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EFFECT OF THE SOLID SUPPORT ON THE CHROMATOGRAPHIC PROPERTIES OF A LIQUID CRYSTAL STATIONARY PHASE

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SUMMARY

The gas–liquid chromatographic (GLC) retention characteristics of the liquid crystal stationary phase N,N′-bis(*p*-methoxybenzylidene)-α,α′-bi-*p*-toluidine (BMBT) are significantly affected by the type of solid support used and the amount of liquid crystal deposited on the support. The solid supports examined were Chromosorb W HP, porous silica glass beads, Porasil C and F. The per cent loading above which the influence of the support is no longer observed varies with the type of support material, being highest for the silica beads of the Porasil C type. The retention volumes of the solute probes, phenanthrene and anthracene, were measured at four temperatures in the nematic range of BMBT coated on Chromosorb W HP and Porasil C. With Chromosorb W HP, the specific retention volume, V_g^0, of a given probe at a given temperature decreases as the loading increases up to 2.5%, beyond which V_g^0 is practically constant. With Porasil C, V_g^0 continuously decreases as the loading increases up to 30%. Differential scanning calorimetry in combination with GLC revealed the presence of two types of configurations of BMBT molecules on coated solid supports; namely, a liquid crystal film on the surface and a bulk liquid region in the capillaries of the support. With low per cent loadings only surface films are observed, while at higher loadings the support capillaries are also filled with bulk liquid. With surface-active support material the GLC working temperature range is extended to lower temperatures, however this advantage is offset by the drastically lower selectivity offered by thin films as compared to the bulk selectivity achieved with high loadings on inert solid supports.

INTRODUCTION

Liquid crystal stationary phases are being used more frequently in the separation of rigid isomeric solute mixtures (*e.g.*, substituted benzenes, naphthalenes, polycyclic aromatic hydrocarbons, aza-arenes, polychlorinated biphenyls, steroids and bile acids[1–4]). In contrast to conventional isotropic stationary phases where the separation mechanism is mainly based on solute volatility and polarity, anisotropic liquid crystals discriminate on the basis of solute shape differences. In comparison with other liquid crystal modifications, nematic liquid crystals are, by far, the most useful

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for this type of application. This is largely due to the availability of chemically and thermally stable nematic phases with low, medium and high nematic temperature ranges. However, one drawback is that the nematic temperature ranges of most of the currently available liquid crystals are restricted, imposing practical limitations on their use for the analysis of complex mixtures, particularly those which require temperature programming.

The objective of this work is to investigate the effect of the solid support on two possible approaches to broadening the nematic temperature range. Namely, the operation of liquid crystal columns at temperatures in the supercooled nematic state, and the use of thin films on surface-active solid supports.

Supercooling of the mesomorphic phase transitions have been observed by several workers with packed[5–7] and capillary[8] columns. This phenomenon is familiar to organic chemists as it occurs with many organic compounds. The extent of supercooling, generally, depends on the cooling rate. The interesting fact about liquid crystals is that for many of the systems studied the crystallization of the supercooled mesophase occurs close to one particular temperature and is reproducible irrespective of the cooling rate[5–7]. Wasik and Chesler[5] reported the use of columns of the nematic liquid crystal N,N′-bis(*p*-methoxybenzylidene)-α,α′-bi-*p*-toluidine (BMBT) down to about 65°C below the normal solid–nematic transition temperature of 181°C, and Hlozek and Gutwillinger[6] were able to extend the nematic range of ethylene 4,4′-diphenylbis(4-methoxybenzoate) down to 65°C which is 103°C below the normal solid–nematic transition temperature. Martire and co-workers[9,10] and Willey and Brown[11] have determined the melting and clearing points of liquid crystals in bulk by differential scanning calorimetry (DSC) and as coated on an inert Chromosorb W support by DSC and gas–liquid chromatography (GLC). Both reported slight depression of the mesomorphic transition temperature, for the coated sample, but the solid support surface effects were dismissed as being insignificant. Armitage and Price[12], on the other hand, used surface-active porous silica supports and observed that the depression of the liquid crystal melting transition is in the order of 10°C.

The effect of solid support activity on the chromatographic properties of the stationary phase has long been a subject of controversy. Ideally one would hope that solute–stationary phase partition coefficients as measured by GLC or static methods are identical. It is only when this condition is met that retention volumes are reproducible from laboratory to laboratory. In practice, retention volumes are affected by the amount of liquid phase and the type and treatment of the solid support[13]. It is only with high per cent loadings deposited on low-surface-area solid supports that the reproducibility of retention data is achieved[9]. In order to explain the variation of retention data with per cent loading and the type of solid support used, Korol[14] studied squalane (non-polar) and oxydipropionitrile (strongly polar) stationary phases. He invoked an argument (originally suggested by Giddings) that the stationary phase is present on the solid support in two types of configurations. Namely, a film on the surface and a bulk liquid in the pores. With low per cent loadings, most of the stationary phase is present as a surface film and solute retention is largely due to adsorption on the gas–liquid interface, and on the gas–solid support surface interface. As the amount of liquid phase is increased the support pores are filled and solute solubility in the bulk predominantly determines the retention process.

