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Preparation and evaluation of nickelmesogen for micropacked gas chromatography

Chiann-Tyng Chou, Yi-Fen Pai, Chun-Chi Lin, Tarun K. Misra, Chuen-Ying Liu*

Department of Chemistry, National Taiwan University, 1, Sec. 4, Roosevelt Road, Taipei 10617, Taiwan

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Abstract

The preparation and mesomorphic properties of a substituted bis(dithiolene)nickel complex derived from 4, 4′-dimethoxybenzil are reported. The phase transition temperatures were based on data obtained by polarized light microscopy and differential scanning calorimetry. The mesogenic phase existed over the temperature range from 77 to 175 °C. A novel micropacked column (1.5 or 3 m × 1 mm i.d.) prepared from the slurry of bis[1,2-bis(4-*n*-undecyloxyphenyl)ethane-1,2-dithiolene] nickel(II) (5%, w/w), coated on Chromosorb W was applied for the separation of dialkyl sulfides. The non-linearity (discontinuity) of Van't Hoff plots suggests that the liquid crystal property existed even in the coated phase. Factors affecting the retention and the sample selectivity on the prepared column were examined by using a flame photometric detector (FPD). The separation might be based on the mechanism of ligand exchange, shape selectivity and polarity interaction besides the vapor pressure. LOD for the determination of dialkyl sulfides was below 1 ng for most of the analytes.

Keywords: Stationary phases, GC; Nickelmesogen; Dialkyl sulfides

1. Introduction

There has been much recent interest in metal-containing liquid crystals, called metallomesogens, because such materials are expected to have not only the intrinsic properties of organic mesogens but also unique properties based on the metal atoms [1]. Various metallomesogens have already been reported [2]. In general, the geometry of the complex is often determined by the metal center incorporated and the organic chelating ligand, and it can vary from square planar to tetrahedral structures for complexes with a coordination number of four. Square planar geometries generally give rise to liquid crystals, whereas tetrahedral geometries are often not mesomorphic [3].

Metallomesogens are certainly a singular example of symbiosis in materials science. Compounds showing interesting magnetic [1], electrical [3], optical [4] and electrooptical [5] properties have already been obtained. Our interest in metallomesogens arose from the analytical application of thermotropic liquid crystals. Such complexes include metal-thiolates and metal-carboxylates. All are potentially of great interest as stationary phases of gas chromatography [6–10]. Both shape selectivity and ligand exchange are the predominant separation mechanisms in these processes, leading to high selectivity for electron-donating compounds. Incorporation of a metal center can often induce the formation of mesophases by a non-mesogenic organic ligand, whereas the mesomorphic properties of an organic ligand may be totally lost upon incorporation of a metal ion. Practical applications of the metallomesogens are limited. This is the reason why only few examples of their applications in gas chromatography is found in the literature.

In the petroleum industry, thiols might arise from thermal cracking of alkyl sulfides and the catalytic cracking of aryl sulfides present in the fossil fuel, the transformation extent of sulfide and the composition of the products were associated with the structure of sulfide and reaction conditions [11]. In 1974, Schurig et al. reported the thermodynamics of dialkyl sulfides with a nickel-chelate dissolved in squalane by GC [12]. Thermodynamic properties and valence-force field of alkane thiols and dialkyl sulfides have been also studied by Turovtsev et al. [13]. Recently, Abalos et. al. [14] reported

* Corresponding author. Tel.: +886 2 23630231; fax: +886 2 23638543.
E-mail address: cyliu@ntu.edu.tw (C.-Y. Liu).

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that determination of volatile alkyl sulfides in wastewater was carried out with headspace solid-phase microextraction followed by gas chromatography-mass spectrometry. Alkanethiols are the most popular passivant for gold nanoparticles and the use of dialkyl sulfides has more recently been reported [15–17]. In other words, dialkyl sulfides are important compounds of wide interest to scientists not only from the view-point of analytical, environmental, synthetic, medicine but also from material science.

In the previous paper [6], packed column with a rod-like dithiolene complex, namely nickel and zinc complexes of 4-decanoxydithiobenzoic acid as the stationary phase have been prepared for the separation of dialkyl sulfides. For further insight into the metallomesogens useful in the field of analytical chemistry, we report herein the preparation of a disk type, columnar shape of nickel-thiolate complex, bis-[1,2-bis(4-*n*-undecyloxyphenyl)ethane-1,2-dithiolene]nickel (II) and its application for the separation of dialkyl sulfides. An advantage of capillary gas chromatography (GC) columns is their high column efficiency and inertness for sample compounds. But in general capillary columns have disadvantages in the analysis of gaseous samples, high volatility compounds and aqueous sample. Here, a novel micropacked column was prepared, for which a nickel-mesogenic phase coated on Chromosorb W was packed into a deactivated fused-silica-lined stainless steel tubing (SILCOSTEEL tube). Examples are given of the applicability of these phases for the separation of dialkyl sulfides.

2. Experimental

2.1. Apparatus

Elemental analyses were carried out with a Perkin-Elmer elemental analyzer (model 2400), provided by the Elemental Analyses Service Center of NSC at the National Taiwan University. IR spectra were obtained on a Bio-Rad spectrophotometer (model FTS-40). Phase transitions were studied by differential scanning calorimetry (DSC) on a TA-3100 apparatus, operating through first heating, cooling and second heating ranging from room temperature to 250 °C at a heating rate of 10 °C min^{-1} under N_2 flow (100 mL min^{-1}). A TA-3100 type thermogravimetric analyzer was used for the measurement of sample thermal stability under a continuous N_2 flow (60 mL min^{-1}) at a rate of temperature rise of 10 °C min^{-1}. Hot stage polarized light microscopy was carried out with an Olympus BX-50 microscope equipped with a Linkam TMS-92. The gas chromatograph used throughout for column evaluation was a Shimadzu Model 17A, equipped with a capillary-column split-injection system and a FPD detector. Dinitrogen (N_2) was used as the carrier gas. Chromatograms were plotted on a Shimadzu CR-6A Chromatopac integrator.

