



ELSEVIER

Journal of Chromatography A, 773 (1997) 199–208

JOURNAL OF
CHROMATOGRAPHY A

Synthesis and characterization of a novel wall coated capillary column for the separation of polycyclic aromatic hydrocarbons

Chuen-Ying Liu*, Cho-Chun Hu, Cheng-Lung Yang

Department of Chemistry, National Taiwan University, Taipei, Taiwan

Received 28 October 1996; revised 17 February 1997; accepted 18 February 1997

Abstract

A mesogenic polymer prepared from the metal complexes of 4-(dec-9'-en-1'-oxy)dithiobenzoate and polysiloxane is described. Differential scanning calorimetry measurements were used for detecting phase transitions. By static coating, wall-coated polymer capillary columns (12 m×0.25 mm I.D.) were prepared and used as the stationary phases for ligand-exchange gas chromatography (LEGC) for the separation of polycyclic aromatic hydrocarbons (PAHs). The results indicate that the nickel complex of the polymer is more appropriate for this usage than the zinc complex. Factors affecting the retention and the sample selectivity were examined. The Van't Hoff plots revealed at least one phase transition. The calibration graphs for most PAHs studied were linear over the range of 3.75–615 $\mu\text{g ml}^{-1}$, while those of fluoranthene and pyrene were linear over the range 30–615 $\mu\text{g ml}^{-1}$. The mass detection limits for most PAHs were in the pg range. Examples of the separation of PAHs indicate that the new wall-coated metallomesogen capillary columns may be useful stationary phases in the LEGC separation of pharmaceuticals, environmental pollutants or biological fluids which are electron-donating compounds.

Keywords: Ligand exchange; Capillary columns; Stationary phases, GC; Metallomesogen stationary phases; Polynuclear aromatic hydrocarbons

1. Introduction

Metallomesogens, metal-containing liquid crystals, combine the physical characteristics exhibited by metal coordination complexes with those of organic molecules which give liquid crystals [1]. Such compounds were first made over 80 years ago but their importance has only recently come to be appreciated.

Ligand-exchange chromatography (LEC) was first recognized by Helfferich and used broadly by Davankov [2]. It is a process in which complex-

forming compounds are separated through the formation and breaking of labile coordinate bonds to a central metal atom, coupled with partition between a mobile and a stationary phase. A great number of metal complexes have been used as stationary phases for ligand-exchange chromatography for the separation of electron-donating compounds. However, there are only a few reports on the use of metallomesogens for this purpose [3–7]. Takayanagi et al. used copper stearate for the separation of amines and dialkyl sulfides. They found that despite the low stability of the metal stearates at high temperature, these stationary phases were efficient and selective [3–5]. Berdagué et al. investigated the thermal

*Corresponding author.

properties of a liquid crystal metal complex by inverse GC on conventional columns and also studied the analytical performance of this complex as stationary phases on glass capillary columns [6]. Hu and Liu used the metal alkoxydithiobenzoates as stationary phases on packed columns of ligand-exchange gas chromatography (LEGC) for the separation of polycyclic aromatic hydrocarbons and dialkyl sulfides [7]. There are some limitations on selection of the metallomesogens in this system; in particular, coordination unsaturation of the central metal ion and thermotropic properties must be taken into account. Additionally, some organic molecules are mesogens, while their metal complexes may not be. The first metallomesogens of dithiolenes complexes with two chains were those of Giroud-Godquin and co-workers, and their synthesis marked the beginning of recent interest in metal-containing systems [8–11]. Metal complexes of 4-alkoxydithiobenzoic acids synthesized by Adams et al. [12] were employed in our first report on metallomesogens as stationary phases for LEGC [7]. The results showed that these columns were promising for the separation of polycyclic aromatic hydrocarbons and dialkyl sulfides. As part of our continuing study on the preparation and application of metallomesogens, double bond containing metallomesogens were prepared and bonded on to a polysiloxane backbone. The separation of polycyclic aromatic hydrocarbons was used as an efficiency test to evaluate the analytical potential of this wall-coated capillary column.

2. Experimental

2.1. Apparatus

All GC analyses were performed on a Shimadzu (Kyoto, Japan) Model GC-9A gas chromatograph equipped with split/splitless injector and flame ionization detector. A Shimadzu data processor (C-R2A) was used for the determination of retention times. The separations were carried out on a fused-silica capillary column (12 m×0.25 mm I.D.) with an external coating of polyimide (J&W, Folsom, CA, USA or Ohio Valley Specialty Chemicals, Marietta, OH, USA) and chemically coated with the metal

complex as described in the following procedures. Ammonia-equilibrated nitrogen (10:90, v/v) and pure nitrogen were used as the mobile phase. The phase behavior was determined using polarizing optical microscopy (BH-2, BHT, Olympus, Japan) equipped with a temperature controller (TMS 92, Linkam, UK) and differential scanning calorimetry (DSC) (TA, Model 910, USA) at a scan rate of 10°C min⁻¹.

2.2. Reagents and chemicals

Most chemicals used were of analytical reagent grade from Merck (Darmstadt, Germany). All liquid reagents and solvents used in moisture-sensitive reactions were distilled and collected over type 4 Å molecular sieves. All solid materials used in moisture-sensitive reactions were dried at 110°C for 24 h prior to the experiment. Polymethylhydrosiloxane (PS 122, $M_n=4500-5000$) was purchased from Petrach Systems (Bristol, PA, USA). This reagent was used without further purification.