Unlike isotropic phases, liquid crystals exhibit a macrostructure which strongly depends on the properties of the surface over which the mesophase is deposited. It is, therefore, expected that the effect of solid support would be even more dramatic with such phases. Rayss *et al.*[15] investigated the properties of the liquid crystal *p*-butyl-*p'*-hexanoylazobenzene using a relatively inert Chromosorb P support. They observed that the solid support modifies the chromatographic properties of the liquid crystal stationary phase, up to a film thickness of 2 nm. Vetrova *et al.*[16] showed that the retention behaviours and the working temperature ranges of liquid crystal stationary phases are significantly affected by the nature of the surface of the solid support.

In this study we will show that the GLC retention characteristics of BMBT are affected to a large extent by the type of solid support used and the amount of liquid crystal deposited on the support. Retention volumes and separation factors for the solute probes phenanthrene and anthracene are reported at different per cent loadings. The solid supports used were Chromosorb W HP, Porasil F, C and glass beads. Plots of ln V_g^0 *vs.* T^{-1} are examined. DSC on bulk and support-coated BMBT samples are presented. The extent of supercooling of the nematic melt and the type of configurations assumed by BMBT molecules on the solid support are discussed in light of these results.

EXPERIMENTAL

Materials

The liquid crystal used was BMBT. It was synthesized by the reaction of 2 mol of *p*-methoxybenzaldehyde with 1 mol of α,α'-bi-*p*-boluidine. The mixture was allowed to reflux in absolute ethanol for several hours, then the product was recrystallized twice from hot absolute ethanol. The reaction yield was greater than 85%. The purity of the product was examined by DSC using a Du Pont 999 instrument, which was calibrated using indium, m.p. 156.6°C, as reference. The solid–nematic and nematic–isotropic phase transition temperatures of BMBT occur at 181°C and 337°C respectively.

The solid supports used were Chromosorb W HP, Porasil C, F and glass beads. The column packings were prepared by dissolving a weighed amount of liquid phase in chloroform and transferring to a chloroform slurry of weighed solid support in a round-bottomed flask. Excess of solvent was gently removed using a rotary evaporator and the slurry was then placed in an evaporating dish and dried in an oven at 60°C with frequent stirring. The dry packing material was then resieved to the appropriate mesh specifications to ensure uniformity of particle size. The per cent loading of each packing was then determined gravimatrically by burning off the organic matter in a crucible. In each case the results of two ashings agreed to within ±1%. Samples of uncoated solid supports were similarly ashed and the slight loss of weight from the solid support material was considered in determining the per cent loadings. The glass bead samples were not ashed as this would result in melting of the particles. Thus for glass beads the per cent loading was that determined from the weights of the stationary phase and solid support. The same procedure was followed for low per cent loadings of BMBT on Porasil C samples.

Apparatus and procedure

A Perkin-Elmer Sigma 1B gas chromatograph equipped with dual columns, forced air oven, two flame ionization detectors, electronic carrier-gas flow controllers and a Sigma 10 data station was employed. The column inlet pressure was measured with an auxiliary instrument pressure gauge accurate to ±0.2 p.s.i., and column outlet pressure was read off a barometer. Oven temperatures were independently calibrated with a thermocouple. The temperature control at 200°C was accurate to ±1.5°C. Retention data were directly recorded by the on-line data station. An average of three measurements was taken for each point. The retention time of benzene (10 ± 1 s at all temperatures above 190°C) was used to correct for column dead volume. At 220°C, the highest column temperature, this value was less than 0.2% of the retention time of phenanthrene. Minimum sample sizes (less than 0.05 µl) of solutions of solutes in benzene were generally injected. At high per cent loadings all solute peaks were symmetrical.

A Du Pont Model 999 differential scanning calorimeter was employed for the phase transition temperature measurements. It was purged continuously at a slow and constant flow-rate with dry nitrogen. Using a scanning rate of 10°C/min, the temperature axis was calibrated with indium (m.p. 156.6°C). A 5- to 10-mg amount of each sample of pure BMBT and BMBT-coated solid supports were hermetically sealed and the program was set for heating and then cooling within the specified temperature ranges. All samples were run in duplicate.

RESULTS AND DISCUSSION

According to Purnell and co-workers[17], who studied the various factors leading to retention, the retention volume, V_N, may be expressed in the form

$$V_N = K_L V_L + K_{SS} A_S + K_{LS} A_L \tag{1}$$

where K, the partition coefficient, refers to the partitioning processes, (i) in the bulk liquid phase (L), (ii) at the liquid phase surface (LS) and (iii) at the support surface (SS), V_L is the volume of liquid phase in the column and A_L and A_S are the surface areas of the liquid phase and solid support, respectively. V_N is related to V_g^0 by the expression

$$V_N = V_g^0 \, W_L \cdot \frac{T_C}{273.2} \tag{2}$$

where W_L is the mass of liquid phase in the column and T_C is the column temperature in °K.