2.2. Reagents and chemicals

Most chemicals were analytical reagent grade from Merck (Darmstadt, Germany). Purified water (18 MΩ cm) from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to prepare all solutions. Deuterated chloroform, 4,4′-dimethoxybenzil, phosphorus pentasulfide, hydrochloric acid, lithium chloride, nickel chloride hexahydrate, potassium bromide, potassium hydroxide, sodium hydroxide, sodium sulfate (Merck), deuterated acetone (Janssen, Belgium), *N*,*N*-dimethyl formamide and 1,4-dioxane (Wako, Japan) were purchased from the indicated sources. 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. The analytes comprising diethyl sulfide, allyl methyl sulfide, *t*-butyl methyl sulfide, diisopropyl sulfide, pentamethylene sulfide, di-*t*-butyl sulfide, and di-*sec*-butyl sulfide were purchased from Aldrich (Milwaukee, WI, USA). Diallyl sulfide, di-*n*-propyl sulfide and di-*n*-butyl sulfide were purchased from TCI (Tokyo, Japan). Chromosorb W AW-DMCS, 80-100 mesh was purchased from Sigma (St. Louis, MO, USA).

2.3. Synthesis of the metallomesogen

2.3.1. Preparation of 4,4′-dihydroxybenzil

Technical grade pyridine (24 ml) was placed in a 100 ml three-necked round-bottomed flask fitted with a thermometer and a magnetic stirrer. With rapid stirring concentrated hydrochloric acid (26.4 ml) was added. The flask was equipped for distillation and water was distilled from the mixture until its internal temperature rose to 210 °C. After cooling to 140 °C, 4,4′-dimethoxybenzil (6.48 g, 24 mmol) was added as a solid. The yellow reaction mixture was stirred and refluxed for 3 h under nitrogen atmosphere. The hot reaction mixture was then diluted with 100 ml water. The precipitate was collected by filtration and dissolved in EtOH–H_2O mixture (1:20, v/v). The pH of the solution was adjusted at 7.2 by the addition of NaOH solution. After the solution had been distilled, the residue was dissolved in EtOH, filtered and after evaporation of the solvent provided the desire light yellow compound. Yield 85%.

^{1}H NMR (DMSO-D_6) (δ in ppm): 6.26 (d, 4H; Ar–H); 7.36 (d, 4H; Ar–H).

IR (KBr): $\delta(\text{O–H})_{\text{out of plane}} = 600\text{–}707\ \text{cm}^{-1}$. The interaction of ν(C–O) and δ(O–H): 1173 cm^{-1}. ν(C–O) = 1230 cm^{-1}, δ(O–H) = 1337 and 1373 cm^{-1}, ν(aromatic C=C) 1603 cm^{-1}, ν(C=O) = 1650 cm^{-1} and ν(O–H) = 3401 cm^{-1}.

2.3.2. Preparation of 4,4′-bis(undecyloxy)benzil

4,4′-Dihydroxybenzil (5.8 g, 24 mmol) was dissolved in *N*,*N*-dimethylacetamide (100 ml) in an inert atmosphere of dinitrogen. Anhydrous potassium carbonate (6.6 g, 48 mmol)

and 1-bromoundecane (14 g, 60 mmol) were added and the mixture was stirred at 90 °C for 17 h. The reaction mixture was extracted with chloroform. The organic layer was washed with water, dried over $MgSO_4$ and the solvent was evaporated. The purification was carried out by recrystallization from hot ethanol to give white crystals of the desired compound. Yield 80%.

^{1}H NMR ($CDCl_3$) (δ in ppm): 6.90–7.92 (Ar–H: d, 8H); 4.02 (–O$\underline{CH_2}$–: t, 4H); 1.32 (–CH_2–: m, 36H); 0.86 (–CH_3: m, 6H). ^{13}C NMR ($CDCl_3$) (δ in ppm): 192.71 (–$\underline{C}$O); 163.82 ($\underline{C}$–CO); 131.94 (Ar–$\underline{C}$–O); 125.64 and 114.39 (Ar–$\underline{C}$); 68.51 (O$\underline{C}H_2$–); 32.22–23.08 (–$\underline{C}H_2$–); 14.59 (–$\underline{C}H_3$).

IR (KBr): $\rho(CH_2) = 728\,cm^{-1}$, $\nu(C–O–C)_{sym} = 1030\,cm^{-1}$, $\nu(C–O–C)_{as} = 1260\,cm^{-1}$, $\delta(CH_2)_{sym} = 1465\,cm^{-1}$, ν(aromatic C=C) $= 1603\,cm^{-1}$, $\nu(C–O) = 1670\,cm^{-1}$, $\nu(CH_2)_{sym} = 2853\,cm^{-1}$, $\nu(CH_2)_{sym} = 2930\,cm^{-1}$and $\nu(CH_2)_{as} = 2955\,cm^{-1}$.

2.3.3. Preparation of bis[1,2-bis(4-n-undecyloxyphenyl)-ethane-1,2-dithiolene]nickel(II)

A mixture of 1.9 g (3.45 mmol) of 4,4′-bis(undecyloxy)-benzil, 1.54 g (6.9 mmol) of phosphorus pentasulfide and 100 ml of 1,4-dioxane was refluxed for 5 h. The hot reaction mixture was filtered to remove the unreacted phosphorus pentasulfide and washed with a small portion of hot dioxan. Then a solution of nickel(II) chloride hexahydrate, 0.41 g (1.70 mmol) in 20 ml of ethanol was added to the filtrate and the reaction mixture was further refluxed for 2 h. After it had been cooled by immersion in an ice-water bath, a brown powder was formed and collected by filtration to give the crude complex. Purification was performed from ethyl acetate. Yield 60%.

