

Synthesis of a Substituted Phthalocyaninato-polysiloxane and its Langmuir–Blodgett Films

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ABSTRACT: Tetrakis-4-(2,4-di-*tert*-amylphenoxy)phthalocyaninato-polysiloxane was synthesized. Its molecular structure was confirmed by elemental analysis, IR and UV-vis spectra. The gas-sensitive properties of its Langmuir–Blodgett films exposed to NH₃, I₂ and NO₂ in air were measured. The results showed that the detection sensitivity on exposure to NH₃ in air can reach 0.1 ppm, while it can reach 100 ppm on exposure to NO₂ and I₂ in air. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: phthalocyaninato-polysiloxane; gas sensitivity; Langmuir–Blodgett films; chemical sensor

INTRODUCTION

A number of sensors for gaseous NH₃, Cl₂ and NO₂ are made from monomeric phthalocyanines [1–4]. The conductivity of these sensors changes with variations in humidity and therefore their usage is limited. In order to improve the stability of the sensors, Wohrle and Schulte [5] synthesized diphthalonitriles. Recently, considerable attention has been focused on polymeric phthalocyanines with oxygen and silicon bridges. Such polymers were first reported by Joyner and Kenney [6]. Owing to their unusual molecular structure, which is a rod-like conformation with cofacial packing of the monomer units along the polysiloxane chain, they exhibit electrical, photoelectronic and gas-sensitive properties. They are also thermally and mechanically stable [7–9]. In this paper we describe the synthesis of tetrakis-4-(2,4-di-*tert*-amylphenoxy)phthalocyaninato-polysiloxane (R₄PcPS) and the conductivity change of its Langmuir–Blodgett (LB) films upon exposure to different gases, e.g. NH₃, NO₂ and I₂.

EXPERIMENTAL

Reagents and Instruments

All reagents used were of analytic grade. They were used without further purification, except for quinoline. Quinoline was distilled in vacuum prior to use. Elemental analyses were performed using an Italy 1106 elemental analysis instrument. UV-vis spectra were obtained with a Shimadzu 365-UV-VIS spectrophotometer. ¹H NMR spectra were recorded with a Varian Unity 400 spectrometer. LB films were prepared in a KSV-5000 twin-compartment trough.

Synthesis of Materials

The synthesis of R₄PcPS is shown in Fig. 1. 4-(2,4-Di-*tert*-amylphenoxy)phthalonitrile (**1**) was synthesized according to the method described by Li *et al.* [10].

5-(2,4-Di-*tert*-amylphenoxy)-1,3-diiminoisoindoline (**2**) [11]. 20 mmol of **1** were dissolved in 83 ml of methanol solution containing 1.5% sodium by weight. Gaseous ammonia was passed through this solution for 1 h at room temperature, then the mixture was heated to 60 °C and reacted at this temperature for 6 h. The product was then dried and used for the next step.

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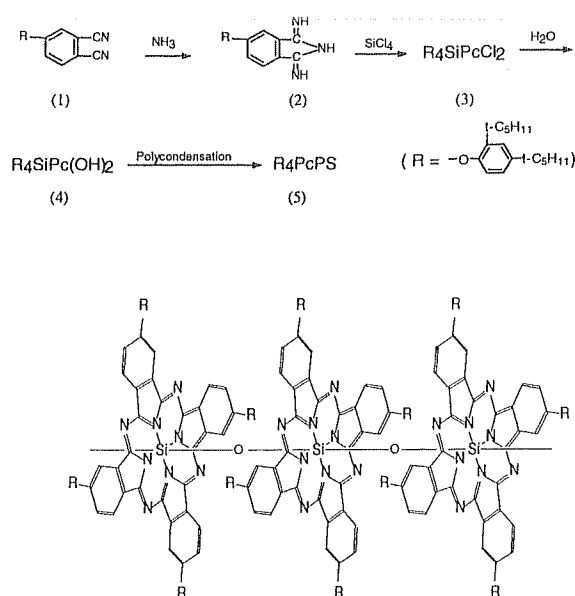


Fig. 1. Synthesis route and molecular structure of R_4PcPS .