Table I lists V_g^0 values for phenanthrene and anthracene at four temperatures in the nematic region of BMBT with columns of different per cent loadings of BMBT on Chromosorb W HP. The values decrease as the per cent loading increases and level off at around 5%, beyond which no change is observed with increasing per cent loading. Table II gives the corresponding V_g^0 values on BMBT-coated Porasil C. With this surface-active support the values are unusually high at low per cent loadings, decrease with increasing surface coverage, but do not level off even at loadings as high as 30%. In dealing with such systems, the retention volume per gram of solid support is more appropriate to use than V_g^0, because it better reveals the effect of the solid support on retention[18]. Dividing eqn. 1 by W_S we obtain

$$V_N/W_S = K_L\, W_L/W_S + K_{SS}A_S/W_S + K_{LS}A_L/W_S \tag{3}$$

TABLE I

SOLUTE-SPECIFIC RETENTION VOLUMES (V_g^0) WITH BMBT-COATED CHROMOSORB W HP

Solute	*% Loading*	$V_g^0 \pm 3\%$			
		190°C	*200°C*	*210°C*	*220°C*
Phenanthrene	0.80	1101	792.3	578.4	435.8
Anthracene	0.80	1529	1083	784.4	586.3
Phenanthrene	2.36	834.2	622.2	467.8	352.0
Anthracene	2.36	1180	864.2	636.0	472.4
Phenanthrene	5.08	748.7	545.7	405.3	306.2
Anthracene	5.08	1057	756.4	547.6	403.5
Phenanthrene	8.57	739.3	546.0	410.8	316.0
Anthracene	8.57	1045	755.5	559.3	421.1
Phenanthrene	19.45	734.9	524.0	386.7	306.7
Anthracene	19.45	1046	727.1	528.2	408.6

TABLE II

SOLUTE-SPECIFIC RETENTION VOLUMES WITH BMBT-COATED PORASIL C

Solute	*% Loading*	$V_g^0 \pm 3\%$			
		190°C	*200°C*	*210°C*	*220°C*
Phenanthrene	0.45	32,120	19,260	13,800	9777
Anthracene	0.45	33,450	19,880	14,130	10,060
Phenanthrene	7.9	2930	1910	1410	1040
Anthracene	7.9	3140	2070	1480	1090
Phenanthrene	10.7	2360	1534	1183	913.7
Anthracene	10.7	2566	1728	1304	1001
Phenanthrene	21.6	1222	841.0	633.1	513.1
Anthracene	21.6	1402	976.3	730.8	568.8
Phenanthrene	30.2	1031	759.3	568.6	429.3
Anthracene	30.2	1261	913.5	677.0	505.5

where W_S is the mass of solid support in the column, $K'_L = K_L/\varrho_L$ and ϱ_L is the density of the stationary phase at the column temperature. A plot of V_N/W_S *vs.* W_L/W_S should give a straight line of slope K'_L if the terms $K_{SS}A_S/W_S$ and $K_{LS}A_L/W_S$ are constant. Furthermore, an intercept of zero indicates complete absence of an adsorption contribution to the retention mechanism.

In Fig. 1, V_N/W_S at 200°C is plotted *vs.* W_L/W_S for the two solute probes on columns of BMBT-coated Chromosorb W HP. Fig. 2 shows a similar plot for the same solutes on BMBT-coated Porasil C. It is clear that in the first case extrapolation of the straight lines for both solutes yields zero intercepts within the experimental error, verifying the inert nature of this low-surface-area support. On the other hand, different straight sections of different slopes and non-zero intercepts are evident with

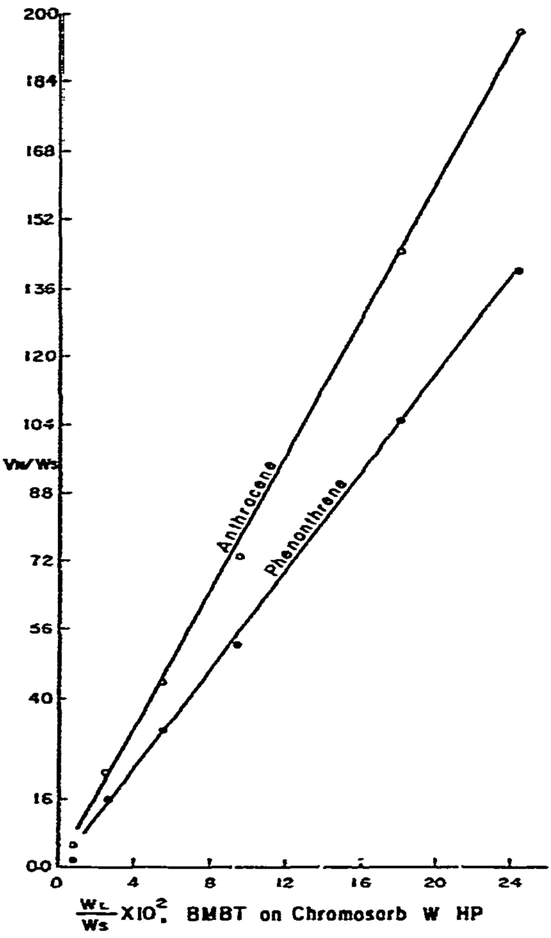


Fig. 1. Retention volumes per gram of solid support (ml/g) for two solutes at 200°C as a function of (W_L/W_S) for BMBT on Chromosorb W HP.

