9169	13,166	2.85
<i>Solid phase</i>											
534.2	252	305	305	1043	5.25	6.35	6.35	21.73	7886	4821	1.69
529.3	290	354	354	1212	6.04	7.38	7.38	25.25	7832	5092	1.94

TABLE VI

SEPARATION FACTORS ON BPhBT (COLUMN 1, TABLE I)

T (°K)	Separation factor*			$t_{R, BaP}$ (min)
	BeP	Per	B(b)C	
555.5	0.783	0.930	—	3.40
552.6	0.800	0.942	3.448	3.58
547.0	0.810	0.952	3.257	4.12
543.3	0.808	0.952	3.297	4.50
538.8	0.808	0.957	3.362	5.03
534.2	0.824	1.000	3.394	5.08
529.3	0.823	1.000	3.437	5.90

* $t'_{R, compound}/t'_{R, BaP}$ Fig. 1. Dependence of the Trennzahl of phenanthrene and anthracene on $1/T$ of column 2 (Table I).

1 column and demonstrates the difference in analysis times. Both columns contain barium carbonate as a surface layer. Fig. 5 shows a chromatogram of three-ring PAHs on a BMBT column (carbonized).

To improve the selectivity and resolution of the capillary systems we studied the possibility of a semibonded phase. The $C\equiv N$ group of the OV-225 molecule is hydrolyzed to the carboxylic acid and then transformed into the acid chloride, which has to be catalytically hydrogenated via the Rosenmund reaction. The aldehyde formed in this way could react with the α, α' -bi-*p*-toluidine which in its turn reacts with the *p*-phenylbenzaldehyde. So this stationary phase has a polar and an apolar side. The apolar side is necessary for the persilylated glass surface and the polar side for the coating of BPhBT.

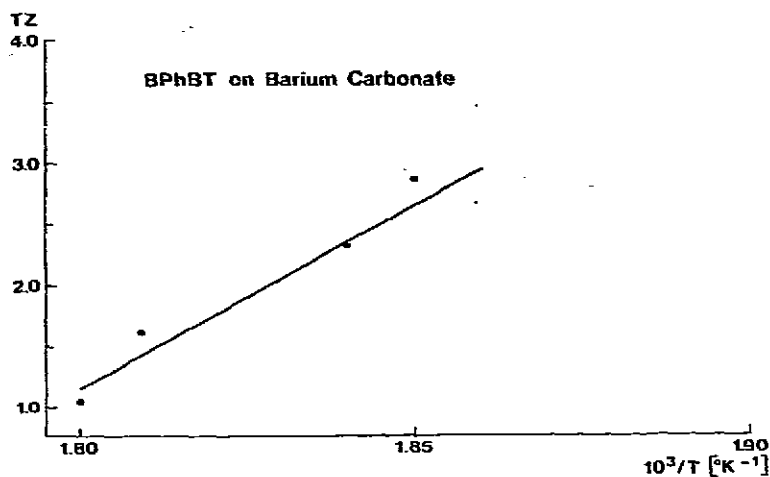


Fig. 2. Dependence of the Trennzahl of 3,4-benzopyrene and 1,2-benzopyrene on $1/T$ of column 1 (Table I).

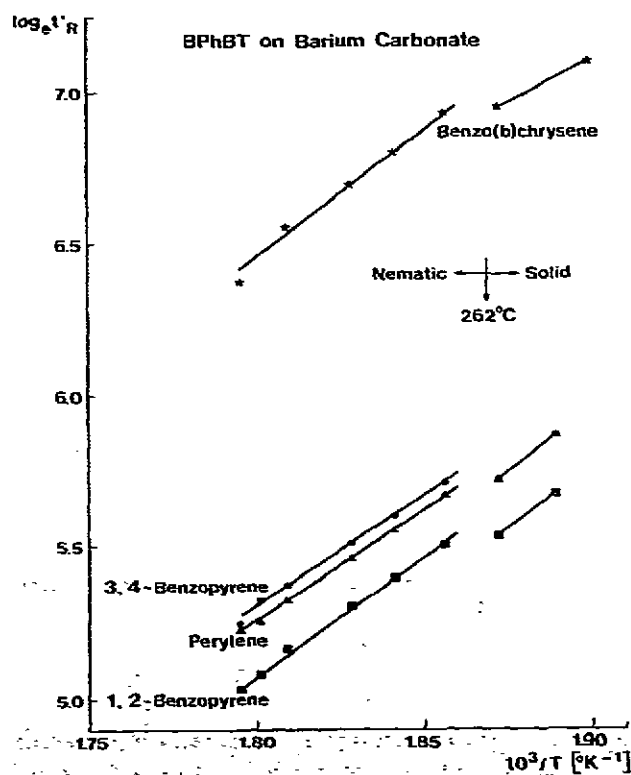


Fig. 3. Dependence of the logarithm of the adjusted retention time (t'_R) on the reciprocal absolute temperature of five-ring PAHs on column 1 (Table I).

