Synthesis of Polystyrene-Supported Dithizone Analogues for Use as Chemical Sensors for Heavy Metals

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Synthesis of Polystyrene-Supported Dithizone Analogues for Use as Chemical Sensors for Heavy Metals

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Abstract

Fiber optic sensors for heavy metal detection require chromogenic ligands which change color upon contact with the metal ions of interest and which can be immobilized onto an insoluble matrix incorporated into the fiber optic system. Diarylthiocarbazonic ligands such as dithizone (diphenylthiocarbazonic) are of particular interest because of the intense and distinct colors of their complexes with heavy metals of environmental concern such as lead and mercury. This paper describes methods for chemical immobilization of a diarylthiocarbazonic unit onto a polystyrene matrix. The key step in the preparation of polystyrene-supported diarylthiocarbazones uses the coupling of nitroformaldehyde β -naphthylhydrazine with diazotized aminopolystyrene. The resulting polystyrene-supported diarylnitroformazan can then be converted to the corresponding polystyrene-supported diarylthiocarbazonic by treatment with aqueous ammonium sulfide followed by oxidation. Using this method samples of polystyrene-supported diarylthiocarbazones have been obtained which undergo distinctive color changes in 0.005 *M* aqueous Pb^{2+} and Hg^{2+} . The properties of such polystyrene-supported diarylthiocarbazones obtained from diazotized aminopolystyrene and nitroformaldehyde β -naphthylhydrazine, including their reactions with heavy metal ions, are compared with materials containing an extra azo chromophore obtained by the method of Chwastowska and Kosiarska using the coupling of diazotized aminopolystyrene with di- β -naphthylthiocarbazonic.

1. Introduction

Fiber optic sensors^{1,2,3,4,5,6,7} require chromogenic ligands for monitoring heavy metals through color changes occurring in the presence of small quantities of the metals of interest. Of particular interest are ligands suitable for monitoring the toxic lead and mercury cations which are "soft" acids in the Pearson sense thereby having a higher affinity for sulfur ligands than oxygen ligands. Ideal chromogenic ligands for such metals should have the following properties:

- (1) The metal-ligand complex must be highly colored even in low metal concentrations and must have a color distinct from that of the uncomplexed reagent. For this reason ligands which have the highly chromophoric azo group are of particular interest.
- (2) The metal complexation should be chemically reversible so that optical sensors containing such ligands can monitor varying metal ion concentrations.
- (3) The chromogenic indicator should be selective for particular metal ions to reduce chemical interference.
- (4) Both the ligand and its metal complexes must be stable in the environment where they are used.

This objective thus requires the development of highly colored chromogenic ligands with selective heavy metal complexing abilities as well as methods for incorporating such ligands into optic sensors through suitably chosen immobilization procedures.

Diverse methods have been used for the immobilization of ligands on the silica surfaces of fiber optic sensors including trapping in porous membranes, chemical bonding to silica-coupled silane molecules or organic membranes, and polymerizing the ligand onto a silica surface. The method chosen for ligand immobilization can affect response time, selectivity, sensitivity, and reversibility.

Among the diverse immobilization methods, the use of chemical bonding of the chromogenic ligand onto a polystyrene matrix appears to be very attractive since polystyrene can be readily converted to aminopolystyrene^{8,9,10} and then diazotized with nitrous acid (Figure 1). The resulting polymer-supported diazonium ion can provide a source of the required polymer-supported azo chromophore through a suitably chosen coupling reaction leading to a ligand of desired type. Most other immobilization methods do not appear to be suitable for the generation of immobilized diazonium ions as synthetic intermediates.

Chromogenic ligands of particular interest in this work are diarylthiocarbazones such as dithizone (diphenylthiocarbazone) and its analogs, which form highly colored complexes with mercury and lead.^{11,12} In this connection a number of methods are available for the synthesis of dithizone and related compounds.^{13,14} The method of

greatest interest in connection with this project is the procedure of Hubbard and Scott¹⁵ based on earlier work by Bamberger, Padova, and Omerod¹⁶ since it provides a method for the conversion of an aromatic amine to the corresponding diarylthiocarbazone (Figure 2b).

The diarylthiocarbazones can be anchored onto a polystyrene matrix by coupling with a polystyrene-supported diazonium salt using a procedure reported by Chwastowska and Kosiarska (Figure 3).¹⁰ However in this case the coupling process introduces a new azo chromophore which might dilute the effect of the heavy metal to be detected on the visible spectrum. This difficulty can be avoided by chemically anchoring a diarylthiocarbazone functionality onto a polymer so that the polymer matrix become an integral part of the diarylthiocarbazone chromophore. Such an approach requires a sequence of reactions such as those depicted in Figures 2a and 4. In the first step a nitroformaldehyde arylhydrazone is prepared by coupling the corresponding arenediazonium salt with the nitromethane anion in a 1:1 ratio (Figure 2a).¹⁶ Subsequent coupling of the nitroformaldehyde arylhydrazone with the diazonium salt of polystyrene (Figure 1) can then give an unsymmetrical diarylnitroformazan in which one of the aryl groups is part of the polystyrene matrix (Figure 4). Such unsymmetrical diarylnitroformazans can be then converted to the corresponding unsymmetrical diarylthiocarbazones by the same methods as used for the symmetrical dithizones (Figure 4).^{14,15} This synthetic approach to the unsymmetrical diarylthiocarbazones through nitroformaldehyde arylhydrazones (Figure 4) has been developed by Pupko and Pel'kis^{17,18} but had not yet been adapted for the preparation of polymer-supported diarylthiocarbazones when the work described in this paper was initiated.