Porasil C. It is clear that the slopes change between W_L/W_S of 0.12 (corresponding to 10.7% loading) and 0.26 (corresponding to 20.6% loading). It is possible to calculate K_L^c and estimate the adsorption terms from eqn. 3, but this requires more points than are shown in Fig. 2. Nevertheless the figure shows the figure shows the complex nature of the retention mechanism with a high-surface-area support. As the per cent loading increases the contribution of the bulk stationary phase partioning process increases, but one could not safely say that the support active sites are blocked at about 30% loading since the values of V_g^0 are still higher at this loading than the average V_g^0 values obtained on BMBT-coated Chromosorb W HP.

It is known that the heat of adsorption is generally higher than the heat of solution. If one assumes that the retention mechanism in our systems is a combination of bulk absorption and surface adsorption, then one would expect that ΔH_2^s obtainable from a plot of log V_g^0 *vs.* reciprocal temperature (Tables III and IV) would be higher with Porasil C than with Chromosorb W HP. Further, one would expect

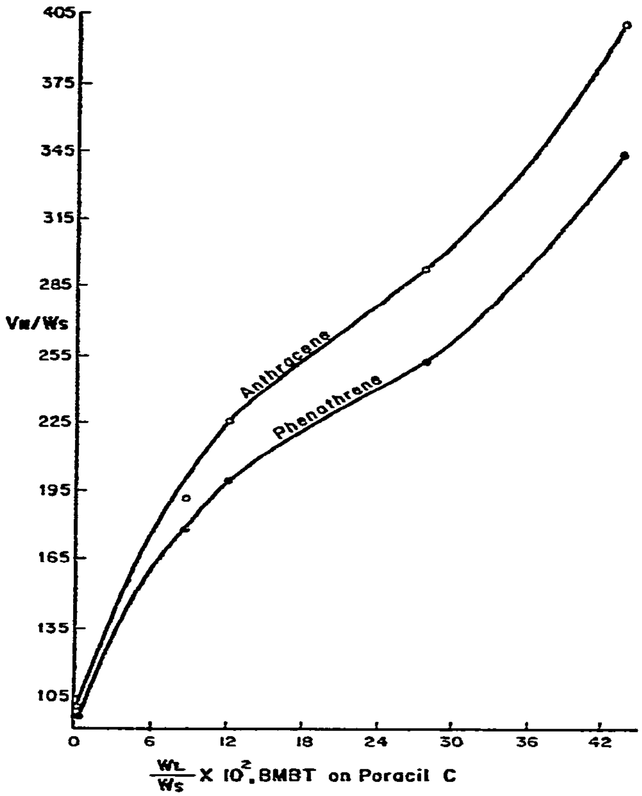


Fig. 2. Retention volumes per gram of solid support (ml/g) for two solutes at 200°C as a function of (W_L/W_S) for BMBT on Porasil C.

ΔH_2^s to decrease as the amount of stationary phase on Porasil C is increased, unlike the case with Chromosorb W HP where ΔH_2^s is not expected to change. Table IV shows that ΔH_2^s with Porasil C starts at a high value with low per cent loading and decreases as the loading is increased. Table III shows that (discounting the ΔH_2^s value at 0.8% loading) the average for the other four BMBT loadings is 55.2 ± 1.4 kJ/mol for phenanthrene and 59.1 ± 1.9 kJ/mol for anthracene.

Vetrova *et al.*[16] observed that when a liquid crystal is applied in sufficient

TABLE III

SOLUTE THERMODYNAMIC DATA WITH BMBT-COATED CHROMOSORB W HP

% Loacing	*$-\Delta H_2^s$ (kJ/mol)*	
	Phenanthrene	*Anthracene*
0.80	58.8	60.8
2.36	54.5	58.0
5.08	56.6	61.0
8.57	53.9	57.5
19.45	55.0	59.7

TABLE IV

SOLUTE THERMODYNAMIC DATA WITH BMBT-COATED PORASIL C

% Loading	$-\Delta H_2^s$ *(kJ/mol)* ± 3%	
	Phenanthrene	*Anthracene*
0.45	74.2	75.03
7.9	64.9	66.8
10.7	59.1	61.8
21.6	54.9	57.0
30.2	55.4	57.8

amount to cover the active surface as a monolayer, a certain orientation and positioning of the liquid crystal molecules occurs on the surface due to the strong adsorption field. If the amount of liquid crystal is increased further the molecules are oriented relative to those already positioned. This type of orientation drastically affects the character of the liquid crystal phase transitions, thus widening the chromatographically useful temperature range. Specifically, they reported that the selectivity of such phases towards the separation of xylene isomers was improved and that the maximum selectivity is observed at a temperature in the solid state and not in the liquid crystalline state as is the case with inert solid support material. Our results are in agreement with their findings regarding the extension of the temperature range below the normal solid–liquid crystal transition temperature, however, contrary to their claims, we observed that the separation power of the liquid crystal phase is drastically reduced when coated on an active solid support. Fig. 3 shows the variations in relative