^{1}H NMR ($CDCl_3$) (δ in ppm): 6.71–7.26 (Ar–H: d, 16H); 3.88 (–O$\underline{CH_2}$–: t, 8H); 1.36 (–CH_2–: m, 72H); 0.81 (–CH_3: m, 12H). ^{13}C NMR ($CDCl_3$) (δ in ppm): 180.46 (–$\underline{C}$S); 159.86 ($\underline{C}$–CS); 134.18 (Ar–$\underline{C}$–O); 130.34 and 114.31 (Ar–$\underline{C}$); 68.1 (O$\underline{C}H_2$–); 31.90–22.68 (–$\underline{C}H_2$–); 14.12 (–$\underline{C}H_3$).

IR (KBr): $\rho(CH_2) = 728\,cm^{-1}$, $\nu(C–O–C)_{sym} = 1030\,cm^{-1}$, $\nu(C–O–C)_{as} = 1250\,cm^{-1}$, $\delta(CH_2)_{sym} = 1470\,cm^{-1}$, ν(aromatic C=C) $= 1603\,cm^{-1}$, $\nu(CH_2)_{sym} = 2858\,cm^{-1}$and $\nu(CH_2)_{as} = 2925\,cm^{-1}$.

2.4. Packed column preparation

SILCOSTEEL tube (Restek, Bellefonte, PA, USA) (1.5 or 3 m length; 1/16 in. o.d.; 0.04 in. i.d.) was rinsed with methanol and dichloromethane (5 ml each) sequentially prior to the packing. Nickelmesogen (0.1 g) dissolved in chloroform (7 ml) was introduced into the container having Chromosorb W (AW-DMCS, 80–100 mesh) (2 g) that was ground to the particle size of 140–230 mesh. The mixture was agitated manually until it became homogeneous. After 24 h, chloroform was removed in a rotary evaporator and the material was filled into the tube. To ensure a homogeneous packing density along the column, the SILCOSTEEL tube was placed in an ultrasonic bath. Vibration and pressure help to transport the packing continuously into the column. It was then installed on a GC apparatus and conditioned at 150 °C for 8 h by a continuous dinitrogen stream.

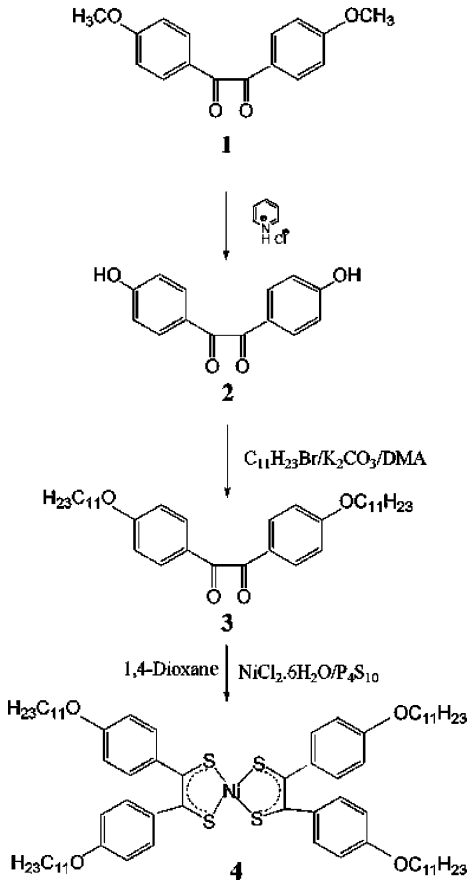

Fig. 1. Synthetic procedures for bis[1,2-di-(*p*-*n*-undecyloxyphenyl)ethane-1,2-dithiolene]nickel.

3. Results and discussion

3.1. Characterization

The synthetic procedures were as those of Horie et al. [18] and Crowley et al. [19] but with slight modification (Fig. 1). The nickelmesogen was characterized after each step of the synthesis by elemental analysis, NMR and IR spectroscopy. The data have been shown in Section 2.

3.1.1. Thermal behavior of the nickelmesogen

In general, liquid crystal properties of the mesogenic substances were characterized via the techniques of polarized light microscopy and thermal analyses. Phase transitions for the mesogenic substance at 81.5, 129.2 and 175.8 °C with ΔH of 18.6, 8.2 and 41.5 J g^{-1} on the first heating cycle