2. Experimental

2.1 Materials

Polystyrene SP5009 (1% divinylbenzene crosslinking) and polystyrene SP5018 (2% divinylbenzene crosslinking) were purchased from Advanced ChemTech. More highly crosslinked polystyrene macroreticular beads (copolymer XFS 4022 with 20% divinylbenzene) were obtained from Dow Chemical Company. The remaining reagents were purchased from standard suppliers.

2.2 Synthesis of nitroformaldehyde β -naphthylhydrazone

The β -naphthylamine hydrochloride (0.4 mole) was stirred overnight in a mixture of 100 mL of water and 120 mL of HCl and then diazotized with 28 g of NaNO_2 dissolved in 60 mL of water at -5 to -8°C using a cold bath of dry ice and *o*-xylene. The sodium salt of nitromethane was prepared in a separate vessel by combining 0.4 mole (22 mL) of

nitromethane in 100 mL of absolute ethanol with 16 g of NaOH in 100 mL of water at -5 to -8°C . The resulting white precipitate of the sodium salt of nitromethane was dissolved in 50 mL of water to give a yellow solution. This solution was added dropwise to the filtered diazonium salt solution kept at -8°C . The final mixture was stirred for 3 hr. The precipitate was filtered off and washed with water. The crude product was purified by dissolving in 5% aqueous sodium hydroxide. After separation of the insoluble fraction the nitroformaldehyde arylhydrazone was precipitated with dilute hydrochloric acid (0.25 *M*). Three such cleaning cycles were required to obtain reasonably pure product. The reaction yield was 42% based on the amine used in the synthesis. Air dried solid nitroformaldehyde β -naphthylhydrazone is orange and melts at 90 – 94°C . It was characterized by infrared and ultraviolet-visible spectroscopy.

2.3 Synthesis of di- β -naphthylnitroformazan

β -Naphthylamine hydrochloride (0.4 mole) was stirred overnight in a mixture of 100 mL of water and 80 mL of HCl and then diazotized with 28 g of NaNO_2 dissolved in 60 mL of water at -5 to -8°C in a cold bath of dry ice and *o*-xylene. The filtered diazotized mixture was then combined with a cold aqueous solution of sodium acetate (87 g in 150 mL of water). In a separate vessel the sodium salt of nitromethane was prepared by mixing at -5 to -8°C solutions of 0.2 mole (11 mL) of nitromethane in 50 mL of absolute ethanol and 8 g of NaOH in 50 mL of water. The white precipitate of the sodium salt of nitromethane was dissolved in 50 mL of water to give a yellow solution. This solution was added dropwise into the diazonium salt solution kept at -8°C . The final mixture was stirred for 2 hr at -5 to -18°C . The temperature was then gradually increased to -4 to 0°C for 2 hr. The di- β -naphthylnitroformazan precipitated as a maroon solid which was separated by filtration and washed with water. The crude moist precipitate was purified by treatment with 150 mL of 50% acetic acid with gentle heat up to 40°C with constant stirring. The mixture was then cooled to room temperature, filtered, and washed with 100 mL of 10% acetic acid followed by water. The air-dried material was ground in a mortar with 200 mL of absolute ethanol. This mixture was brought to the boiling point with stirring and then filtered. The precipitate was washed with 50 mL of hot ethanol and finally air dried. The resulting maroon solid melts at 178 – 180°C . The yields based on amine used in the synthesis were in the range 60 to 85%. These products were characterized by infrared and ultraviolet-visible spectroscopy.

2.4 Synthesis of unsymmetrical phenyl- β -naphthylnitroformazan

This unsymmetrical diarylnitroformazan was synthesized from nitroformaldehyde β -naphthylhydrazone and phenyldiazonium ion. The phenyldiazonium ion (5 mmoles) was prepared from aniline as described above and cooled to -8°C . The solution was buffered at this low temperature by adding a solution of 9.2 g of sodium acetate, 14 mL of acetic acid, and 20 mL of water to give a pH of 5. A cold solution of 0.05 mmoles of nitroformaldehyde β -naphthylhydrazone in methanol was added dropwise and the mixture was stirred for 2 hr at 0 to $+5^{\circ}\text{C}$. The resulting diarylnitroformazan was separated by filtration and washed with deionized water and ethanol until the washings were colorless. The yield of crude material was 94%.

2.5 Preparation of di- β -naphthylthiocarbazine

Di- β -naphthylnitroformazan (18 g) suspended in 200 mL of ethanol was treated with 100 mL of aqueous ammonium sulfide (20% by weight) for 1 hr at room temperature. Gentle heat (up to 40°C) was applied for 2 hr. The mixture was then poured into 500 mL of cold water and the precipitate was separated by filtration. The beige-yellow solid was washed with water and ethanol and then air dried. The yields of product were above 90%.

2.6 Preparation of di- β -naphthylthiocarbazone

The di- β -naphthylthiocarbazine (7.8 g) was treated with 100 mL of 5% ethanolic potassium hydroxide solution for 15 minutes at room temperature to give a dark red solution which was then filtered. The clear filtrate was neutralized to pH ~ 6 with dilute hydrochloric acid and 1 L of cold water was added. The mixture was stirred for 1 hr. The resulting precipitate was separated by filtration and washed with distilled water. Air-dried crude di- β -naphthylthiocarbazone was purified by three subsequent chloroform extractions using 150 mL of solvent each time. The combined chloroform solution was washed with three 100 mL portions of distilled water, the chloroform layer being removed each time to a clean separatory funnel. The washed chloroform solution was filtered and evaporated to ~ 100 mL volume and dried overnight over magnesium sulfate. The solution was once more filtered and 100 mL of absolute ethanol was added. The precipitated di- β -naphthylthiocarbazone was filtered off and air dried.