2.3. Preparation of metallomesogens

In the beginning of this investigation, an olefin-containing chelating agent, 4-(dec-9'-en-1'-oxy)-dithiobenzoate was synthesized as follows (Fig. 1):

Dec-9-en-1-ol (0.075 mol) was added dropwise to a solution of 4-toluenesulfonyl chloride (0.082 mol) in pyridine (60 ml). The reaction was carried out in an ice bath under nitrogen. After 20 h, ice water (200 ml) was added to the above mixture and then extracted with dichloromethane. The organic layer was washed sequentially with 6 M HCl and pure water and then dried with anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the filtrate was concentrated under reduced pressure to give the pale yellow product I, dec-9-en-1-yl tosylate (84.1% yield)

Compound I (0.05 mol) was added dropwise to a solution containing 4-bromophenol (0.055 mol), potassium hydroxide (0.055 mol) and potassium iodide (0.001 mol) in ethanol. The reaction was heated to reflux for 16 h and 30% potassium hydroxide aqueous solution was then added. The reaction mixture was allowed to reflux for 2 h to ensure complete reaction. The mixture was cooled to

room temperature, then concentrated under reduced pressure and extracted with dichloromethane. The organic layer was shaken with a potassium hydroxide aqueous solution (1:10, w/v) and then with water. After repeating the procedures three times, anhydrous magnesium sulfate was added to dry the dichloromethane solution. The magnesium sulfate was removed by filtration and the solution was concentrated to yield the product II, dec-9-en-1-yl 4-bromophenyl ether (82.3% yield).

Under a nitrogen purge, 10 ml of dry tetrahydrofuran was placed in a dry 100-ml round-bottomed flask containing magnesium turnings (0.02 mol) which was connected to a condenser fitted with a balloon filled with nitrogen. With a dry syringe, several drops of II and a small amount of 1,2-dibromoethane as the initiator were added to the THF. After the reaction began, further II (6.3 g) in THF (20 ml) was added dropwise. The mixture was reacted for 2 h with stirring, until the magnesium was used up. The round-bottomed flask was sealed with a rubber septum.

Carbon disulfide (2.5 ml) was introduced dropwise into the round-bottomed flask containing the Grignard reagent in an ice bath. The mixture turned red immediately and reacted with stirring. After 2 h, ice (200 g) and concentrated hydrochloric acid (100 ml) were added to the mixture and extracted with diethyl ether, then dried with magnesium sulfate. The ether was removed with a rotary evaporator. The product, III, was precipitated at -15°C . Because of relatively low stability of the free acids, the ligands, 4-(dec-9'-en-1'-oxy)dithiobenzoate were stored as their sodium salts or directly reacted with metal salts in methanol-dichloromethane (1:1, v/v).

Metallomesogens were prepared by dropwise addition of a methanol solution (10 ml) of nickel chloride hexahydrate (1.0 mmol) or zinc acetate dihydrate (1.0 mmol) to dichloromethane-methanol (1:1, v/v) containing an excess of III (2.1 mmol) in an inert atmosphere. After the solution had been stirred for 8 h, the resulting precipitates were collected by filtration, washed sequentially with pure water, methanol and diethyl ether, then recrystallized from hot toluene to give the nickel complex. Because of low solubility of nickel complex in common solvents at room temperature, no NMR spectrum was given. IR: $\nu_{(\text{CSS})\text{s}}=1164\text{ cm}^{-1}$, $\nu_{(\text{CSS})\text{asymm}}=975$

cm^{-1} , $\nu_{(\text{CSS})\text{symm}}=945\text{ cm}^{-1}$, $\nu_{(\text{SS})}=565\text{ cm}^{-1}$, $\nu_{(\text{C}=\text{S})}=1019\text{ cm}^{-1}$, $\nu_{(\text{C}=\text{C},\text{ aromatic})}=1595\text{ cm}^{-1}$, $\nu_{(\text{C}=\text{C})}=1639\text{ cm}^{-1}$, $\nu_{(\text{C}=\text{H})}=3070\text{ cm}^{-1}$, $\nu_{(\text{C}-\text{H})\text{s}}=2852$ and 2923 cm^{-1} . Anal. calc. for $\text{C}_{34}\text{H}_{46}\text{O}_2\text{S}_4\text{Ni}$: C 60.65, H 6.88; found: C 60.01, H 6.75. The zinc complex was obtained on careful crystallization from toluene-hexane. $^1\text{H NMR}$ (C^2HCl_3): 1.13–1.54 (m, 20H, $-(\text{CH}_2)_5-\text{CH}_2-\text{CH}_2\text{O}$), 1.76–1.83 (m, 4H, $-\text{CH}_2-\text{CH}_2\text{O}$), 2.01–2.04 (t, 4H, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 4.00–4.06 (t, 4H, $-\text{CH}_2-\text{CH}_2\text{O}-$), 4.89–5.01 (t, 4H, $\text{CH}_2=\text{CH}-$), 5.82–5.90 (m, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 6.70–7.35 (dd, 8H, **aromatic protons**). IR: $\nu_{(\text{CSS})\text{s}}=1167\text{ cm}^{-1}$, $\nu_{(\text{CSS})\text{asymm}}=984\text{ cm}^{-1}$, $\nu_{(\text{CSS})\text{symm}}=925\text{ cm}^{-1}$, $\nu_{(\text{SS})}=585\text{ cm}^{-1}$, $\nu_{(\text{C}=\text{S})}=1019\text{ cm}^{-1}$, $\nu_{(\text{C}=\text{C},\text{ aromatic})}=1598\text{ cm}^{-1}$, $\nu_{(\text{C}=\text{C})}=1639\text{ cm}^{-1}$, $\nu_{(\text{C}=\text{H})}=3072\text{ cm}^{-1}$, $\nu_{(\text{C}-\text{H})\text{s}}=2850$ and 2922 cm^{-1} . Anal. calc. for $\text{C}_{34}\text{H}_{46}\text{O}_2\text{S}_4\text{Zn}$: C 60.02, H 6.82; found: C 59.89, H 6.67.