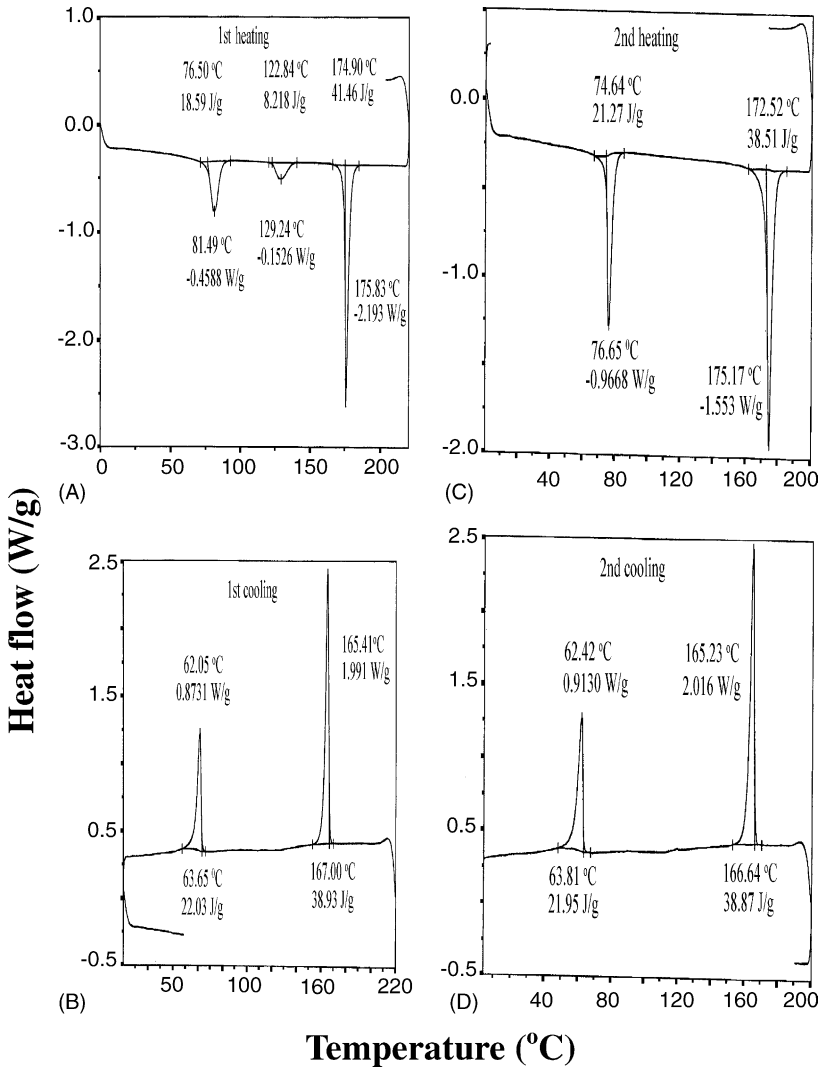

Fig. 2. Differential scanning calorimetry thermogram of bis[1,2-di-(*p*-*n*-undecyloxyphenyl)ethane-1,2-dithiolene]nickel: (A) first heating, (B) first cooling, (C) second heating, (D) second cooling.

were indicated (Fig. 2A). If the sample was then cooled from 220 °C, we obtained two exothermic peaks at 62.1 and 165.4 °C with ΔH of 22.0 and 38.9 J g^{-1}, respectively (Fig. 2B). On the second heating, two endothermic peaks at 76.7 and 175.2 °C with ΔH of 21.3 and 38.5 J g^{-1}, respectively were found (Fig. 2C). We found also two exothermic peaks at 62.4 and 165.2 °C with ΔH of 22.0 and 38.9 J g^{-1}, respectively on the second cooling process (Fig. 2D). The results are summarized in Table 1. In DSC measurements, the peak for the phase transition often showed heating rate dependence. The faster the heating rate was, the higher the

Table 1
Phase transitions (°C) and corresponding enthalpy changes (J g^{-1}) of the metallomesogen

	Discotic liquid crystal	
	Crystalline	Isotropic liquid
First heating	81.49 (K_1, 18.59) 129.24 (K_2, 8.22)	175.83 (41.46)
First cooling	62.05 (22.03)	165.41 (38.93)
Second heating	76.65 (21.27)	175.17 (38.51)
Second cooling	62.42 (21.95)	165.23 (38.87)

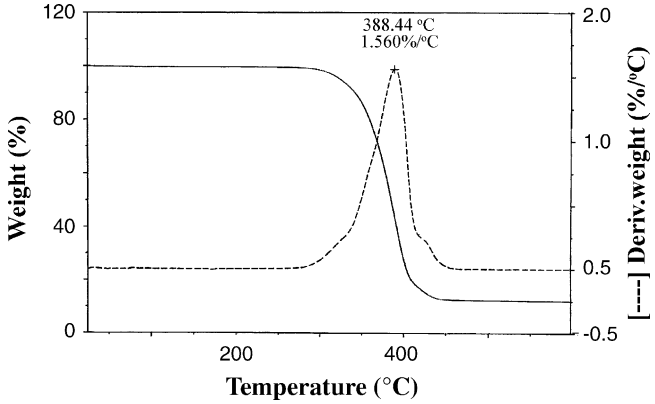

Fig. 3. Thermogravimetric analysis of bis[1,2-di-(*p*-*n*-undecyloxyphenyl)-ethane-1,2-dithiolene]nickel.

transition temperature became. In this work, all DSC profiles are displayed at 10 °C min^{-1}. Ohta et al. in their previous papers [20] reported that the similar $C_{11}O$–Ni complex gives only one mesophase. But recently they revealed that there are two differently colored mesophases [18]. Here we also obtained the same results as in Ohta's recent work (Fig. 2A). Thermal gravimetric analysis (TGA) indicated a significant weight loss at temperatures higher than 300 °C (Fig. 3).

The morphological observations under polarized light microscopy at different temperatures were consistent with those described in the thermal analysis. On first heating, the nickel complex melts to an isotropic liquid. After fast cooling to room temperature, four-alkyl chains around the central metal ion may be responsible for the fan-like texture (Fig. 4A). No sufficient time for the molecules to rearrange to mesogenic phase might be the reason. On cooling down slowly from the isotropic liquid to 172 °C, the development of a feather-like texture can be seen (Fig. 4B). With a thinner film on the slide, the mentioned feather-like texture was as in Fig. 4C. Even on cooling down to 27 °C, it remained with the similar texture but with some crack (Fig. 4D).

3.2. Packing material

In general, a particle size of 60–80 mesh or 80–100 mesh is suitable for the GC packed column of 2–4 mm i.d. Here the column dimension was 1 mm i.d., thus the particle size of 140–230 mesh (106–63 μm) was chosen. The amount of coating of the Chromosorb was usually dependent on the volatility of the analyte. Since a wide range bp (37–188 °C) was employed for the analytes, the amount of 2 and 5% nickelmesogen (w/w) on Chromosorb were evaluated.