2.7 Air oxidation of di- β -naphthylthiocarbazine to di- β -naphthylthiocarbazone in 1,2-dichloroethane

The di- β -naphthylthiocarbazine was dissolved in 1,2-dichloroethane in a two-necked round-bottomed flask placed on a heating mantle. A slow stream of air was bubbled

through the solution which was brought to boiling temperature ($\sim 85^{\circ}\text{C}$). A condenser fitted to the flask reduced evaporation of the solvent. However it was necessary to add further portions of solvent periodically especially during long time oxidations using larger samples ($> 1\text{ g}$). The color of the solution changed gradually after $\sim 3\text{ hr}$ to a very intense green-black. After the oxidation was complete, the solvent was evaporated. The crude di- β -naphthylthiocarbazone was purified by chloroform extraction in the same manner as previously described.

2.8 Hydrogen peroxide oxidation of di- β -naphthylthiocarbazide to di- β -naphthylthiocarbazone

A 1 g portion of di- β -naphthylthiocarbazide or a functionalized polymeric thiocarbazine was treated with 10 mL of 3% hydrogen peroxide solution for 15 min at ambient temperature. The resulting solid was separated by filtration, washed with water, and air dried.

2.9 Preparation of nitro- and aminopolystyrenes

A 30 g-portion of the polystyrene was suspended in a mixture of acetic anhydride and acetic acid and cooled to -4°C . Nitric acid was slowly introduced and the mixture was stirred at low temperature ($\sim -4^{\circ}\text{C}$). After the reaction was completed the solids were filtered off, washed, and air dried. The nitration of polystyrene was also carried out in which the acetic acid-acetic anhydride mixture was substituted by sulfuric acid (samples 3-18, 3-20, 3-22, 3-24). The reaction conditions are listed in Table 1. The nitropolystyrenes were reduced to the corresponding aminopolystyrenes with stannous chloride in hydrochloric acid at room temperature or 90°C (see Table 1).

2.10 Functionalization of diazotized aminopolystyrene with nitroformaldehyde β -naphthylhydrazine and its conversion to thiocarbazone.

A 0.5 to 10 g-portion of aminopolystyrene was suspended in a mixture of hydrochloric acid and water cooled to $\sim -4^{\circ}\text{C}$ and then diazotized with 0.1 mole of NaNO_2 dissolved in 40 mL of distilled water. The mixture was stirred for 1 hr to allow complete reaction. The resulting solid was separated by filtration, washed with cold water to remove an excess of acid, and then immediately transferred into a cold buffer solution of 36 g of sodium acetate, 40 mL of acetic acid, and 20 mL of water. The nitroformaldehyde arylhydrazine (~ 0.5 to 1 g) dissolved in 200 mL of ethanol was filtered and cooled to $0-2^{\circ}\text{C}$. This ethanolic solution was slowly added to the polymer suspension. The final mixture was stirred at -2 to $+4^{\circ}\text{C}$ for 6 hr. The dark colored solid was separated and

washed with water and then with ethanol until the filtrate was clear. In several cases Soxhlet extraction was used to minimize use of ethanol.

In the next step the functionalized polystyrene was treated with an aqueous solution of ammonium sulfide at room temperature for at least 3 hr. Thus a 1 to 10 g-portion of functionalized polymer was treated with 20 to 100 mL of 20% aqueous ammonium sulfide as previously described for di- β -naphthylthiocarbazone. A more rapid reaction was obtained with solutions also containing 5 ml of 21 % ammonium hydroxide .

2.11 Anchoring of di- β -naphthylthiocarbazone to polystyrene (procedure of Chwastowska and Kosiarska¹⁰)

A portion of aminopolystyrene (~5 g) suspended in a mixture of 120 mL of concentrated hydrochloric acid and 100 mL of water was cooled to about -4°C and then diazotized with 18.6 g of sodium nitrite dissolved in 50 mL of water for 4 hr. Solids were filtered off, washed with cold water, and transferred into a cold acetate buffer solution prepared by dissolving 36.4 g of sodium acetate and 50 mL of acetic acid in 100 ml of water. An acetone solution (200 mL) containing approximately 0.5 g of di- β -naphthylthiocarbazone was filtered and slowly added and the mixture was stirred for 4 to 18 hr . After the reaction was complete, the crosslinked polystyrene was washed with water, then with acetone to remove unreacted di- β -naphthylthiocarbazone, and air-dried. Attempts to separate unreacted di- β -naphthylthiocarbazone from the uncrosslinked polymer met with difficulty owing to significant acetone solubility of the polymer itself. Therefore a water-acetone mixture (3:1) rather than pure acetone was used to wash these samples. Air-dried samples obtained from the uncrosslinked polymer did not appear to be homogeneous.

2.12 Spectroscopic methods

The infrared spectra were recorded on a Perkin Elmer 1600 Series FT-IR infrared spectrometer using KBr disks. The electronic spectra of chloroform solutions were recorded on a Hewlett Packard Model 8452A Diode Array Spectrophotometer. The electronic spectra of solid samples were taken in Nujol mulls placed between two methacrylate ultraviolet grade plates. Proton nuclear magnetic resonance spectra of nitroformaldehyde arylhydrazones, diarylnitroformazans and the corresponding diarylthiocarbazones were recorded in CDCl_3 solutions on a Bruker AC-300 spectrometer operating at 300 MHz for protons. However since most of polymers used in the preparation of the functionalized polystyrenes are insoluble in organic solvents, solution NMR spectra of these polymers could not be obtained.

3. Results and Discussion

3.1 Synthesis of nitroformaldehyde β -naphthylhydrazone, di- β -naphthylformazan, and unsymmetrical phenyl- β -naphthylnitroformazan.