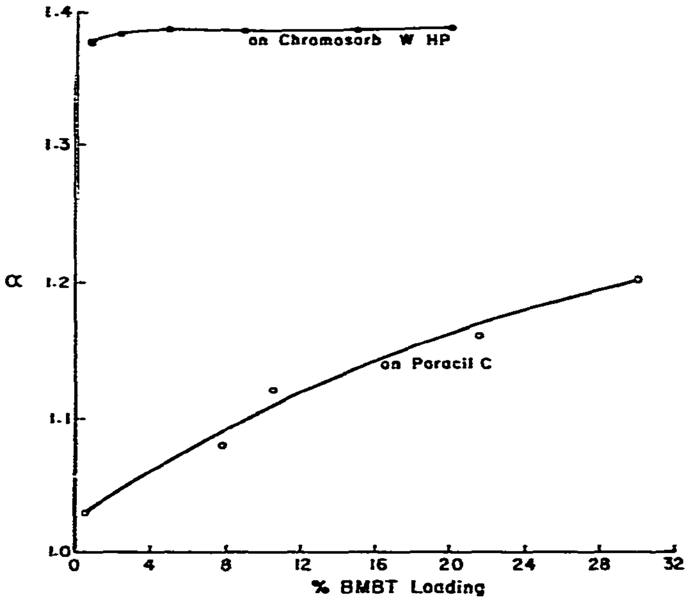


Fig. 3. Relative retention of anthracene to phenanthrene, α(A/P), in the nematic region of BMBT as a function of BMBT loading on two solid supports.

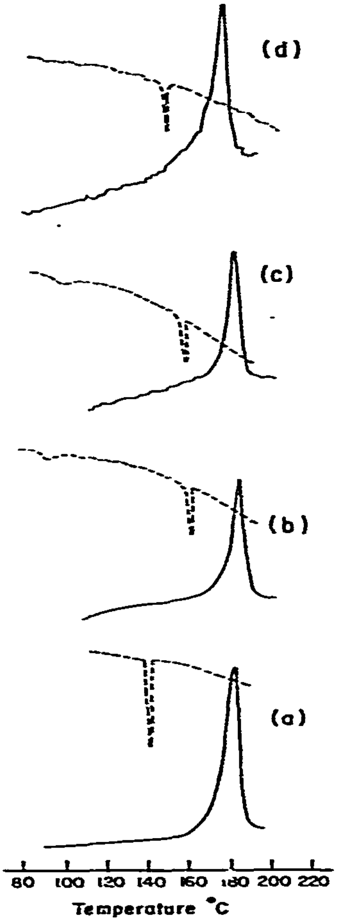
retention of anthracene and phenanthrene, $\alpha(A/P)$, as a function of per cent loading of BMBT on Chromosorb W HP and on Porasil C at 200°C. It is clear that $\alpha(A/P)$ is much higher on Chromosorb W HP than on Porasil C. Furthermore, while a constant value is reached at about 5% loading of BMBT on Chromosorb W HP, $\alpha(A/P)$ increases with loading on Porasil C. The maximum value at about 30% loading of BMBT on Porasil C is still significantly lower than the average value achieved with BMBT-coated Chromosorb W HP.

The choice of a surface-active solid support does not offer the chromatographer any advantage other than extending the working temperatures of liquid crystal phases to lower values. Since the main reason for selecting a liquid crystal stationary phase is to take advantage of the enhanced selectivity exhibited by these phases, the clear choice of solid support is a highly inert low-surface-area material.

We now address the supercooling phenomena observed with pure and support-coated BMBT, and discuss the implications of our GLC and DSC results in relation to the configuration of the BMBT molecules on the support surface.

Liquid crystal phase transitions may be monitored directly by DSC thermograms which could be recorded with heating and cooling programs. Alternatively they may be investigated indirectly by GLC. Typically, the logarithm of the capacity ratio (corrected retention time) of some probe solutes chromatographed on a liquid crystal stationary phase are plotted *versus* reciprocal temperature. Such a plot is virtually a straight line of constant slope as long as the stationary phase does not undergo a phase change. Phase transitions are thus monitored as changes in the slope of the plot.