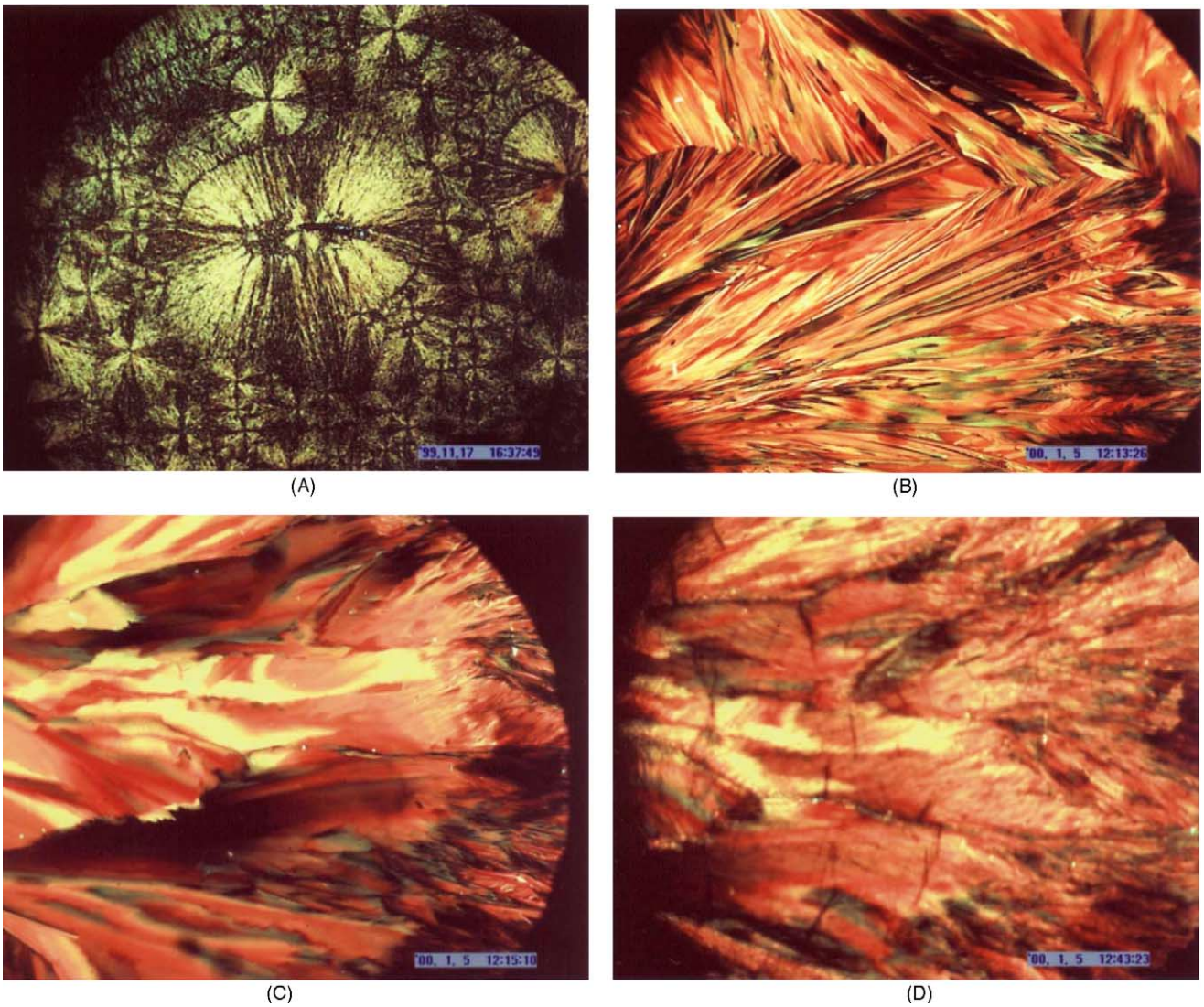

Fig. 4. Optical polarizing micrograph of bis[1,2-di-(*p*-*n*-undecyloxyphenyl)ethane-1,2-dithiolene]nickel: (A) fast cooling to room temperature, (B) cooling from isotropic liquid to 172 °C, (C) cooling from isotropic liquid to 172 °C (a thinner film than that in (B)), (D) cooling from isotropic liquid to 27 °C.

Table 2
The physical properties of dialkyl sulfides

Analyte	Structure	M.W.	bp (°C)
Dimethyl sulfide	$(CH_3)_2S$	62.1	37
Diethyl sulfide	$(CH_3CH_2)_2S$	90.2	92
Allyl methyl sulfide	$(CH_2{=}CHCH_2)(CH_3)S$	88.2	91–93
t-Butyl methyl sulfide	$[(CH_3)_3C](CH_3)S$	104.2	102
Diisopropyl sulfide	$[(CH_3)_2CH]_2S$	118.2	121
Diallyl sulfide	$(CH_2{=}CHCH_2)_2S$	114.2	138
Di-*n*-propyl sulfide	$(CH_3CH_2CH_2)_2S$	118.2	142
Pentamethylene sulfide		102.2	142
Di-*t*-butyl sulfide	$[(CH_3)_3C]_2S$	146.3	147–151
Di-*sec*-butyl sulfide	$[(CH_3CH_2)CH(CH_3)]_2S$	146.3	165
Di-*n*-butyl sulfide	$[(CH_3)(CH_2)_3]_2S$	146.3	188

3.2.1. Column performance evaluation

The prepared columns were evaluated for their performance in the GC separation of dialkyl sulfides. The physical properties of the model compounds are shown in Table 2. The least volatile di-*n*-butyl sulfide was chosen to investigate the injection temperature. The apparatus required a long time for conditioning, and it was not suitable for the split mode. Even if the apparatus was ready, sample elution was difficult because only small inlet pressure and a slow flow rate could be achieved. Direct injection was therefore adopted for this work. The optimum injection temperature was found from 210 to 230 °C.