The synthetic method reported by Pupko and Pel'kis¹⁶ (Figure 2) was investigated in which 1 mole of aryldiazonium salt was coupled with 1 mole of the sodium salt of nitromethane to form the corresponding nitroformaldehyde arylhydrazone. By using this method nitroformaldehyde arylhydrazones were synthesized in which the aryl group was phenyl, 2,4,6-trimethylphenyl and β -naphthyl. However, the phenyl and 2,4,6-trimethylphenyl derivatives were quite unstable at room temperature and decomposed over a period of several days. Therefore we concentrated our efforts on the more stable nitroformaldehyde β -naphthylhydrazone.

Since the paper by Pupko and Pel'kis¹⁶ did not describe adequately the synthesis of nitroformaldehyde β -naphthylhydrazone, the details of the preparative procedure needed to be worked out. In our initial experiments based on the Pupko and Pel'kis procedure¹⁶ 0.1 mole of β -naphthylamine hydrochloride was suspended in water and then diazotized with the stoichiometric amount of NaNO_2 with cooling to -5 to -8°C . The sodium salt of nitromethane (0.1 mole) was prepared separately. The aryldiazonium salt solution was added dropwise to the nitromethane solution at -5 to -8°C and the mixture was stirred for 4 hr. Several cleaning cycles were required to obtain reasonably pure product and the final yield was relatively poor not exceeding 20%. We found that this coupling reaction is strongly pH-dependent and is not a smooth reaction since considerable amounts of tarry byproducts are produced, especially when aniline and 2,4,6-trimethylaniline are used as starting materials. The main side product of the reaction was the corresponding diarylnitroformazan. In a number of experiments we found that if the reaction conditions suggested by Pupko and Pel'kis¹⁶ were used, the final pH of the mixture was about 2.5 and considerable diarylnitroformazan side product was produced at the beginning of the coupling reaction when the mixture still was very basic. Our modification of the Pupko and Pel'kis procedure¹⁶ using an excess of acid for the preparation of the aryldiazonium salt and reversing the order of mixing so that the nitromethane solution was added to the aryldiazonium solution rather than vice versa was found to suppress significantly the formation of the diarylnitroformazan side product by keeping the pH low during the coupling reaction. Such modified conditions were used for synthesis of nitroformaldehyde β -naphthylhydrazone on a large scale.

The di- β -naphthylnitroformazan as well as the diphenyl and di(2,4,6-trimethylphenyl) analogues were synthesized according to the Hubbard procedure¹⁵ which is based

on the coupling of 2 moles of the diazonium salt with 1 mole of the sodium salt of nitromethane. This method was found to give very reproducible results with good yields of the diarylnitroformazans.

The unsymmetrical diarylnitroformazans were synthesized in satisfactory yields from the corresponding nitroformaldehyde arylhydrazone and phenyldiazonium ion using the Pupko and Pel'kis procedure.^{17,18} All samples prepared were characterized by spectroscopic methods, mainly infrared and ultraviolet-visible spectra.

These three β -naphthylnitroformazans exhibit distinct electronic and infrared spectra which can be easily identified. Thus for di- β -naphthylnitroformazan the main absorption is observed at 488 nm whereas for nitroformaldehyde β -naphthylhydrazone the maximum occurs at 412 nm. The main absorbance maxima of the unsymmetrical diarylnitroformazans are distinctly different from those of the symmetrical analogs occurring at 338 and 464-470 nm. The same relationship was observed for phenyl and 2,4,6-trimethylphenyl analogues.

The infrared spectrum of nitroformaldehyde β -naphthylhydrazone consists of sets of bands in the 600-1700 cm^{-1} region. The most intense absorption occurs between 1050 and 1400 cm^{-1} where several bands with shoulders are observed. The di- β -naphthylnitroformazan exhibits a very poor infrared spectrum dominated by bands at 1271, 1343 and 1550 cm^{-1} . The unsymmetrical phenyl- β -naphthylformazan exhibits an infrared spectrum similar to nitroformaldehyde β -naphthylhydrazone with some shifts in band positions to 1279, 1350 and 1543 cm^{-1} , respectively.

3.2 Formation of di- β -naphthylthiocarbazine

The original procedure for converting diarylnitroformazans to the corresponding diarylthiocarbazones used a two-step reaction (Figure 2b). In the first step the diarylnitroformazan was converted into the corresponding diarylthiocarbazine by treatment with gaseous ammonia and hydrogen sulfide in ethanol^{14,15} followed by oxidation to the corresponding diarylthiocarbazonone. Our syntheses of di- β -naphthylthiocarbazine used a modified version of this reaction with commercial aqueous ammonium sulfide. This procedure allowed us to avoid the inconvenience of using gaseous NH_3 and H_2S and was previously used for the synthesis of some dithizone derivatives but not di- β -naphthylthiocarbazonone. Therefore it was necessary to work out the optimum conditions of the reaction. In this connection several batches of di- β -naphthylthiocarbazonone were synthesized and characterized by spectroscopic methods.

The infrared spectra of two samples of di- β -naphthylthiocarbazonone synthesized from the same starting diarylnitroformazan are almost identical confirming the reproducibility of this synthetic method. Some shifts in the band position $\sim + 4 \text{ cm}^{-1}$ and small

changes in the relative intensities can be ascribed to the different levels of impurities. In general the infrared spectra of samples of di- β -naphthylthiocarbazide consist of bands mainly in the 600–800, 1150–1300 and 1400–1700 cm^{-1} regions. The absorption bands between 1200–1300 cm^{-1} indicate the presence of the –SH group. The bands at 1270 and 1343 cm^{-1} present in the spectrum of the starting di- β -naphthylthioformazan completely vanished upon conversion to the corresponding diarylthiocarbazone and were replaced by sets of bands with maxima at 1180, 1220 and 1250 cm^{-1} . Additional infrared bands appeared at 1470, 1510, 1560 and 1600 cm^{-1} .