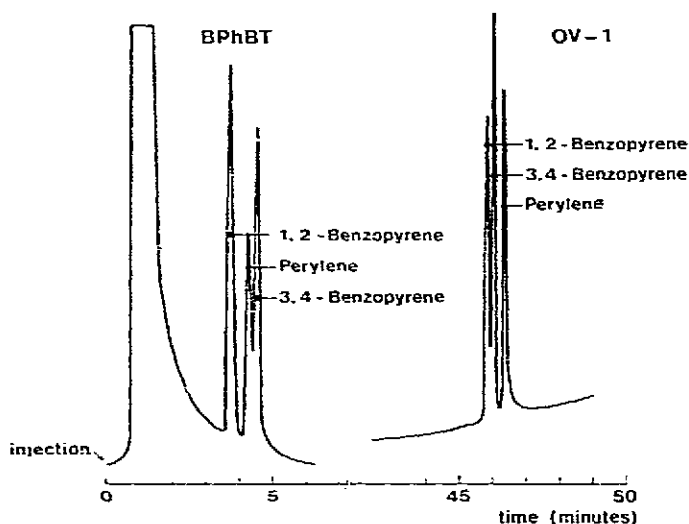


Fig. 4. Glass capillary chromatograms of five-ring PAHs on (left) a 18.5 m \times 0.25 mm column coated *in situ* with BPhBT (0.5 μ m), pressure 0.60 bar, temperature 280 C and (right) a 27 m \times 0.30 mm column coated with 0.15- μ m OV-1, programmed from 60 to 300 C at 6 C min⁻¹.

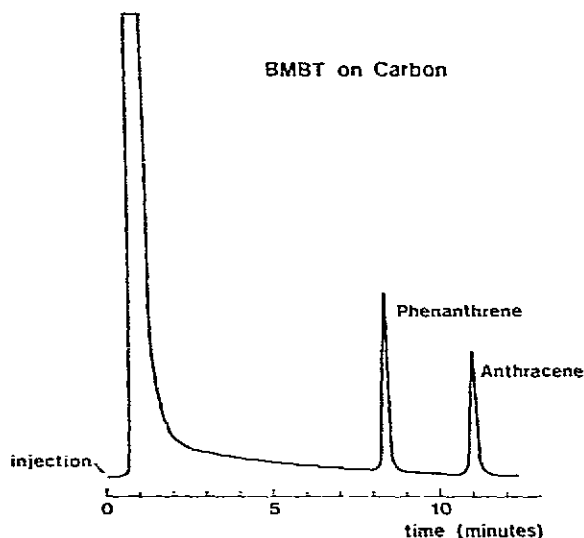


Fig. 5. Glass capillary chromatogram of phenanthrene and anthracene on a 17 m \times 0.25 mm column coated with BMBT on carbon; pressure 0.54 bar, temperature 198°C.

Electron microscopy

Fig. 6 shows the BPhBT coating on a barium carbonate layer and on a carbon layer and before and after heating in the gas chromatograph. In Fig. 6A, some unreacted starting compounds is probably present on the surface. After heating, the surface is covered with a layer (probably BPhBT) and also with large crystals, which