Tetrakis-4-(2,4-di-tert-amylphenoxy)phthalocyaninato Silicon Dichloride (3) ($R_4PcSiCl_2$) [11]. 16.95 mmol of **2** were stirred with 85 ml of freshly distilled quinoline in a 500 ml three-neck flask with a reflux condenser under N_2 gas for 30 min. The mixture was poured into silicon tetrachloride, heated to $190^\circ C$ and kept for 1 h. After the mixture had cooled to room temperature, water was added to it. The mixture was then filtered off and dried in vacuum. A blue-green product was obtained. The product was washed with methanol and acetone, then dissolved in chloroform and precipitated in a large excess of acetone. The mixture was centrifuged at 3000 rpm for 15 min and the precipitate was separated. After the precipitate had been dried, about 2 g of a dark blue-green powder were obtained. The powder was purified by column chromatography (silicon gel 40 μm , chloroform).

Tetrakis-4-(2,4-di-tert-amylphenoxy)silicon Dihydroxophthalocyanine (4) ($R_4Si(OH)_2Pc$) [11]. 1 mmol of **3** was mixed with 0.16 g of sodium hydroxide, 3.6 ml of pyridine and 14 ml of water. The mixture was refluxed for 1 h. The yield of the dark blue, plate-like product was 95%.

Tetrakis-4-(2,4-di-tert-amylphenoxy)phthalocyaninato polysiloxane (5) (R_4PcPS) [12]. 0.1 g of **4** was refluxed with 2 mg of $FeCl_3$ and 10 ml of toluene for 72 h. A dark green powder product was obtained with a mass of 0.09 g and a yield of 90%. The powder was then purified by thin layer centrifugal chromatography.

Preparation of LB Films and Measurement of Gas-sensitive Properties

Surface pressure-area (π - A) isotherms of R_4PcPS were measured on deionized water subphase (resistivity larger than $18 M\Omega cm$) with chloroform as spreading solvent. R_4PcPS concentrations of 1, 0.5, 0.1 and $0.05 mg ml^{-1}$ were used. LB films (10 layers) of R_4PcPS as a gas-sensitive element were deposited in a KSV-5000 twin-compartment Langmuir trough onto a glass substrate with an Al interdigital electrode consisting of 50 pairs of fingers. Each finger was 50 μm wide and the gap between fingers was 50 μm . The deposition of the monolayer was done at 20 $mN m^{-1}$ using a dipping speed of 5 $mm min^{-1}$. All experiments were performed at $20 \pm 1^\circ C$.

In order to obtain the gas-sensing response characteristics, the conductance of the gas-sensitive element was measured upon exposure to NH_3 , NO_2 and I_2 in air. The lateral conductance of the LB film was monitored by a current-voltage (I - V) measuring apparatus linked to a gas test system. The gas test system was made of Teflon and glass and included several gas valves, a mixing chamber and a testing chamber.

RESULTS AND DISCUSSION

Synthesis and Characterization of R_4PcPS

The average degree ($n=3$) of polymerization of R_4PcPS was measured by GPC (gel permeation chromatography). The IR and UV-vis spectra of the compound were determined.

The IR spectra of compounds **4** and **5** are shown in Fig. 2. The Si-OH characteristic peak at about $823 cm^{-1}$ is clear in compound **4** but very weak in compound **5**. The broad band in compound **5** at $1086 cm^{-1}$ is due to the antisymmetrical vibration of the Si-O-Si stretch [13].

The UV-vis spectra of compounds **4** and **5** are shown in Fig. 3. The Q-band of compound **5** is blue-shifted compared with that of compound **4** [14].

The high purity of the R_4PcPS was confirmed by the results of the elemental analysis, which agree with the calculated values (Table 1).

LB Films of R_4PcPS and Their Gas Sensitivity

The surface pressure-area isotherms for different concentrations of R_4PcPS in chloroform solvent are shown in Fig. 4. The isotherms for 0.5, 0.1 and

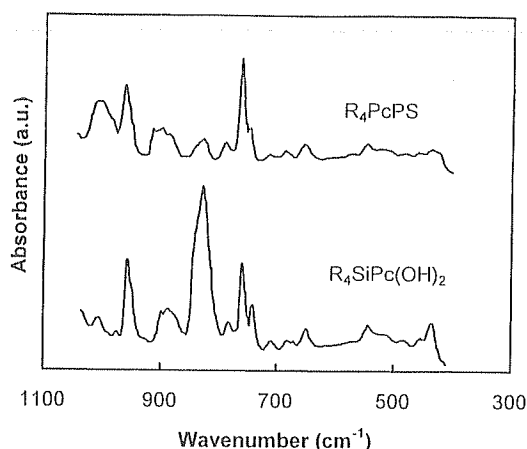


Fig. 2. FTIR spectra of $R_4SiPc(OH)_2$ and R_4PcPS .