2.4. Synthesis of side chain liquid crystal polymer

Side chain liquid crystal polymer was synthesized by treating the metal complexes of III in toluene followed by coupling with polymethylhydrosiloxane in the presence of a catalytic amount of H_2PtCl_6 in butanol (50 μl , 1 $\mu\text{g ml}^{-1}$). The molar ratio of IV to Si-H functional groups of polysiloxane was 1.1. The mixture was refluxed under nitrogen until the Si-H functional group could not be detected with infrared spectroscopy. After cooling to room temperature, the solvent was removed by rotary evaporation and the residue was dissolved in dichloromethane. The unreacted IV was removed by filtration and the filtrate was concentrated under reduced pressure. The procedures were repeated thrice. The crude product was finally recrystallized from methanol to give compound V (Fig. 1).

To compound V (0.5 g) in 20 ml dichloromethane-methanol (1:1, v/v), 0.1 g Pd/C (10%, w/w) was added with stirring. The solvents were then evacuated and reacted under hydrogen at room temperature to ensure complete reaction. The final product was recovered by suction filtration and the solvent was removed by rotary evaporation. The desired products are called Compound VI. Elemental analysis (EA) for VI (M:Ni) before hydrogenation: C 66.09, H 7.14; after hydrogenation: C 62.45, H 7.93.

IR: $\nu_{(\text{CSS})_s} = 1166 \text{ cm}^{-1}$, $\nu_{(\text{CSS})_{\text{asymm}}} = 993 \text{ cm}^{-1}$, $\nu_{(\text{CSS})_{\text{symm}}} = 949 \text{ cm}^{-1}$, $\nu_{(\text{SS})} = 585 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{S})} = 1026 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{C}, \text{aromatic})} = 1596 \text{ cm}^{-1}$, $\nu_{(\text{C}-\text{H})_s} = 2850$ and 2921 cm^{-1} . EA for VI (M: Zn) before hydrogenation: C 65.11, H 6.34; after hydrogenation: C 64.34, H 6.18. IR: $\nu_{(\text{CSS})_s} = 1167 \text{ cm}^{-1}$, $\nu_{(\text{CSS})_{\text{asymm}}} = 984 \text{ cm}^{-1}$, $\nu_{(\text{CSS})_{\text{symm}}} = 950 \text{ cm}^{-1}$, $\nu_{(\text{SS})} = 585 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{S})} = 1023 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{C}, \text{aromatic})} = 1596 \text{ cm}^{-1}$, $\nu_{(\text{C}-\text{H})_s} = 2852$ and 2920 cm^{-1} .

2.5. Column preparation

Fused-silica capillaries were first rinsed with methanol and dichloromethane (5 ml each) sequentially. Then the capillaries were conditioned at 250°C with a gentle flow of nitrogen for about 4 h and coated using static procedure. The apparatus for the coating procedure is as that proposed by Grob et al. [13] with some modification. In order to prepare a capillary column (12 m × 0.25 mm I.D.) with film thickness of 0.25 μm , a solution prepared from 0.020 g linear side-chain liquid crystal polymer in 5 ml dichloromethane (which also contained benzoyl peroxide, 5% w/w of the linear polymer) was filled into the capillary. The column was then slowly dipped into a water bath at 40°C, followed by removal of the solvent under vacuum lasting for 10 h. To improve the reproducibility and efficiency of the coating procedure, we considered the possibility of coating glass capillaries as follows. One end of the fused-silica capillary sealed with silicon rubber was immersed in ice water. The other end was connected to a buffer capillary column to which a 0.5-cm diameter empty glass tube was lined up successively. The latter process was used in order to obtain an almost homogeneous distribution of the deposited material, and as a trap for the vacuum system. After coating, the columns were then placed in the nitrogen-purged oven of a gas chromatograph. The temperature was raised to 200°C at a heating rate of 3°C min⁻¹. After this heat treatment, the interior column wall formed was purged with nitrogen at 200°C for 6 h. The cross-linking was performed at these processes. Then the column was rinsed with dichloromethane (5 ml) to remove any traces of unreacted material and further purged with nitrogen for about 15 min till a constant stable base line was obtained.

3. Results and discussion

3.1. Characteristics of the prepared metallomesogens

The reactions involved in the preparation of metallomesogens are shown in Fig. 1. Poly(methylhydrosiloxane) is reacted with the metal complexes of compound III containing a vinyl group, namely DODTBA–Ni and DODTBA–Zn. Hydrosilation takes place yielding the mesomorphic polysiloxane. The extent of completion of the reaction was assessed by proton NMR which is superior to IR spectroscopy [13]. For the hydrogenation of the unreacted vinyl group in mesomorphic polysiloxane, the intensity of the IR absorption peak at 1685 cm⁻¹ (–C=C) can be used to assess the extent of the reaction. The desired final products were referred to as P-DODTBA–Ni and P-DODTBA–Zn, respectively. In general, it can be assumed that static coating gives a more uniform polymerization than a dynamic procedure [14–16]. Therefore static coating procedures were adopted for the preparation of wall-coated capillary columns.

