OPIC
Office de la propriété intellectuelle du Canada

CIPO
Canadian Intellectual Property Office

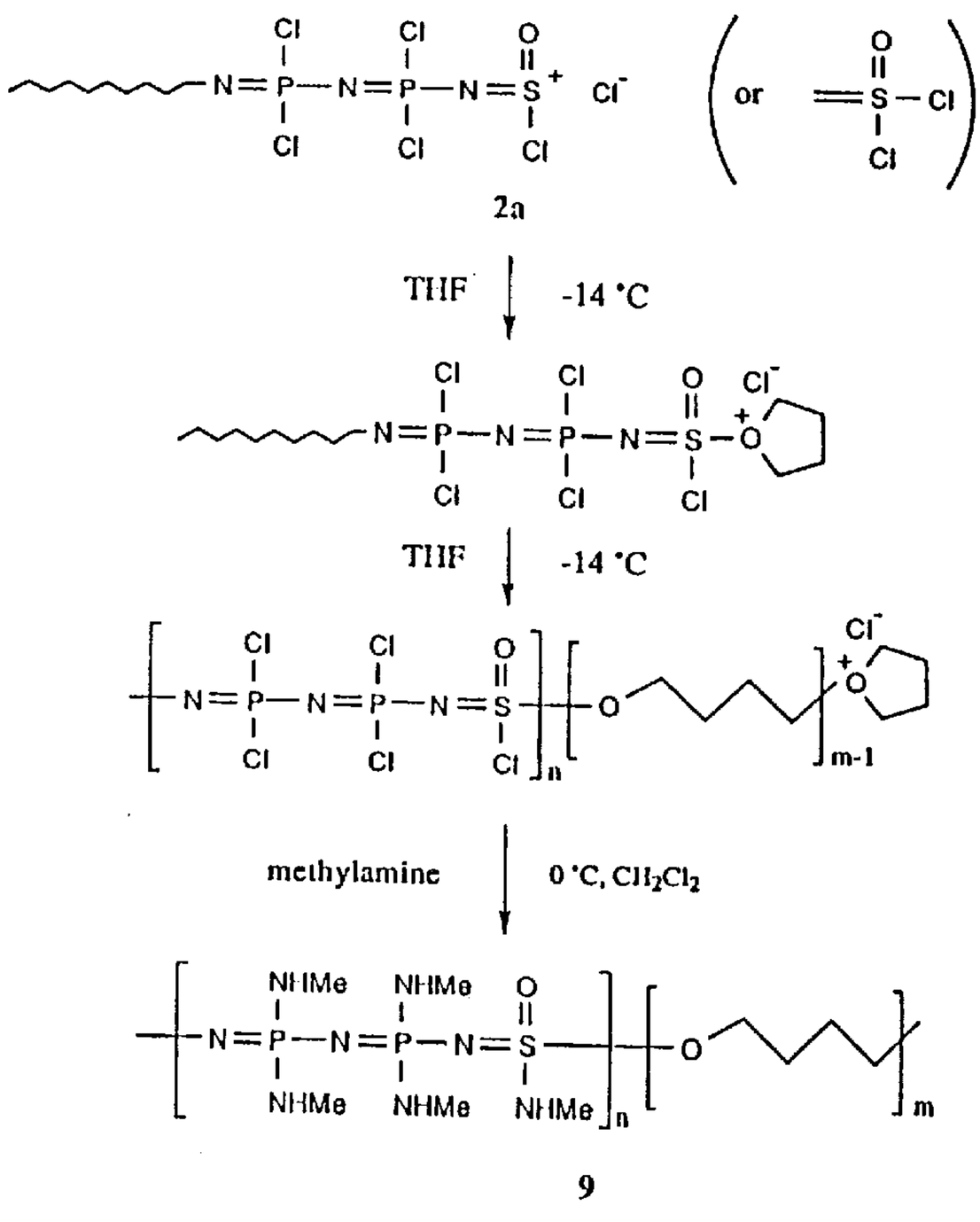
(12) (19) (CA) **Demande-Application**

(21) (A1) **2,227,309**
(22) 1998/01/16
(43) 1999/07/16

(72) MANNERS, Ian, CA
(72) GU, Xijia, CA
(72) WINNICK, Mitchell, CA
(71) MANNERS, Ian, CA
(71) GU, Xijia, CA
(71) WINNICK, Mitchell, CA

(51) Int.Cl.[6] C08G 79/02, G01N 21/64, C09D 5/22, C09D 185/02, C09K 11/06, G01L 11/02

(54) **DETECTEUR PHOSPHORESCENT D'OXYGENE**
(54) **PHOSPHORESCENT OXYGEN SENSORS**



9

Synthesis of Poly[(methylamino)thionylphosphazene]-b-Poly(tetrahydrofuran) Block Copolymer

(57) Disclosed herein is a polymer material formed from a polymeric material having a backbone containing nitrogen and one or more of sulfur and phosphorous, the polymer material further comprising at least one side chain, wherein either the at least one side chain or the backbone bears a phosphorescent dye agent.