Fig. 4 shows DSC thermograms of pure BMBT and packings of various percentages of BMBT on Chromosorb W HP. It is clear that on heating the solid the solid–nematic transition is only slightly affected by spreading the material on the inert support surface. This result is in agreement with the observations of other workers[9–11] on similar systems. On the other hand, upon cooling the nematic melt pure BMBT solidifies at 140°C, about 42°C below the normal solid–nematic transition, while BMBT-coated Chromosorb W HP samples solidify at 163 ± 5°C which is only about 19°C below the normal nematic–solid transition and about 23°C above the solidification temperature of pure BMBT samples. We found that with multiple DSC scans the temperatures reported above were reproducible to within ±3°C irrespective of the cooling rate. Furthermore, as the coated support samples are cooled below the solidification point, a small and broad exothermic peak is observed around 100°C. With low per cent loadings (*i.e.*, 5.8% and lower) this peak was not observed, perhaps because the amount of BMBT in the sample pan is very small. We assign the transition at around 163°C to bulk BMBT present in the pores and around the solid support particles, and the transition around 100°C to BMBT spread as an ordered film on the solid support surface, and present corroborative GLC evidence in support of this assignment. Fig. 5 shows $\ln t'_R$ *vs.* T^{-1} for the solute probe phenanthrene on cooling the nematic melt of BMBT-coated Chromosorb W HP. At 5.8% loading $\ln t'_R$ increases linearly with decrease in temperature, and the nematic solvent properties are preserved at temperatures below the normal nematic–solid transition temperature down to around 110°C. At this temperature the retention drops sharply due to the solidification of the mesophase. This is in agreement with the results of Wasik and Chester[5] with 2.5% BMBT columns. They attributed the linearity of the plot to



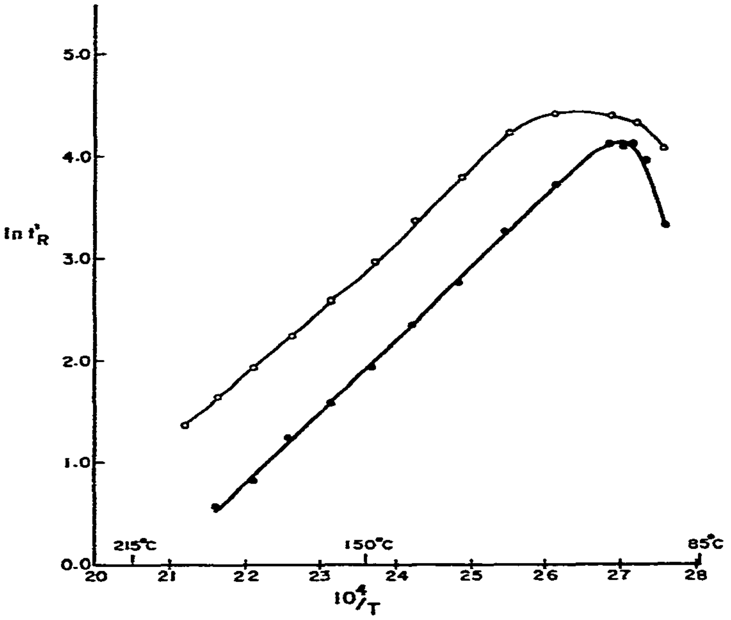
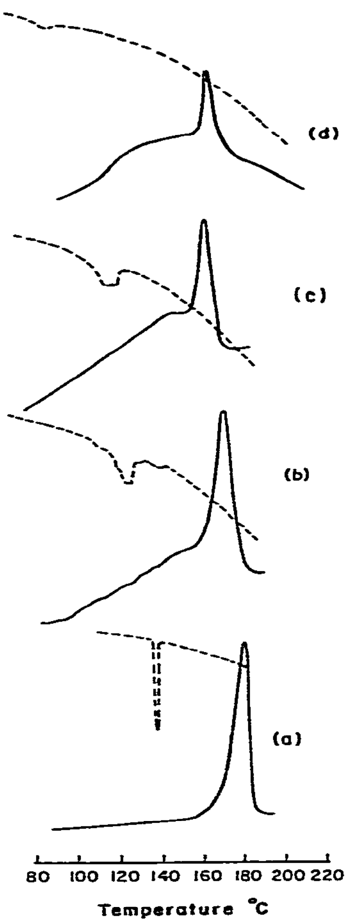


Fig. 4. DSC scans of BMBT, pure and coated on Chromosorb W HP. Scan rate 10°C/min. Solid lines, heating; dashed lines, cooling. (a) pure BMBT; (b) 23%; (c) 12.2%; (d) 5.8% loading.

Fig. 5. Logarithm of the retention time ($t'R$) of phenanthrene *versus* reciprocal temperature on cooling the nematic melt of BMBT-coated Chromosorb W HP. Per cent loadings: ○, 8.5; ●, 12.2.

supercooling of the nematic melt. We, on the other hand, believe that with low per cent loadings ($< \approx 6\%$) most of the BMBT phase is spread on the solid support in some sort of two-dimensional arrangement and the proportion of bulk BMBT is insufficient to affect the linearity of the ln t'_R *vs.* T^{-1} plot. As the amount of BMBT is increased the proportion of bulk BMBT increases and when this portion solidifies a change in the slope of ln t'_R *vs.* T^{-1} appears as demonstrated at the 12.2% loading in Fig. 5.