0.05 mg ml^{-1} R_4PcPS are reproducible with a limiting area of about 100 \AA^2 per molecule. This means that stable monolayers were formed. The smaller limiting area (70 \AA^2 per molecule) of the isotherm for 1 mg ml^{-1} R_4PcPS could be due to the aggregates formed at high concentration of the product in solution. It was discovered that the formation of the LB films is sensitive to subphase temperature and pH, regardless of the subphase cations (e.g. Cd^{2+} and Na^+) [15].

The gas-sensing properties of R_4PcPS LB films exposed to NH_3 , NO_2 and I_2 were measured. The results are shown in Fig. 5. The detection sensitivity of a 10-layer R_4PcPS LB film upon exposure to NH_3 in air can reach 0.1 ppm at room temperature, with a response time of 80 s and a recovery time of 100 s (Fig. 5, top curve). The response and recovery times for the conductance of a 15-layer LB film upon exposure to 100 ppm NO_2 in air are about 32 and 10 s respectively (Fig. 5, middle curve). For 100 ppm I_2 in

Table 1. Elemental analysis results

Compound	C (%)	H (%)	N (%)	Cl (%)
3	Calc.	74.82	7.33	6.98
	Found	74.83	7.36	7.27
4	Calc.	76.59	7.58	7.45
	Found	76.40	7.87	7.27
5	Calc.	77.52	7.54	7.54
	Found	75.95	8.05	7.33

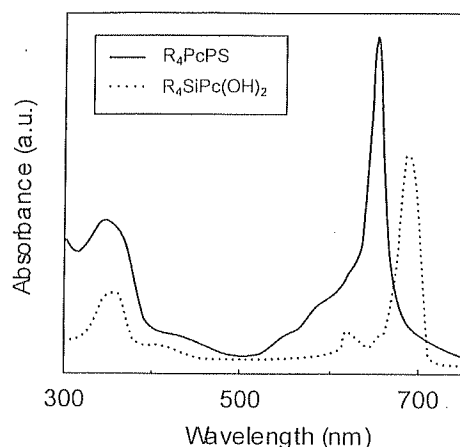


Fig. 3. UV-vis absorption spectra of $R_4SiPc(OH)_2$ and R_4PcPS in chloroform solution.

air the response and recovery times are only 10 and 5 s respectively (Fig. 5, bottom curve).

The R_4PcPS LB film shows much higher sensitivity than other NH_3 gas sensors reported in the literature: copper tetra-4-(2,4-di-*tert*-amylphenoxy)phthalocyanine can only reach 2 ppm with a response time of 32 s [16], copper tetracumyl-phenoxy-phthalocyanine has a sensitivity of 0.5 ppm with a response time of about 30 s [17], and a recently reported NH_3 sensor using polypyrrole as the sensitive material has a sensitivity of 10 ppm [18]. Moreover, R_4PcPS is more stable than those materials. When the R_4PcPS LB film was exposed to 10 sequential pulses of 20 ppm NH_3 , the differences between the response curves were less than 4%.

It is possible that the reactive gas molecules adsorbed on the film surface accept π -electrons from

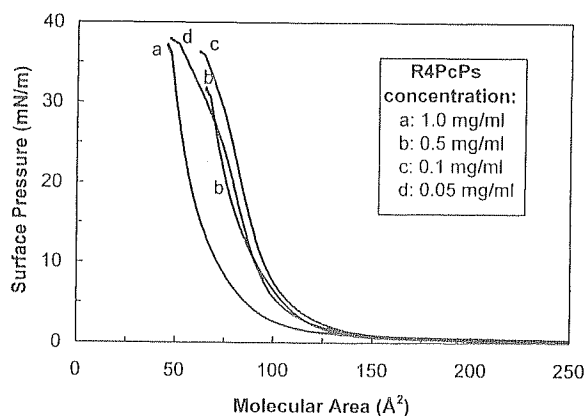


Fig. 4. Surface pressure-area isotherms for R_4PcPS in various concentrations.