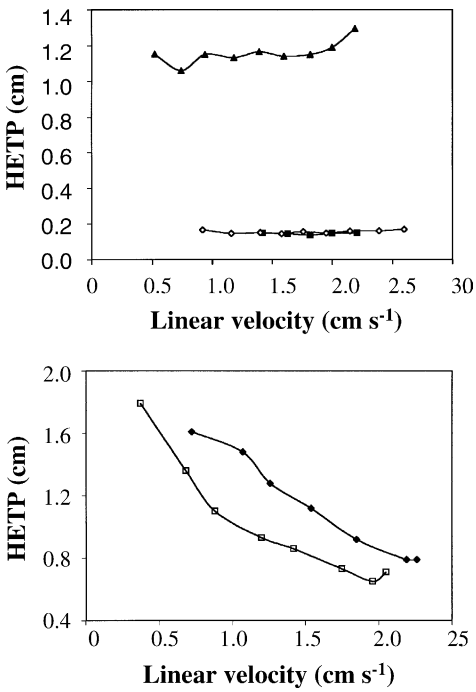

Fig. 5. Effect of mobile phase flow rate on plate height for diethyl sulfide and di-*t*-butyl sulfide. Column dimension: 1.5 m × 1 mm i.d. Stationary phase: bis[1,2-di-(*p*-*n*-undecyloxyphenyl)ethane-1,2-dithiolene]nickel coated on Chromosorb [140–230 mesh, (A) 5% (B) 2%, w/w]; carrier gas: dinitrogen; sample concentration: 50 μg ml^{-1}; injection volume: 1 μl; injector temperature: 210 °C; detector: FPD; oven temperature: (A) diethyl sulfide: (▲), 65 °C; (■),100 °C; di-*t*-butyl sulfide: (◇), 130 °C; (B) diethyl sulfide: (□), 100 °C; di-*t*-butyl sulfide: (◆), 130 °C.

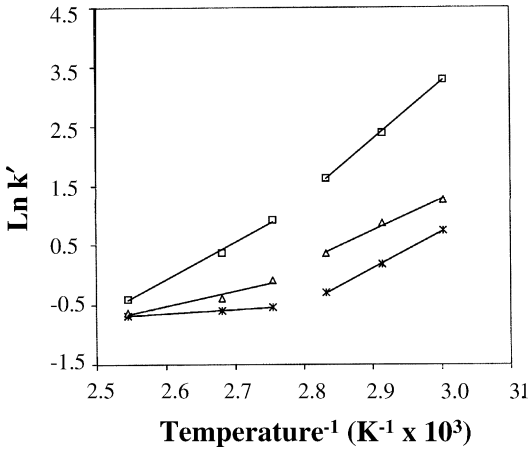

Fig. 6. van't Hoff plot of dialkyl sulfides. Conditions as in Fig. 5 except flow rate: 80 mL min^{-1}; FPD base and head block temperature: 250 and 150 °C; (✱) diallyl sulfide; (Δ) di-*sec*-butyl sulfide; (□) di-*n*-butyl sulfide.

The effect of the flow rate on the plate height have been studied. A constant plate height of 2 mm was found at a linear velocity (over the range) from 0.85 to 2.65 cm s^{-1} for both diethyl sulfide and di-*t*-butyl sulfide with 5% (w/w) nickelmesogen coated on Chromosorb W (Fig. 5A). Separation within this range is highly favorable, but relationships different from those presented in Fig. 5A have been obtained for the lower coating (2%) (Fig. 5B). Most likely, 2% coating leaves large areas of the support uncovered and adsorption on the bare Chromosorb W contributes significantly to zone broadening. In the above study, the oven temperature for diethyl sulfide was 100 °C, while that for di-*t*-butyl sulfide it was 130 °C. By further lowering the oven temperature below the mesogenic phase (65 °C), poorer dissolution of the analyte in the crystalline phase was seen (Fig. 5A).

To elucidate whether the mesogenic property still remains after it was introduced into the support, the dependence of the retention factor on temperature was studied. The results known as the Van't Hoff plot is shown in Fig. 6. The intersection for the lines with different slope was around 85 °C. This point would be indicative of phase changes in the columns, but it was higher than that of the parent mesogen (77 °C). A lower flexibility of the mesogenic phase coated on Chromosorb than that in the free-state may be the reason for this observation.

3.3. Optimization of micropacked column for the separation of dialkyl sulfides

Because of the wide boiling range for the analytes, it is not easy to separate all of them isothermally within a reasonable time. Hence several assays of temperature programming were performed. One of the best conditions was as the following: 40 °C for 3 min, to 80 °C at 5 °C min^{-1} and held 7 min, then to 100 °C for 5 min at 3 °C min^{-1}, finally

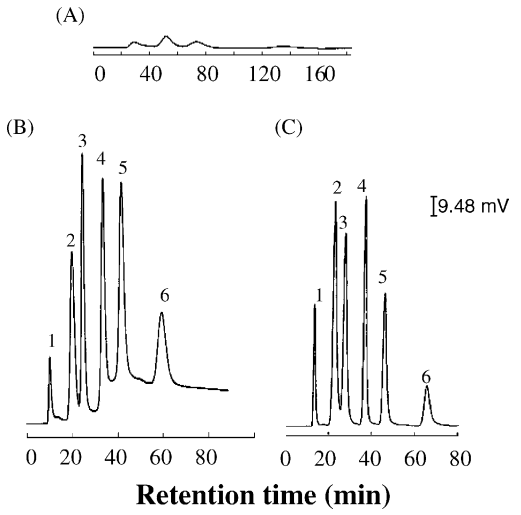

Fig. 7. Comparison of the separation efficiency of bare Chromosorb W with the nickelmesogen coated Chromosorb. Column dimension: (A) and (B) 1.5 m × 1 mm i.d. (C) 3.0 m × 1 mm i.d. Stationary phase: (A) bare Chromosorb W (140–230 mesh), (B and C) nickelmesogen coated Chromosorb W (140–230 mesh, 5%, w/w); carrier gas: nitrogen; flow rate: 40 mL min^{-1}; sample concentration: 150 μg ml^{-1}; injection volume: 0.5 μl; injector temperature: 210 °C; FPD base and head block temperature: 250 and 150 °C; oven temperature: 40 °C (3 min) to 80 °C (7 min) at 5 °C min^{-1}, then to 100 °C (5 min) at 3 °C min^{-1}, then to 115 °C at 3 °C min^{-1}. Peaks: (1) dimethyl sulfide, (2) allyl methyl sulfide, (3) diiospropyl sulfide, (4) di-*t*-butyl sulfide, (5) di-*sec*-butyl sulfide, (6) di-*n*-butyl sulfide.