The liquid crystal property of both DODTBA–Ni and DODTBA–Zn were characterized via the techniques of light microscopy and calorimetric investigation. The DSC thermogram observed for DODTBA–Ni on heating showed a glass transition temperature (T_g) at 122.6°C and two endothermic peaks probably corresponding to the transition from a smectic H to smectic C type at 162.9°C and from the smectic C to isotropic phase at 230°C. The DSC thermogram for DODTBA–Zn showed a glass transition temperature (T_g) at 123.1°C and two endothermic peaks probably corresponding to the transition from a smectic C to nematic mesophase at 140.8°C and that from the nematic to isotropic phase at 162.9°C. In a similar way, the liquid crystal property of the metallomesogen-containing polymer was also investigated. The transition temperatures of each olefin-containing metallomesogen and its corresponding siloxane polymers are summarized in Table 1. A significant variation in phase transition temperature of the olefin-containing metallomesogens in comparison with that of the metallomesogens prepared in the previous paper [7] was observed. Not only did the phase transition temperature of the

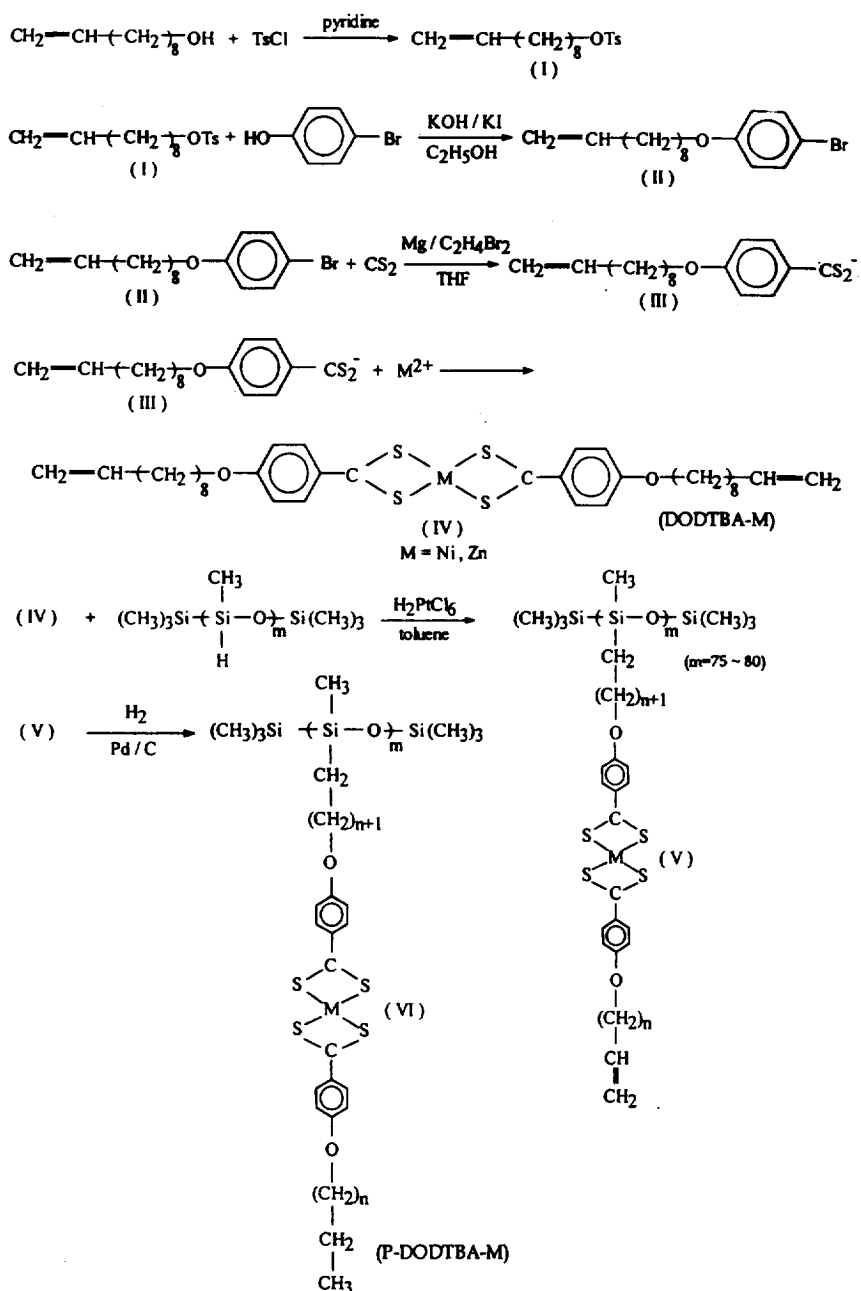


Fig. 1. Procedures for the preparation of metallomesogenic polymer.

metallomesogens containing vinyl groups shift to a lower temperature, but also the thermal stability of these compounds seemed poorer than the previous ones. This behavior might be due to the asymmetry of the molecule for introducing the vinyl group.