Turning our attention to the active support material of the Porasil C type we find that the DSC results shown in Fig. 6 for pure and coated BMBT and the corresponding GLC results shown in Fig. 7 are qualitatively different from those reported for Chromosorb W HP (Figs. 4 and 5). It is observed that the BMBT solidification is shifted to temperatures lower than the nematic–solid transition temperature of pure



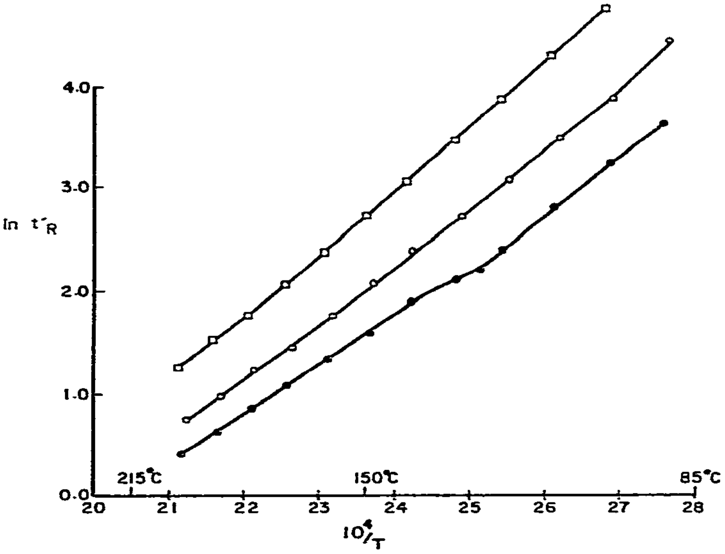
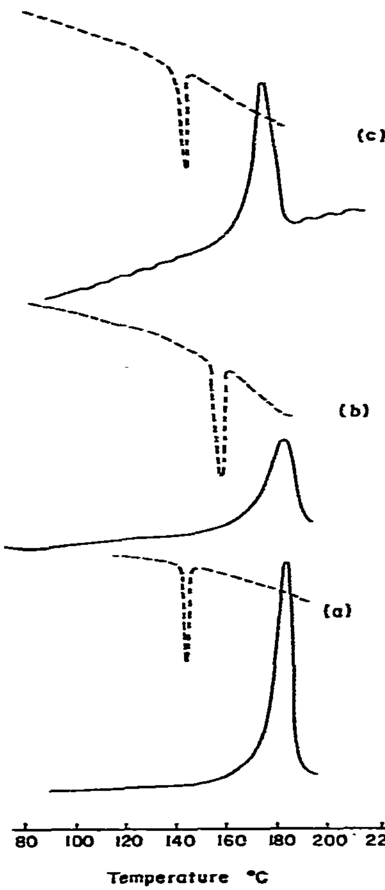


Fig. 6. DSC scans of BMBT, pure and coated on Porasil C. Scan rate 10°C/min. Solid lines, heating; dashed lines, cooling. (a) pure BMBT; (b) 35%; (c) 25%; (d) 15% loading.

Fig. 7. Logarithm of the retention time of phenanthrene *versus* reciprocal temperature on cooling the nematic melt of BMBT-coated Porasil C. Per cent loadings: ●, 35; ○, 25; ◇, 15.

BMBT, and that the transition temperature approaches that of supercooled pure BMBT as the per cent loading is increased. It is believed that the difference in the nematic–solid transition temperatures on cooling BMBT samples coated on Porasil C and Chromosorb W is due to the fact that the force field exerted by the surface of Porasil C is larger than that of Chromosorb W HP. The GLC results, on the other hand, show that ln t'_R *vs.* T^{-1} plots are linear at 15 and 25% loadings and the change of slope around the bulk transition temperature appears only at 35% loading. It is clear that, because of the large surface area of Porasil C, most of the BMBT is present in the surface-adsorbed configuration. As the amount of BMBT is increased the solid support capillaries are filled with bulk mesophase. On the other hand, the solidification temperature of surface-adsorbed BMBT is depressed significantly as our GLC experiment did not reveal the position of the lower temperature transition.

It is interesting that the DSC thermograms obtained on heating BMBT-coated



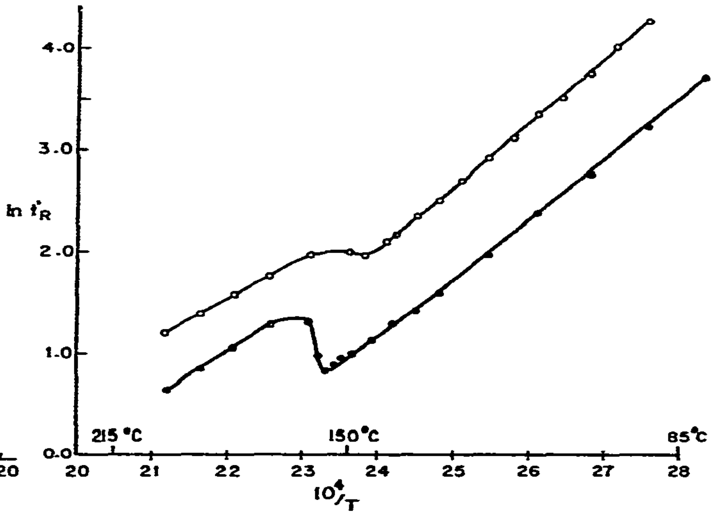


Fig. 8. DSC scans of BMBT, pure and coated on Porasil F. Scan rate 10°C/min, Solid lines, heating; dashed lines, cooling. (a) pure BMBT; (b) 12.5%; (c) 6.5% loading.