The diarylthiocarbazides are not very stable in air as they readily undergo oxidation to the corresponding diarylthiocarbazones. Our samples were exposed to air for different periods of time before the infrared spectra were registered and thus are probably contaminated with oxidation products to varying extents.

The electronic spectra taken on freshly synthesized di- β -naphthylthiocarbazide and samples exposed to air for several days show differences indicating that the diarylthiocarbazides are not very stable in air as they readily undergo oxidation to the corresponding diarylthiocarbazones. The fresh synthesized sample exhibits a major maximum at 256 nm with low intensity absorptions at 416 and 650 nm. Upon exposure to air for 3 days the band at 650 nm increases in intensity. This band is characteristic for di- β -naphthylthiocarbazone.^{11,15,19,20}

3.3 Oxidation of di- β -naphthylthiocarbazide to di- β -naphthylthiocarbazone

A critical step in the preparation of the diarylthiocarbazones is the oxidation of the corresponding diarylthiocarbazides. The original method^{14,15} for preparation of diarylthiocarbazones used oxidation by air in strongly basic ethanolic KOH solution. This is actually a disproportionation reaction with a maximum yield of 50 % of the diarylthiocarbazone. It was found²¹ that at least in some cases the yields of diarylthiocarbazones could be increased to 80–90% by air oxidation in a neutral organic solvent. Both methods were used for oxidation of diarylthiocarbazides to the corresponding diarylthiocarbazones. We have found that the yield of di- β -naphthylthiocarbazone yield by oxidation/disproportionation in ethanolic KOH solution depends on reaction time with longer reaction times leading to lower yields. We thus recommend a reaction time of only 15 min for the KOH oxidation/disproportionation.

The infrared spectra of the purified products confirm formation of di- β -naphthylthiocarbazone. Samples treated with potassium hydroxide for longer times exhibit additional bands and changes in the relative intensity patterns. Oxidation with air in a chlorinated solvent (e.g., 1,2-dichloroethane) was found to produce much purer products

in higher yields but required longer reaction times. In a sample oxidized for 4 hr the infrared bands of unreacted di- β -naphthylthiocarbazine were still observed in addition to the bands characteristic for di- β -naphthylthiocarbazone indicating incomplete oxidation. Such bands vanished from the infrared spectrum of samples oxidized for longer times. Attempts to substitute acetone for the chlorinated solvent in the air oxidation procedure failed. The infrared spectrum of the solid separated from acetone after aeration corresponds to unreacted di- β -naphthylthiocarbazine. The reason for this behavior is not clear. It can arise from the lower solubility of di- β -naphthylthiocarbazine in acetone compared to 1,2-dichloroethane as was previously observed for dithizone derivatives²¹ or simply from the lower boiling temperature of acetone (56°C versus 84°C for 1,2-dichloroethane). Oxidation of di- β -naphthylthiocarbazine with dilute hydrogen peroxide produced a dark brown solid that exhibited an infrared spectrum similar to di- β -naphthylthiocarbazone but with a different pattern of relative intensities. Moreover an additional relatively strong band around 1022 cm^{-1} was observed suggesting the presence of a sulfoxide group.²² On the other hand sulfonic acids derivatives were previously identified as oxidation products of dithizone and their infrared spectra also exhibit such a band.²³ In any case our sample obtained by hydrogen peroxide oxidation exhibited a different electronic spectrum and was completely inactive in reactions with mercury and lead cations.

In order to confirm formation of di- β -naphthylthiocarbazone in the oxidation of di- β -naphthylthiocarbazine either in potassium hydroxide solution or a chlorinated solvent, the electronic spectra were obtained in chloroform solution. In general the electronic spectra of the di- β -naphthylthiocarbazone samples exhibited a strong absorption maximum around 650 nm that is consistent with literature data for di- β -naphthylthiocarbazone.^{11,15,24,25} This band is shifted to lower wavenumbers upon complexation with lead and mercuric cations to ~540 and ~510 nm, respectively. Such changes are consistent with reported electronic spectra.^{11,15,19,20,23,25}

3.4 Preparation of aminopolystyrene

We studied the functionalization of the following three samples of commercially available polystyrenes of different particle sizes and crosslinked with different amounts of divinylbenzene (DVB).

- (1) Polystyrene SP5009 with a 100-200 mesh particle size and containing 1% DVB.
- (2) Polystyrene SP5018 with a 200-400 mesh particle size and containing 2% DVB.
- (3) Copolymer XFS 4022 consisting of beads and containing 20% DVB.

We also studied a sample of commercially available uncrosslinked polystyrene (Polystyrene MW 45,000) in form of crushed plates.

The samples of crosslinked polystyrene with different divinylbenzene (DVB) contents and different particle sizes as well as the sample of uncrosslinked polystyrene as suspensions were nitrated either with nitric acid in a mixture of acetic anhydride and acetic acid according to the published procedures^{8,9} or in the standard sulfuric acid medium frequently used for nitrations of benzenoid derivatives (samples 3-18, 3-20, 3-22, 3-24 as listed in Table 1). The samples of the resulting nitropolystyrene were then reduced to the corresponding aminopolystyrenes using stannous chloride in hydrochloric acid solution (Table 1).

In order to follow changes in the polymers after nitration and reduction infrared spectra of starting materials were recorded. The infrared spectra of starting polystyrenes were found to be similar. Some changes in the relative intensity of bands were noticeable presumably owing to the different DVB content. The uncrosslinked polymer was found to exhibit a poor spectrum. A set of bands between 1400 and 1700 cm^{-1} was found to be more intense in the crosslinked polymers.