to 115 °C at 3 °C min^{-1}. The chromatograms are shown as Fig. 7B, in which a complete separation of the six compounds is demonstrated. By increasing the column length to 3 m, a more satisfying result was obtained (Fig. 7C). But the 3 m column did not double the retention time compared with the result shown in Fig. 7B. Different packing density might be the reason. By further injecting eleven analytes, only eight peaks could be found (Fig. 8). Evidently delicate investigation for the resolution of *t*-butyl methyl sulfide, allyl methyl sulfide and diethyl sulfide will still be necessary. Each analyte was then injected individually. The results (Table 3) showed that strong interaction with the stationary phase resulted in a broadened peak.

3.4. Mechanism of the separation

Most of the compounds were eluted following the order of their boiling points, except *t*-butyl methyl sulfide and di-*t*-butyl sulfide. Other factors responsible for the elution order of the dialkyl sulfides were considered to be the following.

3.4.1. Polarity interaction

The nickelmesogenic phase is of low polarity. All dialkyl sulfides are symmetrical except allyl methyl sulfide and *t*-butyl methyl sulfide, which are also of low polarity. Therefore, a strong interaction between analytes and the stationary phase might be expected.

3.4.2. Ligand exchange

The sulfur atom in the analyte could form association complexes with the stationary phase having an empty orbital at the central metal atom [12]. The presence of longer alkyl groups on the analyte might lead one to expect a greater electron density on the sulfur atom. Hence, the retention time decreased in the order: di-*n*-butyl sulfide > di-*n*-propyl sulfide > diethyl sulfide (Fig. 8). We note also that di-*t*-butyl sulfide (bp 147–151 °C) is eluted before di-*n*-propyl sulfide (bp 142 °C), which is unexpected and might be due to steric hindrance for coordination. Cyclic pentamethylene sulfide might have less steric hindrance than di-*n*-propyl sulfide. Thus a greater affinity toward the stationary phase was shown.

3.4.3. Molecular shape

Here a disk type, columnar shape metallomesogen was prepared. Solutes most similar to the disk-type ordered environment would interact more strongly with the stationary

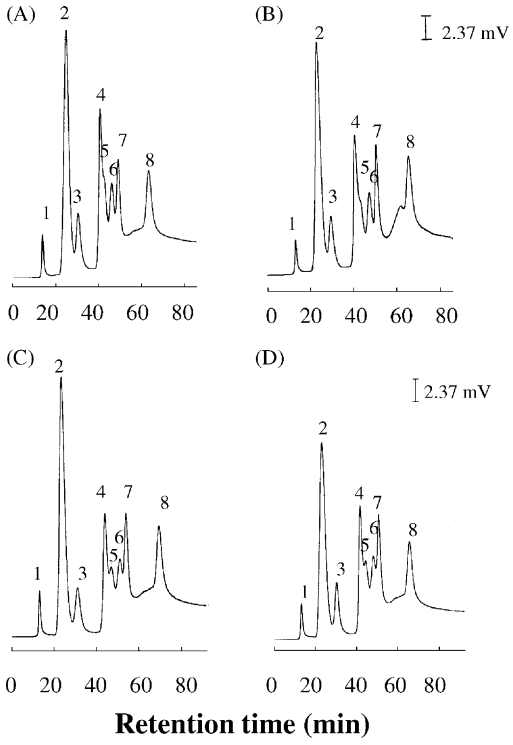

Fig. 8. The separation of dialkyl sulfides at various temperature programs. Conditions as in Fig. 7C, except sample concentration: 25 μg ml^{-1} and oven temperature: (A) 40 °C (5 min) to 100 °C (10 min) at 3 °C min^{-1}, then to 130 °C at 2 °C min^{-1}; (B) 40 °C (3 min) to 70 °C at 3 °C min^{-1}, then to 82 °C (7 min) at 4 °C min^{-1}, then to 94 °C (7 min) at 4 °C min^{-1}, then to 104 °C (7 min) at 2 °C min^{-1}, finally to 130 °C at 4 °C min^{-1}; (C) 40 °C (3 min) to 70 °C (10 min) at 4 °C min^{-1}, then to 82 °C (7 min) at 4 °C min^{-1}, then to 94 °C (7 min) at 4 °C min^{-1}, finally to 130 °C at 2 °C min^{-1}; (D) 40 °C (3 min) to 70 °C (10 min) at 5 °C min^{-1}, then to 80 °C (7 min) at 5 °C min^{-1}, then to 100 °C (7 min) at 5 °C min^{-1}, then to 130 °C at 2 °C min^{-1}. Peaks: (1) dimethyl sulfide (2) allyl methyl, di-*t*-butyl, diethyl sulfide (3) diiospropyl sulfide (4) diallyl, di-*t*-butyl sulfide (5) di-*n*-propyl sulfide (6) pentamethylene sulfide (7) di-*sec*-butyl sulfide (8) di-*n*-butyl sulfide.

Table 3
Retention behavior of dialkyl sulfides with micropacked nickelmesogenic column under temperature program[a]

Analyte	Retention time (min)	Peak width at half height (s)
Dimethyl sulfide	13.09	62.9
t-Butyl methyl sulfide	23.12	145.2
Allyl methyl sulfide	24.41	93.3
Diethyl sulfide	25.03	157.2
Diisopropyl sulfide	30.80	123.9
Di-*t*-butyl sulfide	42.32	103.6
Diallyl sulfide	43.46	171.2
Di-*n*-propyl sulfide	45.96	156.7
Pentamethylene sulfide	49.59	167.7
Di-*sec*-butyl sulfide	52.75	110.8
Di-*n*-butyl sulfide	68.09	155.0

[a] Column dimension: 3 m × 1 mm i.d.; stationary phase: bis[1,2-bis(4-*n*-undecyl-oxyphenyl)ethane-1,2-dithiolene]nickel(II) coated on Chromosorb (140–230 mesh, 5%, w/w); carrier gas: nitrogen; flow rate: 40 mL min^{-1}; sample concentration: 25 μg ml^{-1}; injection volume: 0.5 μl; injector temperature: 210 °C; FPD base and head block temperature: 250 and 150 °C; oven temperature: 40 °C (3 min) to 70 °C (10 min) at 5 °C min^{-1}, to 80 °C (7 min) at 5 °C min^{-1}, then to 100 °C (7 min) at 5 °C min^{-1} and finally to 130 °C at 2 °C min^{-1}.