ABSTRACT

PHOSPHORESCENT OXYGEN SENSORS

Disclosed herein is a polymer material formed from a polymeric material having a backbone containing nitrogen and one or more of sulfur and phosphorous, the polymer material further comprising at least one side chain, wherein either the at least one side chain or the backbone bears a phosphorescent dye agent.

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The present invention relates to phosphorescent oxygen sensors and more particularly to compositions for forming coatings therefor.

2. DESCRIPTION OF THE RELATED ART

The field of luminescent barometry has developed as a result of continuing difficulties encountered with other mechanical means to measure pressure distributions over aerodynamic surfaces. The theories of luminescent barometry are described in detail in U.S. Patent 5,359,887 and U.S. Patent 5,151,603. Luminescent barometry is based on the phenomenon that some phosphorescent materials emit light at a unique wavelength and which is 'quenched' by the presence of particular molecules such as oxygen. This quenching effect can be quantified so that the phosphorescent material, provided in an oxygen permeable matrix, can be used to measure, for example, the partial pressure of oxygen passing over aerodynamic surfaces.

As a consequence of their considerable fabrication advantages, the use of polymeric materials for the construction of sensing devices using this quenching effect is an area of intense current interest. Luminescent sensors based on composites comprising transition metal phosphorescent dyes immobilized in polymer matrices have attracted attention as oxygen sensors for both biomedical and barometric applications. Conventional phosphorescent dyes such as Pt (platinum) octaethylporphyrin (OEP) derivatives or Ru^{II}

(ruthenium) bipyridyl (bipy) or phananthroline (Phen) derivatives with oxygen quenchable excited states have been dispersed in a silicone (otherwise known as polysiloxane) based polymer matrices due to their high gas permeability.

However, these conventional silicone-based polymer systems tend to be incompatible with the dyes and can lead to undesirable local concentrations and thus reduced sensitivity. Most PtOEP based systems in cross-linked silicone polymer matrices also have non-linear dependence on air pressure thereby making measurements less accurate.

Furthermore, conventional polysiloxane coatings tend to continue cross-linking as their temperature rises which causes irreversible changes in their phosphorescent properties as a result, making their data subject to error and generally unsuitable for measurements taken in fluctuating temperature conditions.

It is therefore an object of the present invention to provide a novel composition for a phosphorescent oxygen sensing coating.

SUMMARY OF THE INVENTION

Briefly stated, the invention involves a polymer material formed from a polymeric material having a backbone containing nitrogen and one or more of sulfur and phosphorous, the polymer material further comprising at least one side chain, wherein either the at least one side chain or the backbone bears a phosphorescent dye agent.

Preferably, the sulfur and phosphorus have side groups

selected from the group consisting of oxygen, a halogen, methyl, a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group.

Preferably, the polymer has a plurality of side chains at least one of the side chains bearing the phosphorescent dye agent. More particularly, the sulfur has a first side group including oxygen and a second side group, the phosphorous has first and second side groups, the first and second side groups on phosphorus and the second side group on sulfur being either NHBu^n or a group bearing the dye agent.

In another aspect, the invention involves a phosphorescent oxygen sensor comprising a substrate having a surface, a polymer material as defined hereinabove and applied to the surface to form a coating.

In still another of its aspects, the invention provides a polymer material formed from a phosphorescent dye agent contained in a polymeric material of formula A, wherein:

E1, E2 and E3 are the same or are different and are selected from sulfur or phosphorus;

R1 to R6 are the same or different and are selected from the group comprising oxygen, a halogen, hydrogen, methyl a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or

branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group, and wherein at least one of R1 to R6 is a group bearing a phosphorescent dye agent.

Preferably E1 is sulfur VI, while E2 and E3 are each phosphorus. Each of R2 to R6 includes an oxygen or a nitrogen substituent. More particularly, each of R3 to R6 includes an aryloxy group or an alkamine group, and each is selected from the group consisting of $NHBu^n$, OBu^n, OC_6H_4, $OC_6H_4CF_3$-m, $OCH_2CH=CH_2$ and $OC_6H_4CF_3$-p, and the group bearing the dye agent.

More preferably, R2 is a halogen, and more particularly R2 and R3 to R5 are the same and R6 is the group bearing the dye agent. Still more particularly, R2 and R3 to R5 are each $NHBu^n$ and the group bearing the dye agent includes a ruthenium substituent. Still more particularly, the group bearing the dye agent is Ru(4,7-diphenylphen)$_3$.

In one embodiment, the group bearing the dye agent includes a heterocyclic group selected from the group comprising a substituted C_{3-20} cycloalkyl group, a substituted C_{6-20} aryl group and a substituted or unsubstituted C_{6-20} aralkyl group.