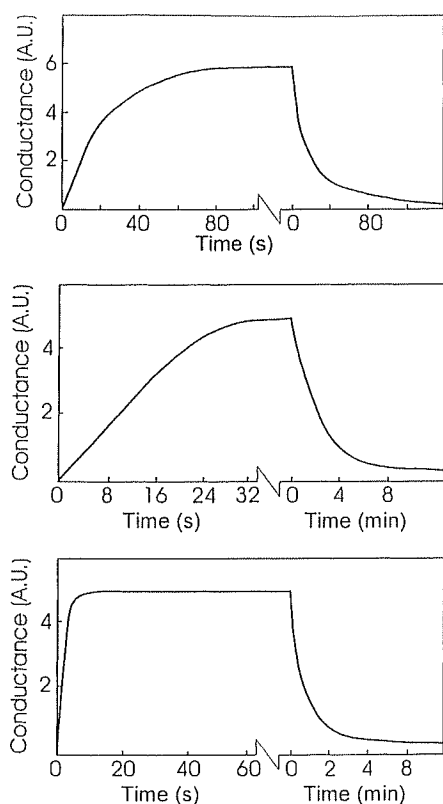


Fig. 5. Response and recovery curves of R_4PcPS LB films in air: top, 10 layers, 0.1 ppm NH_3 ; middle, 15 layers, 100 ppm NO_2 ; bottom, 15 layers, 100 ppm I_2 .

the Pc macrocycles and result in an increase in the hole concentration, i.e. an increase in conductance. The response time is possibly related to the size of the adsorbed gas molecule and the layer structure of the LB films.

The mechanism behind the change in conductance of R_4PcPS LB films and the influence of humidity on it are being studied.

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REFERENCES AND NOTES

1. B. Bott and T. A. Jones, *Sens. Actuat.* **5**, 43 (1984).
2. T. A. Jones and B. Bott, *Sens. Actuat.* **9**, 27 (1980).
3. W. Barger, J. Dote, M. Klusty, R. Mowerg, R. Price and A. Snow, *Thin Solid Films* **159**, 369 (1988).
4. S. D. L., D. P. Jiang, Y. J. Li, W. N. Liu, X. M. Pang, Y. Fan, W. Q. Chen, T. J. Li, X. J. Dong and Z. Q. Zhu, *Thin Solid Films* **210–211**, 606 (1992).
5. D. Wohrle and B. Schulte, *Makromol. Chem.* **189**, 1167 (1988).
6. R. D. Joyner and M. E. Kenney, *Inorg. Chem.* **1**, 717 (1962).
7. T. Sauer and G. Wegner, *Macromolecules* **24**, 2240 (1991).
8. O. E. Sielcken, L. A. Vandekuyl, W. Drenth, J. Schoonman and R. J. M. Nolte, *J. Am. Chem. Soc.* **112**, 3086 (1990).
9. H. Wang and J. B. Lando, *Langmuir* **10**, 790 (1994).
10. Y. Li, X. Pang, C. Cai and W. Chen, *Chinese J. Appl. Chem.* **8**, 52 (1991).
11. T. Sauer and G. Wegner, *Mol. Cryst. Liq. Cryst.* **97**, 16 213 (1988).
12. T. Sauer and G. Wegner, *Makromol. Chem. Rapid Commun.* **7**, 243 (1986).
13. C. W. Dirk, T. Inabe, K. F. Schoch and T. J. Marks, *J. Am. Chem. Soc.* **105**, 1539 (1983).
14. W. Caseri, T. Suner and G. Wegner, *Makromol. Chem. Rapid Commun.* **9**, 651 (1989).
15. Y. Fan, Y. Li, D. Jiang, L. Zhang, Z. Wang and A. Lu, *J. Funct. Mater.* **26**, 639 (1995) (in Chinese).
16. D. P. Jiang, A. D. Lu, Y. J. Li, X. M. Pang and Y. L. Hua, *Thin Solid Films* **199**, 173 (1991).
17. H. Wohltjen, W. R. Barger, A. W. Snow and N. L. Jarvis, *IEEE Trans. Electron Devices* **ED-32**, 1170 (1985).
18. M. Penza, E. Milella, M. B. Alba, A. Quirini and L. Vasanelli, *Sens. Actuat. B* **40**, 205 (1997).