Several batches of nitropolystyrene were prepared (Table 1). An initial batch (sample 1-16A) was synthesized using the method of King and Sweet⁹ including purification with different mixtures of organic solvents. The materials were then washed with pure water to remove acids following by ethanol. The degree of nitration was estimated from the infrared spectra of the solid nitropolystyrenes, which were yellow solids exhibiting infrared bands around 1520 and 1345 cm^{-1} not present in the original polystyrenes indicative of aromatic nitro groups. The 1345 cm^{-1} band overlaps with the ~1320 and 1370 cm^{-1} bands of polystyrenes. The product of the nitration in THF solution (sample 3-2) exhibited very low intensity bands in this region. The intensity of these bands increased for samples synthesized in a sulfuric acid medium. The degree of nitration was found to depend on the particle size of solid rather than the divinylbenzene content with smaller particles leading to lower degrees of nitration.

The nitropolystyrenes were reduced to the corresponding aminopolystyrenes using stannous chloride in hydrochloric acid at room temperature or 90°C (Table 1). The uncrosslinked nitropolystyrene can be completely reduced to the corresponding aminopolystyrene by increasing the reduction time at room temperature. In the infrared spectra of the aminopolystyrenes the bands at 1345 and 1520 cm^{-1} assigned to nitro groups are no longer observable. The crosslinked nitropolystyrenes are more resistant towards reduction so that higher temperatures are recommended for complete reduction to aminopolystyrenes. However the rate of reduction depends on the particle size of the solid rather than the DVB content as we have previously observed for the nitration reaction discussed above. For the

partially reduced samples the infrared bands at $\sim 1520\text{ cm}^{-1}$ and $\sim 1345\text{ cm}^{-1}$ are still observed but in lower intensities.

3.5 Functionalization of diazotized aminopolystyrene with nitroformaldehyde β -naphthylhydrazine

Several batches of each type of aminopolystyrene functionalized with nitroformaldehyde β -naphthylhydrazine were prepared and characterized by infrared and ultraviolet spectroscopy. In a typical experiment aminopolystyrene was diazotized with an excess of sodium nitrite in hydrochloric acid and then coupled with the nitroformaldehyde β -naphthylhydrazine to give a polymer-supported diarylnitroformazan (Figure 4) following the reaction pathway described earlier for synthesis of unsymmetrical diarylnitroformazans.^{17,18} The best results in the synthesis of unsupported diarylnitroformazans were obtained when the reaction mixture was buffered to pH about 4 to 5 as noted above. However the diazotization reaction required a very low pH of $\sim 0-1$. Therefore in order to avoid neutralization of excess acid with alkali the coupling procedure was modified. The aminopolystyrene diazotized at low pH was quickly filtered off from the reaction mixture, washed generously with cold water, and immediately transferred into a cold buffer solution of sodium acetate and acetic acid followed by coupling with the nitroformaldehyde arylhydrazine dissolved in ethanol. The dark colored solids were separated and washed with water to remove acetates followed by ethanol to remove excess nitroformaldehyde arylhydrazine. In several cases Soxhlet extraction was used to minimize the use of ethanol.

The electronic spectra of these products showed a very broad absorption in the 400-700 nm range without distinct maxima similar to the spectra of solid diarylnitroformazans. The infrared spectra of functionalized polymers in general exhibit changes in the relative intensities of bands in the $1100-1700\text{ cm}^{-1}$ range as well as new bands at 1273, 1320, 1520, 1541, 1628 and 1653 cm^{-1} compared to the starting aminopolystyrene. Those absorptions can be observed as distinct bands or as shoulders depending on the degree of functionalization which would depend of course on the number of active sites on the polymer generated during diazotization. The positions of new bands or shoulders in general are comparable with the those of most intense bands for di- β -naphthylnitroformazan and the corresponding unsymmetrical phenyl- β -naphthylnitroformazan.

In the next step the functionalized polystyrenes were treated with an aqueous solution of ammonium sulfide at room temperature for at least 3 hr. In some cases this reaction was carried out for 18 hr in order to observe visually a color change to beige in accord with expectations based on the color of the corresponding di- β -naphthylthio-

carbazine. However in many cases the products after treatment with aqueous ammonium sulfide displayed dark green or gray colors similar to solid diarylthiocarbazones.

After treatment with aqueous ammonium sulfide the infrared spectra of the functionalized polystyrenes exhibited bands characteristic of polystyrene and some shifts in the band positions compared to the β -naphthylnitroformazan modified polymers. The most significant difference is that the band at $\sim 1273\text{ cm}^{-1}$ originally present in the infrared spectra of polystyrenes functionalized with nitroformaldehyde β -naphthylhydrazone vanished after treatment with ammonium sulfide similar to observations with unsupported di- β -naphthylnitroformazan indicating conversion of the supported diarylnitroformazan functionalities to the corresponding diarylthiocarbazide functionalities.

The green or olive color of the solid products suggests that the supported diarylthiocarbazides were at least partially oxidized to the corresponding diarylthiocarbazones. Therefore we decided to test the products at this stage of the reaction sequence with heavy metal cations. In this connection these solids were shaken vigorously with aqueous solutions of Pb^{2+} and Hg^{2+} . The green or olive colors of these solids were replaced with reddish or pinkish colors indicating metal complexation. These metal-containing polymers were separated and air dried and their infrared spectra were recorded giving the following results:

Lead-containing polymer: 672, 752, 834, 905, 1016, 1067, 1160, 1178, low intensity 1230, 1341, 1438, 1498, 1578 with several shoulders, 1654 cm^{-1} .