In still another of its aspects, the invention provides a polymeric material of the formula B wherein:

E1, E2 and E3 are the same or are different and are selected from sulfur or phosphorus;

R1 to R6 are the same or different and are selected from the group comprising oxygen, a halogen, hydrogen, methyl a

substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group; and wherein at least one of R1 to R6 is a group bearing a phosphorescent dye agent.

R7 is selected from oxygen, nitrogen or from groups 15 and 16 of the periodic table of elements;

R8 is selected from the group comprising methyl, a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group.

In still another of its aspects, the invention provides a method of forming a copolymeric material of the formula B, comprising the steps of:

providing a first polymeric block of the formula A, wherein:

E1, E2 and E3 are the same or are different and are selected from sulfur or phosphorus;

R1 to R6 are the same or different and is selected from the group comprising oxygen, a halogen, hydrogen, methyl a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched

alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group; and wherein at least one of R1 to R6 is a group bearing a phosphorescent dye agent.

carrying out a ring opening polymerization of an unsaturated heterocyclic group having at least one electron rich site therein to form a copolymeric material of formula B wherein:

R7 is selected from oxygen, nitrogen or from groups 15 and 16 of the periodic table of elements;

R8 is selected from the group comprising methyl, a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group.

In yet another of its aspects, the present invention provides a coating composition comprising a polymer material, said polymer having a backbone and at least one side group with a phosphorescent dye agent as a constituent member of said backbone or said side group, said polymer being capable of being applied as a coating. Preferably, said polymer material is in a solvent mixture and the solvent mixture is homogeneous.

BRIEF DESCRIPTION OF THE DRAWINGS

Several preferred embodiments of the present invention will be provided, by way of example only, with reference to the appended drawings, wherein:

Figure A is a schematic diagram of a polymerization;

Figure 1 is a plot of a luminescence intensity ratio versus pressure ratio for one exemplified coating of the present invention;

Figure 2 is a PSP image of a wing model coated with the coating of figure 1; and

Figure 3 is a comparison of pressure distribution measurements.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Briefly stated, the invention involves a polymer material formed from a polymeric material having a backbone containing nitrogen and one or more of sulfur and phosphorous, the polymer material further comprising at least one side chain, wherein either the at least one side chain or the backbone bears a phosphorescent dye agent.

Preferably, the sulfur and phosphorus have side groups selected from the group consisting of oxygen, a halogen, methyl, a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group.

Preferably, the polymer has a plurality of side chains at least one of the side chains bearing the phosphorescent dye agent. More particularly, the sulfur has a first side group including oxygen and a second side group, the phosphorous has first and second side groups, the first and second side groups on phosphorus and the second side group on sulfur being either $NHBu^n$ or a group bearing the dye agent, as shown, for example, at 2a.

In another aspect, the invention involves a phosphorescent oxygen sensor comprising a substrate having a surface, a polymer material as defined above and applied to the surface to form a coating.

In still another of its aspects, the invention provides a polymer material formed from a phosphorescent dye agent contained in a polymeric material of formula A, wherein:

E1, E2 and E3 are the same or are different and are selected from sulfur or phosphorus;

R1 to R6 are the same or different and are selected from the group comprising oxygen, a halogen, hydrogen, methyl a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group, and wherein at least one of R1 to R6 is a group bearing a phosphorescent dye agent.

More particularly, the polymer material has a plurality of side chains at least one of the side chains bearing the

phosphorescent dye agent. The sulfur has a first side group including oxygen and a second side group, the phosphorous has first and second side groups, the first and second side groups on phosphorus and the second side group on sulfur being either $NHBu^n$ or a group bearing the dye agent.

At least one of the side groups on the phosphorous bears the dye agent and the other side groups of the phosphorous are the same as the second side group on the sulfur.

Preferably, the group bearing the dye agent includes a ruthenium substituent, more particularly a ruthenium phenanthroline complex.

The polymeric material A provides particular advantages as an ingredient in phosphorescent oxygen sensors and coatings therefor. The polymeric material A is polar, owing to the presence of electron rich sites in its backbone. The constituents making up formula A should be selected having regard to the oxygen environment in which the sensing is to take place and in particular the expected temperature ranges in which the sensor so formed is to be expected to be operable and this may be measured by the Glass Transition Temperature (T_g), and which may be considered as the boundary of the temperatures substantially above which there is sufficient permeability for gases such as oxygen.

Preferably, the sulfur and phosphorus have side groups selected from the group consisting of oxygen, a halogen, methyl, a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or

unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group.

The group bearing the dye agent includes a heterocyclic group selected from the group comprising a substituted C_{3-20} cycloalkyl group, a substituted C_{6-20} aryl group and a substituted or unsubstituted C_{6-20} aralkyl group.

Preferably, E1 is sulfur VI and R1 is oxygen, while each of E2 and E3 are phosphorus, providing a repeating PN segment in the backbone along with a relatively small terminating S=O segment. The S=O segment contributes an asymmetry to the backbone to discourage crystallization, which is sensitive to the regularity of the polymer chain. Moreover, the S=O segment contributes to an amorphous structure which is a contributing factor to the gas permeability of resulting polymers.