Fig. 9. Logarithm of the retention time of naphthalene *versus* reciprocal temperature on cooling the nematic melt of BMBT-coated Porasil F. Per cent loadings: ●, 12.5; ○, 6.5.

Porasil C samples show broad peaks below the normal solid–nematic transition temperature. Armitage and Price[12] reported similar observations with naphthalene coated on Porasil B. They interpreted the depressed transition as that due to material in the pores, while the normal transition is due to material existing between the Porasil particles.

Fig. 8 shows DSC thermograms of samples of pure BMBT and BMBT coated on Porasil F. The surface area of Porasil F ($1.5\ m^2/g$) is only slightly higher than that of Chromosorb W HP (0.6–$1.3\ m^2/g$), however while Chromosorb W HP is silanized, Porasil F is not so treated. Fig. 9 shows GLC plots of $\ln t'_R$ *vs.* T^{-1} for the same samples as in Fig. 8. The DSC results are qualitatively similar to those reported for Chromosorb W HP, with the bulk solidification temperature being higher than that of pure BMBT. However, the solidification temperature approaches that of pure BMBT as the per cent loading is increased and no broad peaks are observed at lower temperatures. The GLC results for this support material are different from those

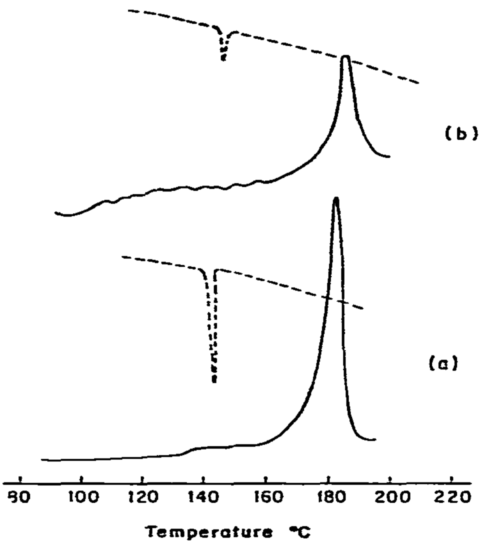


Fig. 10. DSC scans of BMBT, pure and coated on DMCS-treated glass beads. Scan rate 10°C/min. Solid lines, heating; dashed lines, cooling. (a) pure BMBT; (b) 1 % loading.

reported for Chromosorb W HP and Porasil C. With Porasil F, the BMBT solidification temperature is accompanied by a more pronounced change in the slope of ln t'_R *vs.* T^{-1} plots. It is apparant that further experimental data are needed to explain the difference in the chromatographic behaviour between BMBT/Porasil F and BMBT/Chromosorb W HP columns.

Finally, Fig. 10 shows DSC thermograms of samples of pure BMBT and BMBT coated on dimethylchlorosilane (DMCS)-treated glass beads, and Fig. 11 shows the corresponding GLC plots of ln t'_R *vs.* T^{-1}. Glass beads are the most inert types of solid supports used in GLC, however, because of their very low surface area the capacity of glass bead columns is limited. At 1 % loading, the DSC thermogram shows that the solidification temperature of coated BMBT is the same as that of pure BMBT. The GLC ln t'_R *vs.* T^{-1} plot showed only one transition at around 130°C. The relative retention, α(A/P), was measured on a column containing 1 % BMBT on glass

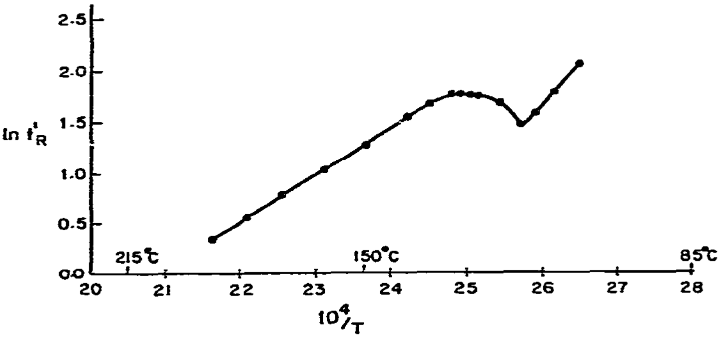


Fig. 11. Logarithm of the retention time of phenanthrene *versus* reciprocal temperature on cooling the nematic melt of 1 % BMBT coated on DMCS-treated glass beads.

beads at 200°C and a values of 1.39 was obtained. This is comparable to the average value obtained on BMBT/Chromosorb W HP columns.

It is therefore concluded that the nematic–solid transition temperatures for the supercooled material, obtained from indirect GLC measurements, do not correspond to the real bulk liquid crystal, but rather to some sort of oriented configuration of the substrate on the solid support surface. The presence of bulk liquid crystal material in the solid support capillaries is revealed by direct DSC measurements.

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