Mercury-containing polymer: 675, 752, 829, 903, 1015, 1054, 1154, 1268, 1326, 1340, 1432, 1465, 1471, 1508, 1560, 1576, 1654 cm^{-1} .

It was not surprising that in these experiments only low intensity bands corresponding to the metal complexes were observed in addition to those of the diarylthiocarbazide since the degree of the oxidation of the functionalized polymer is presumably very low. However some changes in the infrared spectra are visible. The infrared band around 1382 cm^{-1} in the metal-free polymers vanished from spectra of samples treated with the heavy metals. Instead a set of bands at 1320 , 1342 and 1360 cm^{-1} were observed. The bands at ~ 1022 , 1067 , 1179 , 1490 , and 1597 cm^{-1} for supported β -naphthyl species are shifted to 1016 and 1015 , 1059 and 1054 , 1160 and 1154 , 1500 and 1474 , 1578 and 1576 cm^{-1} for samples treated with Pb^{+2} and Hg^{+2} , respectively. Such changes in the infrared spectra are consistent with literature data^{19,26,27,28,29,30} concerning formation of heavy metal complexes of diphenylthiocarbazone and di- β -naphthylthiocarbazone.

Since there are no data in the literature concerning oxidation of polymer-supported diarylthiocarbazides to the corresponding diarylthiocarbazones, it was necessary to find suitable conditions for these oxidations. In this connection the polymer-supported

diarylthiocarbazides were oxidized using methods described above including treatment with ethanolic KOH, air oxidation in a chlorinated solvent (1,2-dichloroethane), and treatment with dilute hydrogen peroxide.

Polymer-supported diarylthiocarbazides were expected to be more difficult to oxidize than unsupported diarylthiocarbazides. Therefore the polymer-supported diarylthiocarbazides were allowed to react with potassium hydroxide solution for 1 or 2 hr instead of the 15 min used for di- β -naphthylthiocarbazide. The infrared spectra of these products indicated no significant differences between those two samples, which is not surprising since diarylthiocarbazides and diarylthiocarbazones absorb in similar regions. However some changes in the relative intensities and band positions are observed, especially around 1152, 1179 1342 and 1654 cm^{-1} indicative of thiocarbazon formation. Air oxidation in 1,2-dichloroethane appeared to give the same product. Oxidation with dilute hydrogen peroxide produced an almost black solid. The infrared spectra exhibited changes in the 1000-1340 cm^{-1} region with domination of a band around 1152 cm^{-1} .

Presently available methods do not allow a quantitative comparison of supported diarylthiocarbazones obtained by different oxidation methods. Therefore these products were tested in reactions with heavy metals (Pb^{2+} and Hg^{2+}). In this connection all samples were found to give a positive reaction with Pb^{2+} and Hg^{2+} . There were changes in the infrared spectra of such samples treated with heavy metals similar to those discussed above.

Both KOH oxidation/disproportionation and air oxidation were found to give similar products based on infrared spectroscopy and reactions with heavy metal cations. However owing to the properties of uncrosslinked polystyrene, the KOH oxidation/disproportionation was chosen for further experiments.

All types of functionalized polystyrenes were converted into the corresponding polystyrene-supported diarylthiocarbazides. The longest time required to observe color changes upon treatment of the polystyrene-supported diarylnitroformazan with aqueous ammonium sulfide occurred with samples prepared from polystyrene containing 2% DVB. Furthermore, treatment of these polystyrene-supported diarylthiocarbazides with potassium hydroxide gave no observable color changes; however the resulting products appeared to react with heavy metal cations giving pinkish to violet reflections in the solutions. However, such reactions were not spontaneous requiring some time (up to 18 hr). to develop these color changes. For polystyrene-supported dithizones made from polystyrene containing 2% of DVB, these color changes with heavy metals could not be observed visually. In experiments using different polystyrenes it was found that the reactions of polystyrene-supported diarylnitroformazans with aqueous ammonium sulfide in basic

ethanolic suspension were more rapid than those in neutral solution giving observable color changes after 3 hr of stirring. All samples appeared to react with heavy metal cations (Pb^{2+} and Hg^{2+}) but a long time up to 3 days was required to observe the color changes.

3.6 Anchoring of di- β -naphthylthiocarbazono to polystyrene using the procedure of Chwastowska and Kosiarska

The second approach to the synthesis of spectroscopic indicators for heavy metal cations is based on work of Chwastowska and Kosiarska¹⁰ in which previously synthesized diarylthiocarbazones are anchored to the diazotized aminopolystyrene through an additional coupling reaction (Figure 3). Several batches of polymers functionalized in this way were synthesized from the corresponding aminopolystyrene derived from uncrosslinked as well as crosslinked polystyrene. The products of this reaction are brown or black solids, which were characterized by infrared and ultraviolet spectroscopy.

The electronic spectra of polystyrenes functionalized by the method of Chwastowska and Kosiarska¹⁰ display a maximum around 268 nm and a very flat, broad absorption between 400–700 nm. The solid di- β -naphthylthiocarbazono itself in a Nujol mull exhibits absorptions at 270, 340 and 600–750 nm but the maxima cannot be estimated precisely. In the infrared spectra of polystyrenes functionalized by the method of Chwastowska and Kosiarska¹⁰ new bands noticeable as shoulders around 1200, 1383, 1475 and 1583 cm^{-1} indicate anchored di- β -naphthylthiocarbazono.