More preferably, each of R2 to R6 includes an oxygen or a nitrogen substituent and each of R2 to R6 may be provided in the form of an aryloxy group, an alkoxy group, arylamine group or an alkamine group and may include therein a phenyl group. In this case, the aryloxy and the arylamine tend to increase T_G due to the fact that these groups tend to be relatively more rigid. In contrast, the alkoxy and alkamine groups tend to be more flexible, contributing to a lower T_G and higher permeability. In each of the oxy and amine groups, polarity is increased by the presence of oxygen and nitrogen substitutents. These oxy and amine groups can be selected with increased polarity by providing for increasing numbers of polar substituents such as oxygen and nitrogen.

If desired, the permeability, T_G and polarity can be

tailored by the selection, or for that matter, a mixture of groups along the polymer depending on the contribution of each group.

In a preferred embodiment, E1 is sulfur and E2, E3 are each phosphorus. In a still further preferred embodiment, each of R2 to R5 are an arylamine group and R6 is a ruthenium phenanthroline complex, such as Ru(4,7-diphenylphen)$_3$. Synthesis of an exemplified version of this further preferred version of the polymeric material A is shown by the structures 1 to 3 and involves the thermal ring-opening polymerization of the cyclic monomer 1 followed by treatment of the halogenated polymeric material 2 with an excess of n-butylamine and is further described below.

The polymeric material 3 is a hydrolytically stable amorphous elastomeric material and possesses a Tg of -17°C giving it both relatively high free volume and gas permeability. The polymeric material can also be formed as a high quality film coating with dimensional stability without the need for cross-linking.

The intensity characteristics of a phosphorescent material are modeled by the Stern-Volmer equation which can be expressed as follows:

$I_{1.00}/I = A + B(P/P_{1.00})$, where

$I_{1.00}/I$= Luminescence Intensity Ratio (the 'LIR')

I = luminescence intensity,

$I_{1.00}$ = luminescence intensity at 1.00 atmosphere. (used as a reference;

P = air pressure in atmospheres;

A = Coefficient for vacuum condition;

B = Coefficient corresponding to gradient of curve, or rate of change of the Luminescence Intensity Ratio;

Compositions containing the polymeric material 3 together with phosphorescent dye agents show well-defined Stern-Volmer behaviour and significantly improved sensitivity.

Preferably, the dye agent includes a platinum or a ruthenium substituent. More preferably, the dye agent is selected from the group consisting of Pt octaethylpophyrin, Ru^{II} bipyridyl and Ru^{II} phenanthroline derivatives, though other known organic and inorganic dye agents are contemplated.

Compositions made according to the present invention have been shown to be usable on substrates such as stainless steel and alumina, though other substrates such as glass, plastics and metals are also contemplated.

In another aspect of the present invention, there is provided a copolymeric material of the formula B wherein

E1, E2 and E3 are the same or are different and are selected from sulfur or phosphorus;

R1 to R6 are the same or different and are selected from the group comprising oxygen, a halogen, hydrogen, methyl a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl

group; and wherein at least one of R1 to R6 is a group bearing a phosphorescent dye agent.

R7 is selected from oxygen, nitrogen or from groups 15 and 16 of the periodic table of elements;

R8 is selected from the group comprising methyl, a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group.

The copolymeric material of the formula B may be formed by first providing a first polymeric block of the formula A; and then carrying out a ring opening polymerization of an unsaturated heterocyclic group having at least one electron rich site therein.

Conveniently, the second polymeric block can be formed by a ring opening polymerization of a heterocyclic group in the presence of the first polymeric block, wherein the heterocyclic group is selected from the group comprising a substituted C_{3-20} cycloalkyl group, a substituted C_{6-20} aryl group and a substituted or unsubstituted C_{6-20} aralkyl group.

More preferably, the heterocyclic group is an unsaturated C_{3-5} cyclic group with the oxygen or nitrogen substituent therein. Still more preferably, the unsaturated heterocyclic group is tetrahydrofuran, ethylene oxide or propylene oxide.

Preferably, E1 is sulfur VI, while E2 and E3 are each

phosphorus and R7 is an electron rich site such as sulfur, oxygen, nitrogen or any one of groups 15 or 16 in the periodic table and provides the electron rich site by virtue of their lone pair of unpaired electrons. The electron rich site is thus able to form a stable electron bond with the electron deficient sulfur and thereby initiate the ring opening polymerization in the presence of the first polymer block.

Preferably, the sulfur in the first polymeric block is in the form of sulfur VI in view of the fact that sulfur in other forms such as sulfur IV may be unstable in some cases, such as for example polythiophosphazene. Further examples of unstable sulfur IV polymers may be found in I. Manners (COORDINATION CHEMISTRY REVIEWS, 137, 1994, 109-129).