3.2. Separation with the wall-coated capillary column

The analytical capabilities of the prepared metallomesogens were established by use of a 12-m wall-

Table 1
Phase transition temperatures and enthalpies for the metallomesogens^a

Compounds	Phase transition temperature, °C (corresponding enthalpy changes, kJ mol ⁻¹)			
	K	S _H	S _C	N
DDTBA–Ni ^b	140.2 (14.2)	167.5 (11.4)	235 (---)	I
DDTBA–Zn ^b	131.4 (27.0)	160.9 (5.2)	173.2 (---)	I
DODTBA–Ni	122.6 (10.8)	162.9 (9.8)	230 (---)	I
DODTBA–Zn	123.1 (18.4)	140.8 (2.7)	162.9 (---)	I
P-DODTBA–Ni	116.1	154.1	240	I
P-DODTBA–Zn	84.1	123.1	140.8	I ^c

^a Abbreviations: K: crystalline; S_C: smetic C; S_H: smetic H; N: nematic; I: isotropic. DDTBA: 4-(dec-1'-oxy)dithiobenzoate; DODTBA: 4-(dec-9'-en-1'-oxy)dithiobenzoate. P-DODTBA: DODTBA corresponding polymer.

^b [7]

^c Decomposed at 170°C.

coated capillary column. In this investigation, polycyclic aromatic hydrocarbons (PAHs) are chosen to evaluate the column efficiency since PAHs can form metal complexes via interaction with electrons of the carbon–carbon double bonds [17].

Preliminary test show that a serious base line drift is indicated for the zinc complex at oven temperature higher than 160°C, only PAHs with lower boiling point could be analyzed with zinc complex, so the nickel complex was selected as the stationary phase for the separation of PAHs. Optimization of the LEGC separation with the new column was carried out using the model PAHs, naphthalene (b.p. 218°C; length-to-breadth ratio, *L/B* 1.244), 2-methylnaphthalene (b.p. 242°C; *L/B* 1.381), 1-methylnaphthalene (b.p. 245°C; *L/B* 1.208), biphenyl (b.p. 255°C; *L/B* 1.748), diphenylmethane (b.p. 265°C; *L/B* 1.651), acenaphthylene (b.p. 280°C; *L/B* 1.076), acenaphthene (b.p. 279°C; *L/B* 1.111), dibenzofuran (b.p. 288°C), fluorene (b.p. 295°C; *L/B* 1.542), phenanthrene (b.p. 338°C; *L/B* 1.569), anthracene (b.p. 340°C; *L/B* 1.579), fluoranthene (b.p. 383°C; *L/B* 1.200), and pyrene (b.p. 393°C; *L/B* 1.259).

The effect of temperature on selectivity showed that in the temperature range where metallomesogens are liquid crystals (130°C–230°C), the retention of samples was reduced and the peak shape was improved with increasing column temperature (Fig. 2). However, shorter retention times caused poor sample selectivity for early eluting samples. In order to test the column efficiency, the number of theoretical plates (*N*) for the separation of dibenzofuran, fluorene and phenanthrene were determined as a function of temperature (Table 2). The plate number

shows a maximum at ~160°C, we therefore consider this temperature to be the optimum with isocratic elution. Fig. 3 shows the separation of PAHs with the prepared column operated at 150°C for 5 min and then ramped up to 190°C at 3°C min⁻¹. These 13 isomers were almost completely resolved from each other on the column. Moreover, the resolution of 2-methylnaphthalene and 1-methylnaphthalene as well as that of the phenanthrene and anthracene is poorer compared with other pairs of PAHs. The elution order of these PAHs is almost consistent with their b.p. except acenaphthylene and acenaphthene. Similar cases occurring in the stationary phases of a nematic liquid crystal and its cupric complex were reported by Guermouche and coworkers, except for the inversion of 1-methylnaphthalene and 2-methylnaphthalene [6]. Only nine compounds and no biphenyl, diphenylmethane, dibenzofuran and fluoranthene reported by them could be compared with each other.

In this investigation, either helium, or ammonia in nitrogen was also tested as mobile phases (Fig. 4). Compared with nitrogen, helium gave a smaller peak with poorer resolution. While the presence of ammonia in nitrogen drastically reduced the retention time of samples, it was found to be effective in improving the peak shape. The expected decrease in analysis time with helium as carrier gas compared to nitrogen was not observed. Based on the separation mechanism which predominantly concerns both ligand exchange and shape selectivity, the phenomenon seems rational. The resolution between the geometric isomers, 1-methylnaphthalene and 2-methylnaphthalene was increased slightly by the addition of am-