Table 4
Summary for the determination of six dialkyl sulfides with nickelmesogen coated micropacked column[a]

Analyte	Linear equation[b] (*y*: 1/2 log (peak area, μV s); *x*: log (concentration, μg ml^{-1}))	Correlation coefficient	Detection limit[c] (ng; μg ml^{-1})
Dimethyl sulfide	$y = 0.898x + 1.536$	0.9578	1.24 (2.48)
Allyl methyl sulfide	$y = 0.885x + 1.924$	0.9954	0.67 (1.35)
Diisopropyl sulfide	$y = 0.878x + 1.862$	0.9959	0.87 (1.73)
Di-*t*-butyl sulfide	$y = 0.795x + 2.031$	0.9983	0.86 (1.72)
Di-*sec*-butyl sulfide	$y = 0.789x + 1.997$	0.9943	1.54 (3.08)
Di-*n*-butyl sulfide	$y = 0.765x + 1.943$	0.9970	0.59 (1.17)

[a] Column dimension: 3 m × 1 mm i.d.; stationary phase: bis[1,2-bis(4-*n*-undecyloxyphenyl)ethane-1,2-dithiolene]nickel(II) coated on Chromosorb (140–230 mesh, 5%, w/w); carrier gas: nitrogen; flow rate: 40 mL min^{-1}; injection volume: 1 μl; injector temperature: 210 °C; FPD base and head block temperature: 250 and 150 °C; oven temperature: 40 °C (3 min) to 80 °C (7 min) at 5 °C min^{-1}, then to 100 °C (5 min) at 3 °C min^{-1} and finally to 115 °C at 3 °C min^{-1}.
[b] Linear range: 625–200 μg ml^{-1}.
[c] Detection limit: three times standard deviation for the peak with the least amount that could be detected ($n = 4$).

phase. The molecular shape of pentamethylene sulfide is more susceptible to the column phase. Hence longer retention than di-*n*-propyl sulfide which has similar b.p. was demonstrated. In other words, the former might be inserted more easily into the ordered liquid crystal structure.

For further testing whether the separation performance originated from the nickelmesogen, a comparison of the retention behavior for dialkyl sulfides on bare and nickelmesogen coated Chromosorb with similar dimension was studied (Fig. 7A and B). Six well resolved peaks were demonstrated for the coated phase (Fig. 7B), whereas only four broad and weak signals were found with testing time of 180 min (Fig. 7A). The contribution of metallomesogen for the separation was obvious.

3.5. Linear calibration range

At the conditions in Fig. 7C, highly reproducible for the determination of dialkyl sulfides assessed from five measurements was demonstrated. The R.S.D. for retention time was less than 0.25% and that for peak area was less than 4.91% except dimethyl sulfide which was 7.95%. The column could be continuously used over 2 months and it showed no significant difference for the retention time.

The relation between FPD detector response and the sample concentration was also studied. The calibration graphs of 1/2 log (peak area, μV s) against log [concentration, μg ml^{-1}] for each analyte are listed in Table 4. The linear range was from 6.25 to 200 μg ml^{-1}. The correlation coefficients were greater than 0.9943, except that of dimethyl sulfide (0.9578). This might be due to high volatility (b.p. 37 °C) resulting in loss of the analyte. The detection limit defined by three times standard deviation for the peak with the least amount that could be detected is less than 1 ng, except for dimethyl sulfide and di-*sec*-butyl sulfide.

4. Conclusions

In this work, a short micropacked disk-type metallomesogen coated column (5%, w/w) (1.5 m × 1 mm i.d.) was prepared. Examples are given of the applicability of this phase for the separation of dialkyl sulfides. The separation of six dialkyl sulfides is demonstrated. To elucidate possible effects caused by the used mesogenic phase, more compounds were analyzed under similar conditions. The elution order decreased as follows: dimethyl sulfide > allyl methyl sulfide, di-*t*-butyl sulfide, diethyl sulfide > diiospropyl sulfide > diallyl sulfide, di-*t*-butyl sulfide > di-*n*-propyl sulfide > pentamethylene sulfide > di-*sec*-butyl sulfide > di-*n*-butyl sulfide. By comparison with the retention behavior of the rod-type metallomesogen-coated column (5%, w/w) (2.1 m × 3.2 mm i.d.), the elution order was diethyl sulfide > diisopropyl sulfide > diallyl sulfide > di-*t*-butyl sulfide > di-*sec*-butyl sulfide > di-*n*-butyl sulfide > di-*n*-hexyl sulfide [6]. A similar elution order but a much longer retention time was observed for each corresponding analyte in this work. Taking into account the rule “like dissolves like” we assume a stronger interaction force of the dialkyl sulfides with the disk type metallomesogen than those with the rod type metallomesogen due to the fact that symmetrical dialkyl sulfides are more easily soluble in the former.

The dialkyl sulfides quantitated at the optimum condition (Table 4), highly reproducible and low detection limit could be achieved. From the retention behavior discussed, the separation mechanism might include ligand exchange,

shape selectivity, and polarity interaction besides the vapor pressure difference. Taking advantage of the mentioned property, the column would be promising for the separation of structure similar, symmetrical or compounds having electron-donating atom.

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