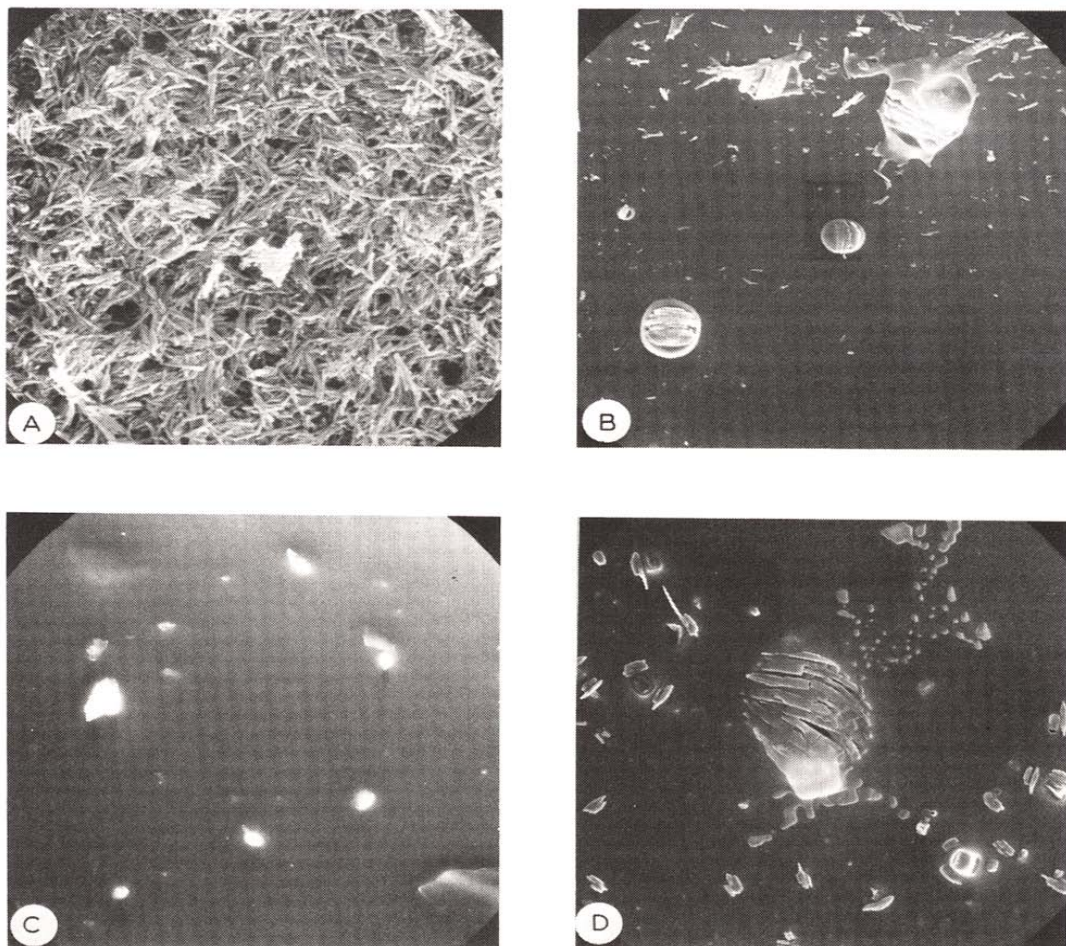


Fig. 6. Scanning electron micrographs of BPhBT: A, on BaCO_3 at room temperature ($\times 3672$); B, on BaCO_3 after heating for 2 h at 300°C in a helium flow ($\times 3672$); C, on a carbonized surface at room temperature ($\times 680$); D, on a carbonized surface after heating for 2 h at 300°C in a helium flow ($\times 3672$).

have the same shape as BPhBT crystals. The completion of the layer is supported by the fact that the barium carbonate crystals are not longer visible, as in Fig. 7A.

In case of the carbonized surface the BPhBT crystals become visible only after heating (Fig. 6C and D) in the gas chromatograph. So during the heating and the cooling of the columns a recrystallization process takes place. The carbon layer consists of very small spheres (Fig. 7B) surrounded by smaller homogeneously divided carbon particles. We expect the crystals on a carbonized surface to be smaller than on a surface with a barium carbonate layer because the surface area is greater.

In the case of BMBT the situation is different. Fig. 8B shows that there are still barium carbonate crystals left and the integrity of the stationary phase film is being disrupted at room temperature. So the wettability of BMBT is poor in comparison with that of BPhBT on barium carbonate. The BMBT forms droplets on the barium

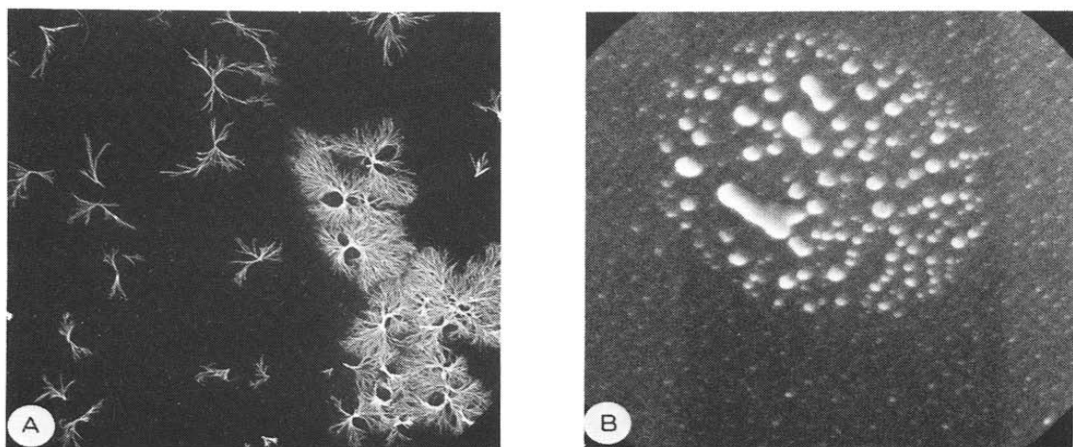


Fig. 7. Scanning electron micrographs ($\times 680$): A, BaCO_3 on the wall of a capillary column; B, carbon deposits on the wall of a capillary column.