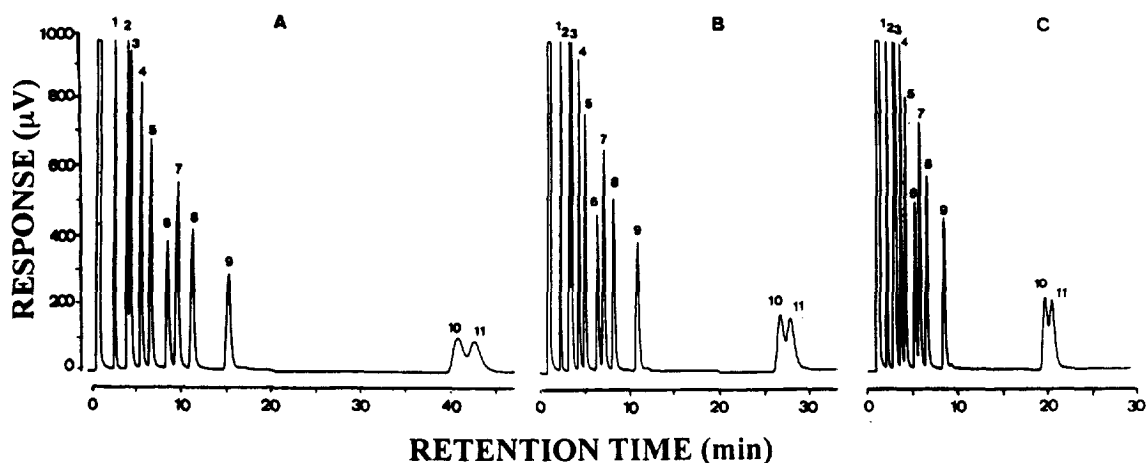


Fig. 2. Separation of PAHs at various oven temperature. Stationary phase: P-DODTBA–Ni, 12 m×0.25 mm I.D.; sample concentration: 480 $\mu\text{g ml}^{-1}$; injector volume: 1 μl ; injector temperature: 260°C; total flow-rate of carrier gas (N_2): 25 ml min^{-1} ; split ratio: 1:25; make-up gas flow-rate: 50 ml min^{-1} ; oven temperature: (A) 150°C; (B) 160°C; (C) 170°C. Peak identification: (1) naphthalene; (2) 2-methylnaphthalene; (3) 1-methylnaphthalene; (4) biphenyl; (5) diphenylmethane; (6) acenaphthylene; (7) acenaphthene; (8) dibenzofuran; (9) fluorene; (10) phenanthrene; (11) anthracene.

monia in nitrogen. Meanwhile, the more double bonds, the longer the retention time and the more pronounced were the effects of the ammonia–nitrogen (10:90, v/v) carrier gas. This phenomena might be due to the competitive coordination of ammonia with PAHs in the stationary phase. Moreover, pure nitrogen without the addition of ammonia as carrier gas was adopted for the further investigation owing to the high corrosion of ammonia.

One possible method for detecting the presence of liquid crystalline properties is a plot of $\ln k'$ of PAHs against reciprocal absolute temperature for the column prepared. A change in slope at a temperature of

160°C can be seen (Fig. 5), which indicates that a different retention mechanism becomes effective around this temperature. Temperature dependencies observed in the stationary phase, indicate that partition of samples into the liquid crystal structure must be taken into account in addition to the ligand exchange reaction. Chang et al. reported that the elution patterns of eleven PAHs on a smectic liquid crystal phase were almost consistent with their L/B ratios [18]. The more rod-like molecule was retained longer. While solute elution only roughly correlates to the degree of solute rod-like, L/B character in our work.

Table 2
Column efficiency for the separation of PAHs^a

T (°C)	t_R (min)		$W_{1/2}$ (s)		N		HETP (cm)	
	A	B	A	B	A	B	A	B
140	15.33	21.21	35.40	47.40	3742	3993	0.32	0.30
150	11.00	14.90	24.30	32.00	4087	4324	0.29	0.28
160	7.74	10.24	17.10	21.80	4086	4399	0.29	0.27
170	6.07	7.88	14.20	16.90	3647	4333	0.33	0.28
180	4.49	5.69	10.60	12.40	3570	4192	0.34	0.29
190	3.57	4.43	8.40	10.00	3596	3910	0.34	0.31

^a Experimental conditions as in Fig. 2.

Abbreviations: T : column temperature; t_R : retention time; $W_{1/2}$: peak width at half-height; N : the number of theoretical plates; HETP: height equivalent to a theoretical plate; A: dibenzofuran; B: phenanthrene.

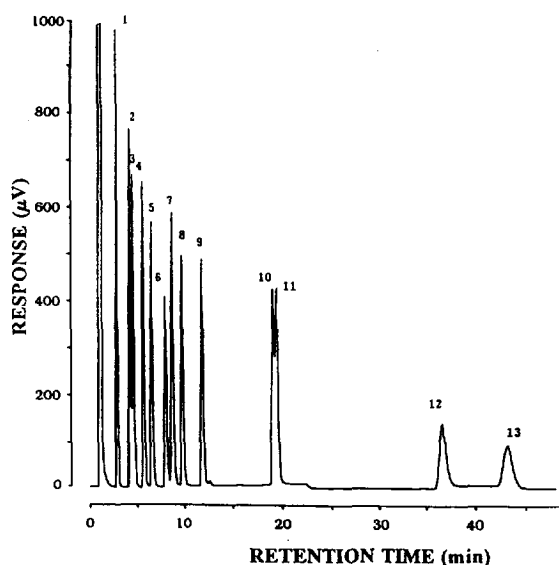


Fig. 3. Separation of PAHs with the optimized programmed temperature. Stationary phase: P-DODTBA-Ni, 12 m \times 0.25 mm I.D.; sample concentration: 480 $\mu\text{g ml}^{-1}$; injector volume: 1 μl ; injector temperature: 260 $^{\circ}\text{C}$; oven temperature: 150 $^{\circ}\text{C}$ (5 min) to 190 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C min}^{-1}$; total flow-rate of carrier gas (N_2): 25 ml min^{-1} ; split ratio: 1:25; make-up gas flow-rate: 50 ml min^{-1} . Peak identification: (1) naphthalene ($t_{\text{R}}=2.80$ min); (2) 2-methylnaphthalene ($t_{\text{R}}=4.17$ min); (3) 1-methylnaphthalene ($t_{\text{R}}=4.51$ min); (4) biphenyl ($t_{\text{R}}=5.62$ min); (5) diphenylmethane ($t_{\text{R}}=6.52$ min); (6) acenaphthylene ($t_{\text{R}}=7.99$ min); (7) acenaphthene ($t_{\text{R}}=8.71$ min); (8) dibenzofuran ($t_{\text{R}}=9.77$ min); (9) fluorene ($t_{\text{R}}=11.91$ min); (10) phenanthrene ($t_{\text{R}}=19.18$ min); (11) anthracene ($t_{\text{R}}=19.58$ min); (12) fluoranthene ($t_{\text{R}}=36.83$ min); (13) pyrene ($t_{\text{R}}=43.15$ min).