The copolymeric material made according to the present invention provides improved integrity and one example of the copolymeric material is shown at 4. While the polymeric material 3 may provide the coating with a generally tacky consistency, the copolymeric material 4 may be used to form a layer of material capable of withstanding its own weight. In other words, the copolymeric material is envisaged in uses beyond mere coatings but perhaps in the formation or fabrication of devices with an inherent phosphorescent oxygen sensing capability.

Nonetheless, it is also contemplated herein to form a polysiloxane polymer with a phosphorescent dye agent as described herein as a constituent member of the polymer matrix.

A sample formed from polymeric material 3 or copolymeric material 4 with a T_G of -17 °C will typically allow the sample

to be used in environments whose temperatures will substantially exceed -17 °C, that is where the sample will allow for the permeation of oxygen and hence allow for the subsequent quenching of luminescence.

The present invention provides a coating which provides superior characteristics over those currently available. Like their polysiloxane counterparts, the present coatings based on the polymeric material A or the copolymeric material B present phosphorescent properties that change with temperature. However, due to the lack of cross linking in the matrix, the repeatability of the data presented by coatings based on the polymeric material 3 or the copolymeric material 4 is substantially improved over their polysiloxane counterparts.

The present coatings forms improved films which with faster drying times and without supplemental curing which is necessary for polysiloxane polymers. The present coatings have improved mechanical integrity and are believed to have substantially no long term flow (creep) on the surface.

Tables 1 to 4 are provided to illustrate a selection of possible groups for R1 to R6 in the polymeric material of the formula A . These tables are obtained from several published papers, namely I. Manners (COORDINATION CHEMISTRY REVIEWS, 137, 1994, 109-129) and Y. Ni et al (MACROMOLECULES 1992, 27, 7119). It is worth noting that a number of R groups have T_g in the region of -18°C to 25°C and these may be considered desirable R groups for some applications.

Further details of the formation of copolymeric material 4 can be seen in figure A and is believed to be representative of one method of forming in general the copolymeric materials

of formula B. In this case, the sulfur VI cation from poly(thionylphosphazene) attacks an oxygen site on a THF molecule to form an oxonium ion. Further reaction of this oxonium ion with more monomer generates a poly(THF) block.

In yet another of its aspects, the present invention provides a coating composition comprising a polymer material, the polymer having a backbone and at least one side group with a phosphorescent dye agent as a constituent member of the backbone or the side group, the polymer being capable of being applied as a coating. Preferably, the polymer material is in a solvent mixture and the solvent mixture is homogeneous.

In yet another of its aspects, the present invention provides a phosphorescent dye agent, comprising a phenanthroline complex which is reactive to form a polymer with the dye agent as a constituent thereof. Preferably, the complex is a ruthenium phenanthroline complex.

In still another of its aspects, the present invention provides a polymer material comprising the phosphorescent dye agent as defined above as a constituent thereof.

In still another of its aspects, the present invention provides a method of forming a phosphorescent dye agent, comprising the steps of:

providing a phenanthroline complex with a dye agent as a constituent thereof; and

forming a reactive site on the complex which is reactive to form a polymer.

Preferably, the complex is a ruthenium phenanthroline complex.

In yet another of its aspects, the present invention provides a method of forming a phosphorescent polymer material, comprising the steps of:

providing a phenanthroline complex with a dye agent as a constituent thereof;

forming a reactive site on the complex; and

reacting the complex with a monomer to form a polymer.

Thus, the materials as described above provide for the use of poly(thionylphosphazenes) as shown at 3 which contain the phosphorescent dye agent as part of the polymer structure. The materials described herein provide increased loading of the dye agent which allows higher intrinsic intensity of phosphorescence making observation of light emission from the coatings easier. The materials herein also provide improved compatibility between the dye agent and the polymer matrix which leads to more predictable Stern-Volmer behaviour. The fact that the dye agent loading also raises the potential use of thinner films which would thus allow more rapid response. This would permit measurements in such applications as fluctuating pressure systems.

Embodiments of the present invention will be described with reference to the following examples which are presented for illustrative purposes only and are not intended to limit the scope of the invention.

EXAMPLE: SYNTHESIS OF A DYE-BOUND POLYMER

5-amino-1,10-phenanthroline:

To a solution of 5-nitro-1,10 phenanthroline (1.00g) in ethanol (40 ml) with Pd/C (0.40 g) were added sodium borohydride (2.00 g) in several portions over 2 hours. The resulting solution was kept stirring for 12 hours under N_2. The solution was filtered and the filtrate was concentrated. Then ether was added to the filtrate to crystallize the product (0.33 g, yield: 38%).

4-aminomethyl-1,10-phenanthroline:

This synthesis was accomplished in 3 steps from 4-methyl-1,10-phenanthroline.