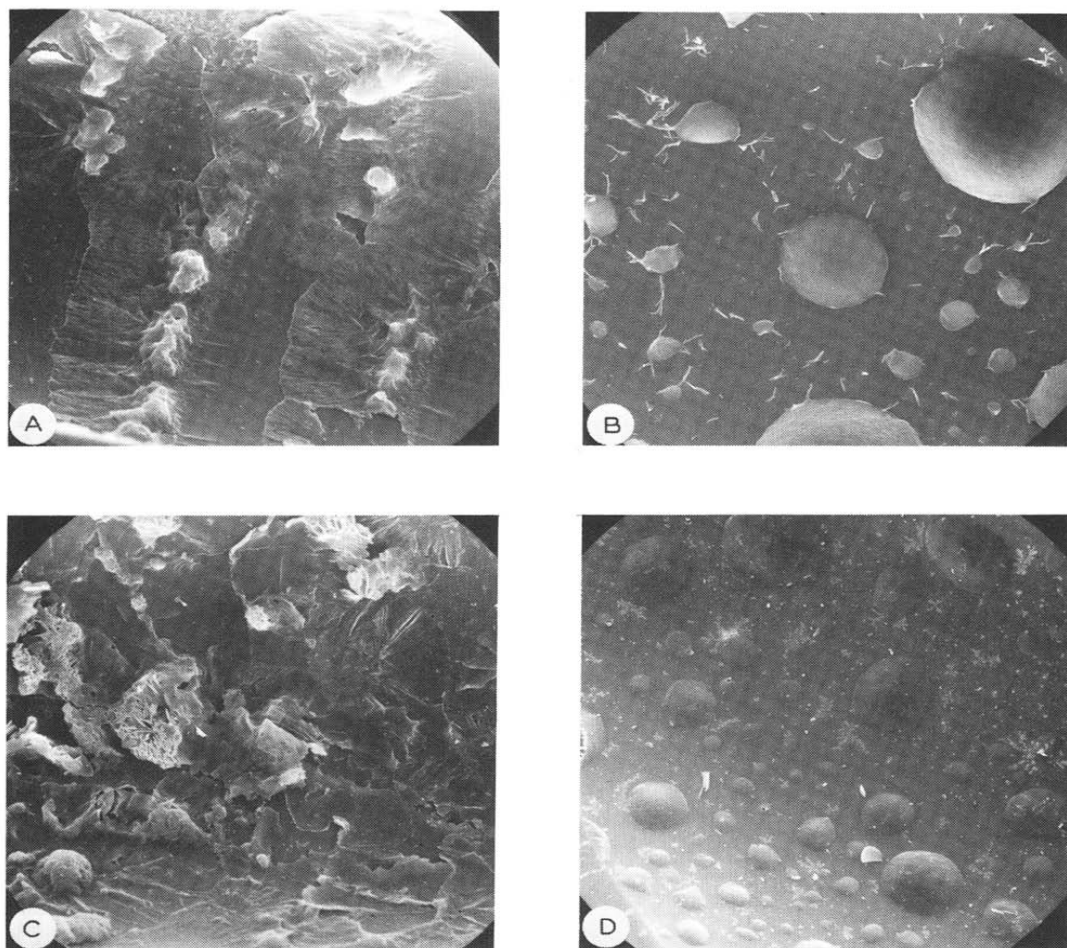


Fig. 8. Scanning electron micrographs of BMBT; A, on BaCO_3 at room temperature ($\times 272$); B, on BaCO_3 after heating for 2 h at 300°C ($\times 680$); C, on a carbonized glass surface at room temperature ($\times 272$); D, on a carbonized glass surface after heating for 2 h at 300°C in a helium flow ($\times 367$).

carbonate layer as well as on the carbonized layer. However, on the latter these droplets are smaller than on the former.

However, it should be remembered that the electron-microscope investigations were carried out at "room temperature". In future studies we hope to investigate the surface layers at elevated temperatures, especially at the solid-nematic transition point, to approach the actual situation in a capillary column during chromatographic separations.

CONCLUSIONS

A carbonized surface forms a good substrate for BMBT as stationary phase in a capillary column, probably better than that formed by barium carbonate. In contrast, barium carbonate is a better substrate for BPhBT. We could not prepare a carbonized column with comparable qualities to the barium carbonate column.

The film thickness should have a value between 0.05 and 0.5 μm . A 0.05- μm layer improves the selectivity, but the Trennzahl and the number of plates decrease²⁹ in the case of BPhBT.

The time required for analyses of five-ring PAHs on a BPhBT column is very short, about 3–6 min for 3,4-benzopyrene (Table V). Even a short column shows a good selectivity and resolution.

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