Other parameters such as injector temperature, total flow rate of carrier gas, split ratio, make-up gas flow-rate etc. were also investigated. The optimum conditions for the separation of PAHs with the proposed system are summarized in Table 2.

3.3. Mechanism of chiral recognition

The elution order of these PAHs, except acenaphthylene and acenaphthene, is almost consistent with their b.p.s. However, ligand-exchange interaction and shape selectivity with liquid crystal would explain the resolution with the prepared stationary phase, since the coordination unsaturation of the central metal ion in the metallomesogens is available [7]. Some experiment results favor this explanation.

In the smectic region of P-DODTBA-Ni, the solute geometrical factor is a significant factor. However, the elution order is not consistent with the L/B ratios. This is contrary to the Chang et al.'s results [18]. The reason for this discrepancy is possibly that the mechanism acting in the present case is more complex, involving both solute geometrical factors and ligand-exchange considerations. The assumption is rational, since the C=C in the PAHs might form a chemical bond with the empty orbital of the central metal ion of the metallomesogens. The more double bonds, the stronger is the interaction with the stationary phase and the greater is the retention time.

3.4. Stability of the wall-coated capillary column

Naphthalene, 1-methylnaphthalene, diphenylmethane and acenaphthene were selected to test the reproducibility of the proposed system. The results were quantitative, the relative standard deviation of the retention time being less than 0.3%, and that of the peak area being less than 2% for ten measurements. After operation for two months, no significant deterioration in performance was observed for the wall-coated capillary column.

Solution mixtures containing known amounts of 13 PAHs were prepared and used for the construction of calibration graphs. At the optimized conditions, the calibration graphs for most PAHs studied were linear over the range 3.75–615 $\mu\text{g ml}^{-1}$, while those of fluoranthene and pyrene were linear over the range 30–615 $\mu\text{g ml}^{-1}$. Within the concentration ranges studied, good linear correlation ($r>0.9993$) between peak areas and concentrations were obtained for each species. The mass detection limits of all PAHs, defined as the minimum weight of analyte that can be detected at a known confidence level (95%) [20], are in the pg range within extreme values between 6.2–38 pg.

4. Conclusion

An olefinic group containing metallomesogen was synthesized for attachment to a siloxane polymer. The combination of the high selectivity of ligand-exchange and liquid-crystal stationary phase as well

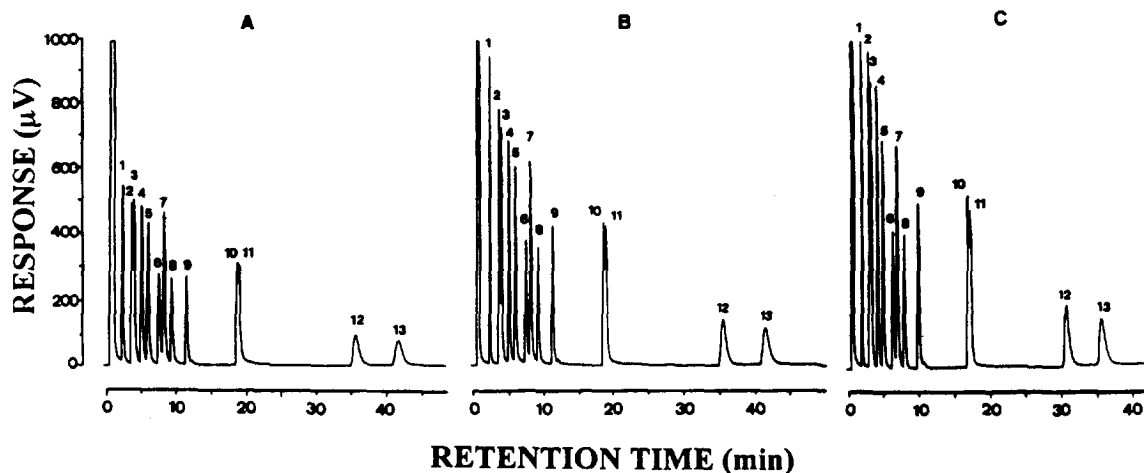


Fig. 4. Separation of PAHs with various carrier gas. Conditions as Fig. 3 except carrier gases are (A) He; (B) N_2 ; (C) NH_3-N_2 (10:90, v/v). Peak identification: (1) naphthalene; (2) 2-methylnaphthalene; (3) 1-methylnaphthalene; (4) biphenyl; (5) diphenylmethane; (6) acenaphthylene; (7) acenaphthene; (8) dibenzofuran; (9) fluorene; (10) phenanthrene; (11) anthracene; (12) fluoranthene; (13) pyrene.