1,10-phenanthroline-4-carboaldehyde: SeO_2 (1.22 g, 99%) was dissolved in 20 ml refluxing dioxane/water (v/v, 94:4). 4-methyl-1,10-phenanthroline (1.00 g) in 80 ml dioxane/water (v/v, 94:4) was added drop wise over 1 hour. Refluxing was continued for 2 hours under N_2. The resulting solution was filtered through celite when hot. The product (1.00 g, containing selenium residues) crystallized as yellow solids and were used without further purification.

1,10-phenanthroline-4-carboaldoxime: A solution of the 1,10-phenanthroline-4-carboaldehyde product (1.00 g), hydroxyamine hydrochloride (2.00 g) and pyridine (4 ml) in ethanol (60 ml) was heated under reflux for 12 hours under N_2. The resulting grey solids were separated from the ethanol solution. The grey solids were recrystallized in hot ethanol. The product was dried in vacuo (0.65 g, yield: 61%).

4-aminomethyl-1,10-phenanthroline: A suspension solution of 1,10-phenanthroline-4-carboaldoxime (0.5 g) in 100 ml ethanol containing 2% perchloric acid was hydrogenated at atmospheric pressure, over 10% Pd/C (150 mg) for 12 hours and then was refluxed for 2 hours. The solution was filtered and the filtrate was concentrated. Ether was added to the filtrate to crystallize the product (0.44 g, 97%).

Synthesis of Ru Dyes Functionalized with Amino Groups

Cis-Dichlorobis (4,7-diphenyl-1,10-phenanthroline)ruthenium: Ruthenium trichloride (2.0 g), 4,7-diphenyl-1,10-phenanthroline (5.8 g), lithium chloride (2.2 g) were heated at reflux in 30 ml of DMF for 3 hours. The solution was then added with 80 ml of acetone and stored at 0°C overnight. Purple solids were collected by suction filtration and washed by water. The crude products were stirred in the cold acetone for 3 hours and filtered. The product suspended in water (100 ml) was heated under reflux for 2 hours and treated with lithium chloride (5.0 g). The purple solids precipitated from the cold solution and were filtered and dried in vacuo (2.5 g).

$Ru[4,7\text{-diphenyl-1,10-phenanthroline})_2(L)][ClO_4]_2$ (L=5-amino-1,10-phenanthroline or 4-aminomethyl-1,10-phenanthroline):

$Ru(4,7\text{-diphenyl-1,10-phenanthroline})_2Cl_2$ (200 mg) and 60 mg of L were heated under reflux in 200 ml ethanol/water (v/v 70:30) for 18 hours under N_2. The resulting solution was treated with $LiClO_4$ (4.0 g). Red orange solids were collected by filtration and washed by water, hexane and ether (200 g, yield: 90%).

Synthesis of Dye Bound Polymer:

A CH_2Cl_2 solution of Ru[4,7-diphenyl-1,10-phenanthroline)$_2$(L)]$_2$ (L=5-amino-1,10-phenanthroline or 4-aminomethyl-1,10-phenanthroline) (1.0 mg) was added to poly(pentachlorothionylphosphazene) (200 mg) in CH_2Cl_2 solution while being stirred at room temperature. After 4 hours, the mixture was cooled to 0°C and excess n-$BuNH_2$ (10 equiv.) was added into the mixture and was stirred for overnight. After this reaction finished, the polymer was precipitated in water (three times) and then precipitated in water methanol (three times). Characterization was achieved by 1H NMR and 31P NMR. Films were spray coated from organic solvents such as CH_2Cl_2 or 1,2-dichloroethane.