The di- β -naphthylthiocarbazono-supported polystyrenes functionalized by the method of Chwastowska and Kosiarska¹⁰ were tested in reactions with Pb^{+2} and Hg^{+2} cations in aqueous solution. In this connection several mg of modified polymer were shaken with aqueous solutions of Pb^{+2} and Hg^{+2} cations for several minutes. The resulting suspensions exhibited pink and violet-red reflections in contrast to the corresponding metal-free polymers. The solids were filtered off, washed with water, and air dried. The amounts of solids were not sufficient to obtain reasonable electronic spectra in the solid state but allowed us to obtain their infrared spectra.

The most significant differences in the infrared spectra of di- β -naphthylthiocarbazono-supported polystyrenes functionalized by the method of Chwastowska and Kosiarska¹⁰ upon treatment with heavy metals were observed in the 1100–1600 cm^{-1} region. Thus the infrared band around 1382 cm^{-1} vanished from spectra of samples treated with Pb^{+2} and Hg^{+2} . Instead a set of bands around 1310, 1341, and 1360 cm^{-1} was observed. The bands at ~1152, 1474 and 1583 cm^{-1} for anchored di- β -naphthylthiocarbazono were shifted to 1176 and 1173 cm^{-1} , 1491 and 1486 cm^{-1} , and 1594 and 1597 cm^{-1} for Pb^{+2} and Hg^{+2} treated samples, respectively. Such changes in the infrared

spectra are consistent with literature data concerning formation of metal dithizonates.^{19,26,27,28,29,30}

We were uncertain if chemically anchored or unwashed physically adsorbed di- β -naphthylthiocarbazone was responsible for the color reactions with heavy metal cations in di- β -naphthylthiocarbazone-supported polystyrenes functionalized by the method of Chwastowska and Kosiarska.¹⁰ Therefore we prepared samples containing 1% by weight of the diarylthiocarbazone by making a tetrahydrofuran solution containing both the pure uncrosslinked polymer and di- β -naphthylthiocarbazone and allowing this solution to evaporate at room temperature in a big Petri dish. After evaporating overnight a polystyrene thick film was obtained. This film had the characteristic dark green color of the di- β -naphthylthiocarbazone ligand but did not undergo color changes with Pb^{+2} and Hg^{+2} even after 3 days. The infrared spectrum shows only changes in the relative intensities of bands owing to low loading. Similar results were obtained by using polyvinylchloride (PVC) rather than polystyrene films containing di- β -naphthylthiocarbazone. A very thin PVC film prepared by coating a very dilute solution on a large surface exhibited an infrared spectrum similar to a pure PVC matrix with some shifts in band positions. Thus the band at $\sim 1097 \text{ cm}^{-1}$ in PVC is shifted to 1064 cm^{-1} for the film and a shoulder at $\sim 1131 \text{ cm}^{-1}$ can be observed. The electronic spectra of the modified PVC film exhibited absorptions at 328 and 650 nm characteristic of pure di- β -naphthylthiocarbazone. Samples prepared in this way appeared to react with heavy metal cations (Pb^{+2} and Hg^{+2}) after 3 days.

4. Summary

This work demonstrates a method for chemical immobilization of a diarylthiocarbazone unit onto a polystyrene matrix using the coupling of nitroformaldehyde β -naphthylhydrazone with diazotized aminopolystyrene followed by treatment with aqueous ammonium sulfide and oxidation. This method has been used to prepare samples of polystyrene-supported diarylthiocarbazones which undergo distinctive color changes in 0.005 M aqueous Pb^{2+} and Hg^{2+} . Materials of this type are potentially useful as chromogenic ligands in fiber optic sensors for heavy metal detection.

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Table 1

Conditions for preparation of nitro- and amino- polystyrenes

Nitration of Polystyrenes						Reduction of Nitropolystyrenes					
Sample number	Polystyrene (g)	mL of HNO ₃	mL acetic anhydride	mL acetic acid	Time (hr)	Sample number	g of sample	g of SnCl ₂	mL of aq. HCl	Temp. °C	Time (hr)
2-112	60	15	150	50	2	2-113	57	125	250	room	24
3-2	59	20	150	45	4	3-7	57	125	250	room	48
3-24	30	15	50 H ₂ SO ₄		4	3-25	28	125	250	room	72
1-16A	10	3.2	41	9	5	1-16B	5	5	5	room	48
2-60	32	50	120	30	2.5	2-61	34	125	250	reflux	30
2-88	50	15	200	45	1	2-94	45	125	250	reflux	28
3-20	30	15	50 H ₂ SO ₄		3	3-21	28	125	250	room	72
2-87	50	30	200	45	3	2-97	58	150	250	reflux	48
3-22	30	15	50 H ₂ SO ₄		4	3-23	28	125	250	room	72
2-89	50	15	200	45	0.5	2-93	58	125	250	reflux	48
3-18	30	15	50 H ₂ SO ₄		3	3-19	28	125	250	room	72

Figure Captions

Figure 1: Conversion of polystyrene to aminopolystyrene followed by diazotization.

Figure 2: (a) Conversion of a primary aromatic amine to the corresponding nitroformaldehyde arylhydrazone; (b) Conversion of a primary aromatic amine to the corresponding diarylthiocarbazine.

Figure 3: The procedure of Chwastowska and Kosiarska¹⁰ for coupling diazotized aminopolystyrene with diphenylthiocarbazine (dithizone). This procedure leads to a supported diarylthiocarbazine with the indicated "extra" azo chromophore. An analogous procedure is used in this work to couple diazotized aminopolystyrene with di- β -naphthylthiocarbazine.

Figure 4: The procedure used in this work to anchor a diarylthiocarbazine chromophore onto a polystyrene matrix.

**Nitroformaldehyde
Arylhydrazone**

Diarylnitroformazan

- a) NH_3
b) H_2S
c) H_2O

Diarylthiocarbazone

Diarylthiocarbazide