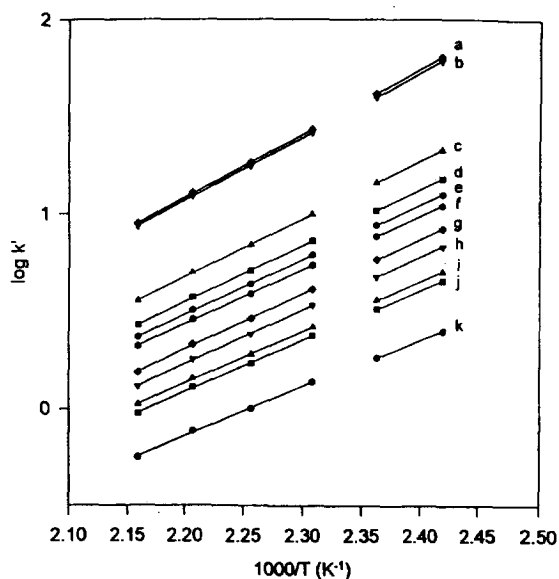


Fig. 5. Van't Hoff plot of PAHs. Stationary phase: P-DODTBA-Ni, 12 m \times 0.25 mm I.D.; sample concentration: 480 $\mu g ml^{-1}$; injector volume: 1 μl ; injector temperature: 260°C; total flow-rate of carrier gas (N_2): 25 $ml min^{-1}$; split ratio: 1:25; make-up gas flow-rate: 50 $ml min^{-1}$. (a) anthracene; (b) phenanthrene; (c) fluorene; (d) dibenzofuran; (e) acenaphthene; (f) acenaphthylene; (g) diphenylmethane; (h) biphenyl; (i) 1-methylnaphthalene; (j) 2-methylnaphthalene; (k) naphthalene.

as the high efficiency of the capillary column have contributed greatly to the good separations of many complex mixtures. These examples show that the polymeric metallomesogen is useful for the separating di-, tri- and tetracyclic PAHs. Comparison of the performance of nickel and zinc metallomesogens show that the former is more appropriate for the separation of PAHs. In GC, nematic liquid crystals are usually used, but not exclusively [19]. The smectic structure of the nickel complex possesses selectivity at the wide temperature range of the existence of the mesophase which enables column temperature programming for the separation of PAHs. Although the highest temperature used was 190°C, and the largest PAH eluted was pyrene, further work is needed before extending the application of the prepared column. The wall-coated capillary column has been found to be useful as a universal stationary phase in the separation of PAHs, dialkyl sulfides, phthalates, phenols etc. The results will be reported in a later paper. LEGC with this new column for the determination of PAHs is attractive. However, this method fails if applied to samples polluted at very low levels. The combination of supercritical fluid extraction with GC applied to the exhausted gas has been evaluated by us and is now in progress.

Acknowledgments

Financial support from the National Science Council of Taiwan is gratefully acknowledged.

References

- [1] S.A. Hudson, P.M. Maitlis, *Chem. Rev.* 93 (1993) 861.
- [2] V.A. Davankov, J.D. Navratil and H.F. Walton, *Ligand Exchange Chromatography*, CRC Press, Boca Raton, FL, 1988.
- [3] K. Fujimura, M. Kitanaka, H. Takayanagi, T. Ando, *Anal. Chem.* 54 (1982) 918.
- [4] H. Takayanagi, M. Hashizume, K. Fujimura, T. Ando, *J. Chromatogr.* 350 (1985) 63.
- [5] H. Takayanagi, M. Akita, K. Fujimura, T. Ando, *J. Chromatogr.* 350 (1985) 75.
- [6] P. Berdagué, F. Perez, J. Courtieu, J.P. Bayle, O. Abdelhadi, S. Guermouche, M.H. Guermouche, *J. High Resolut. Chromatogr.* 18 (1995) 304.
- [7] C.C. Hu, C.Y. Liu, *Anal. Chim. Acta* 332 (1996) 23.
- [8] A.M. Giroud-Godquin, P.M. Maitlis, *Angew. Chem., Int. Ed. Engl.* 30 (1991) 375.
- [9] G.N. Pain, G.I. Christiansz, R.S. Dickson, G.B. Deacon, B.O. West, K. McGregor, R.S. Rowe, *Polyhedron* 9 (1990) 921.
- [10] P. Zanella, G. Rossetto, N. Brianese, F. Ossola, M. Porchia, J.O. Williams, *Chem. Mater.* 3 (1991) 225.
- [11] D.W. Bruce, in D.W. Bruce and D. O'Hare (Editors), *Metal-containing Liquid Crystals in Inorganic Materials*, Wiley, New York, 1992.
- [12] H. Adams, A.C. Albeniz, N.A. Bailey, D.W. Bruce, A.S. Cherodian, R. Dhillon, D.A. Dunmur, P. Espinet, J.L. Feijoo, E. Lalinde, P.M. Maitlis, R.M. Richardson, G. Ungar, *J. Mater. Chem.* 1 (1991) 843.
- [13] M.A. Apfel, H. Finkelmann, G.M. Janini, R.J. Laub, B.H. Lüthmann, A. Price, W.L. Roberts, T.J. Shaw, C.A. Smith, *Anal. Chem.* 57 (1985) 651.
- [14] K. Grob, G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.* 5 (1982) 119.
- [15] R.J. Kominar, *J. Chem. Educ.* 68 (1991) A249.
- [16] C.L. Woolley, B.J. Tarbet, K.E. Markides, J.S. Bradshaw, K.D. Bartle, M.L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.* 11 (1988) 113.
- [17] D. Cagniant (Editor), *Complexation Chromatography*, Marcel Dekker, New York, 1992, p. 197.
- [18] H.-C.K. Chang, K.E. Markides, J.S. Bradshaw, M.L. Lee, *J. Chromatogr. Sci.* 26 (1988) 280.
- [19] Z. Witkiewicz, J. Mazur, *LC-GC* 8 (1990) 224.
- [20] D.A. Skoog and J.J. Leary (Editors), *Principles of Instrumental Analysis*, Saunders College Publishing, New York, 1992, p. 7.