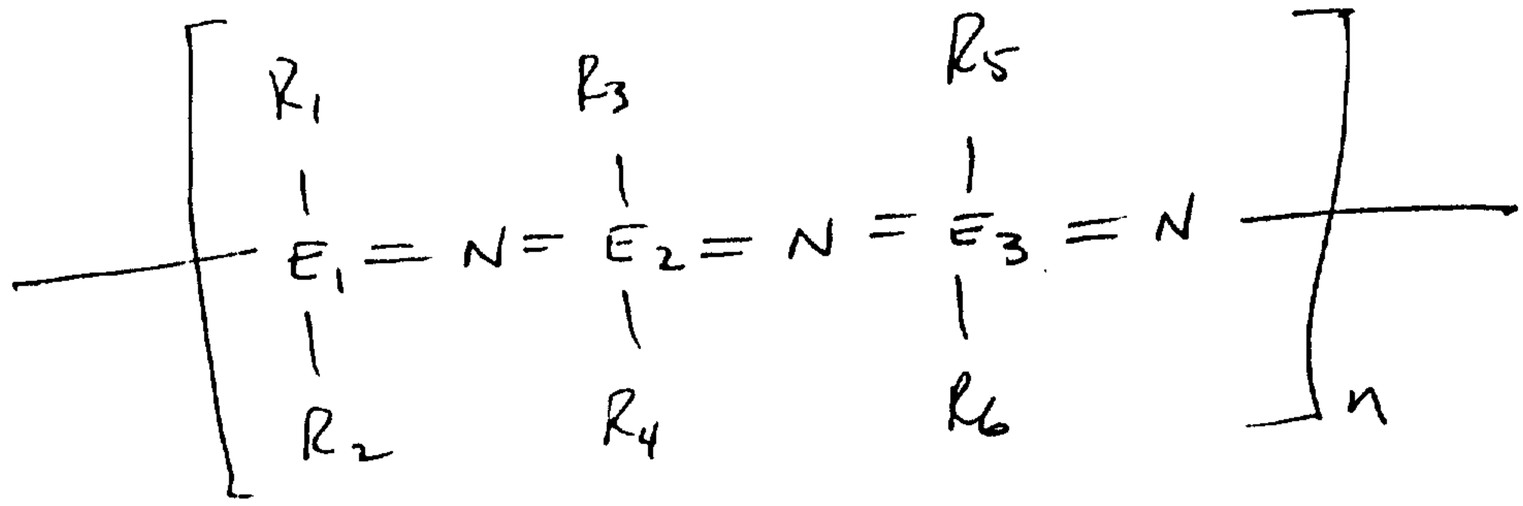
ANALYSIS

Samples were placed in a pressure chamber which was equipped with a viewing window to permit in-situ pressure measurements. The pressure chamber was equipped with an adjustable pressure supply of compressed air. All the measurements were made at room temperature (22 ± 1°C).

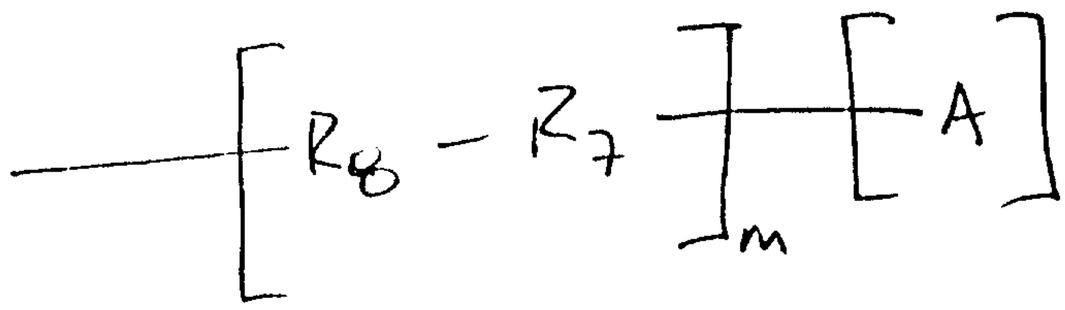
An imaging system was used to detect changes in luminescence intensity as a function of pressures. A 75 Watt tungsten Halogen lamp was used as a light source with a 40 nm band pass filter centred at 450 nm to obtain the blue light. A cut-off filter, corresponding to OG 590 nm for the Ruthenium dye-bound polymer, was placed in front of a liquid nitrogen cooled CCD detector (MODEL LN/CCD, PRINCETON INSTRUMENTS, INC.) with 578 x 384 pixels in a cell size of 13.25 X 8.83 mm^2. Luminescent light from the sample surface was collected with a camera lens (NIKON, 55mm, 1:1.2) and imaged onto the

CCD detector. The pressure of the sample chamber was measured by a pressure gauge (MODEL FA233, WALLACE AND TIERNAN) with an accuracy of ± 0.1 psi. The results are shown in figure 1, as a plot of a luminescence intensity ratio versus pressure ratio, showing a substantially linear relationship therebetween.

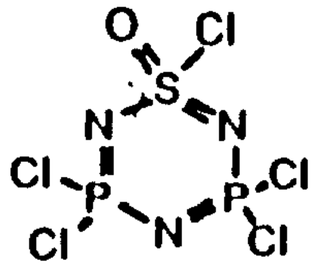
A scale wing model was also coated with the dye-bound polymer as discussed hereinabove and was positioned in a 5X5 foot wind tunnel and subjected to wind speeds of Mach 0.8. Two images were taken in order to calculate the pressure distribution over the model surface. One image (hereinafter referred to as the 'wind-on' image) was taken when the wind speed was Mach 0.8 where the pressure distribution on the model is unknown. The other image (hereinafter referred to as the 'wind-off' image) was taken when the wind was off so that the pressure distribution on the model was a constant of 1 atm. The wind-off image was divided by the wind-on image and the resulting image was shown in figure 2, which presents a complete static pressure mapping. Figure 2 also demonstrates, for example, the transition from relatively low pressure present at the leading edge of the wing (as shown by the dark colour) to a relatively high pressure at the trailing edge of the wing, as would be expected. Figure 3 is a comparison of pressure distribution measurements on a wing model at Mach 0.8. The solid circles are pressure tap measurements and the solid line is a pressure sensitive paint measurement.



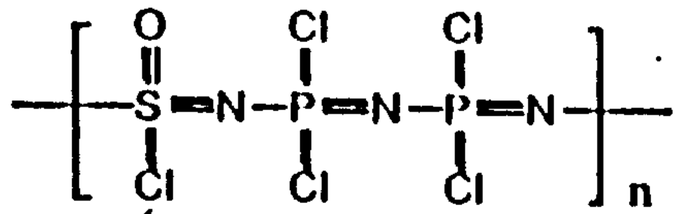
A



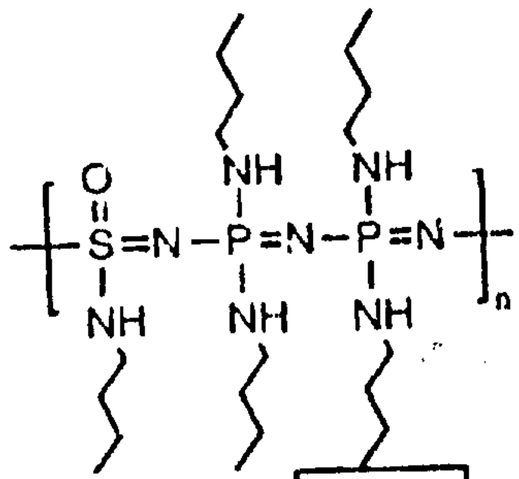
B.



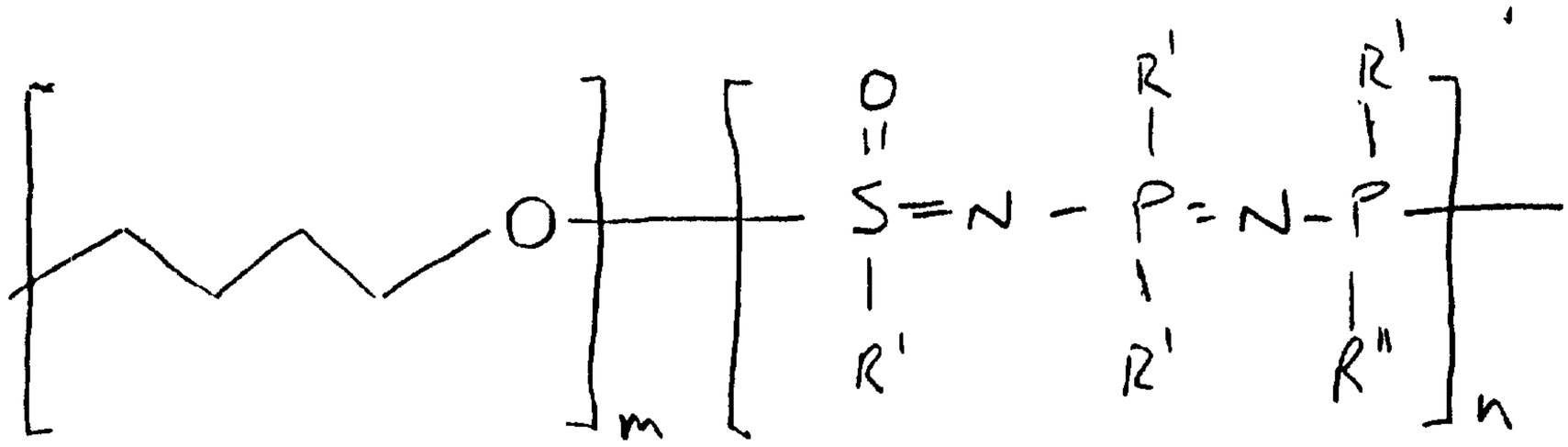
(1)



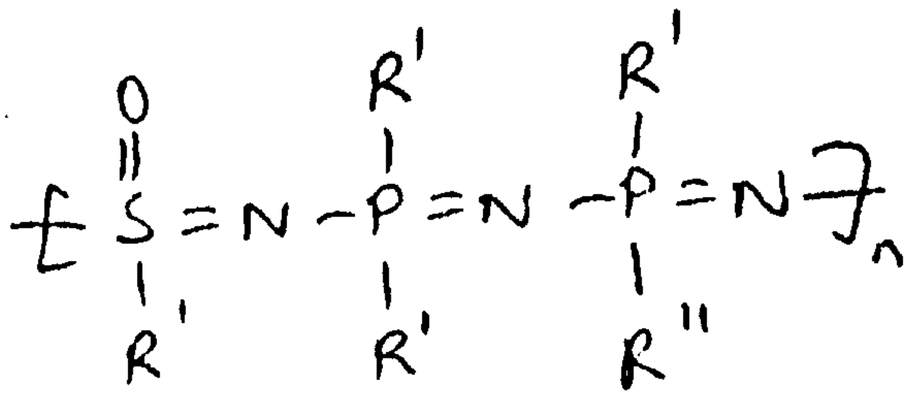
(2)



2a)



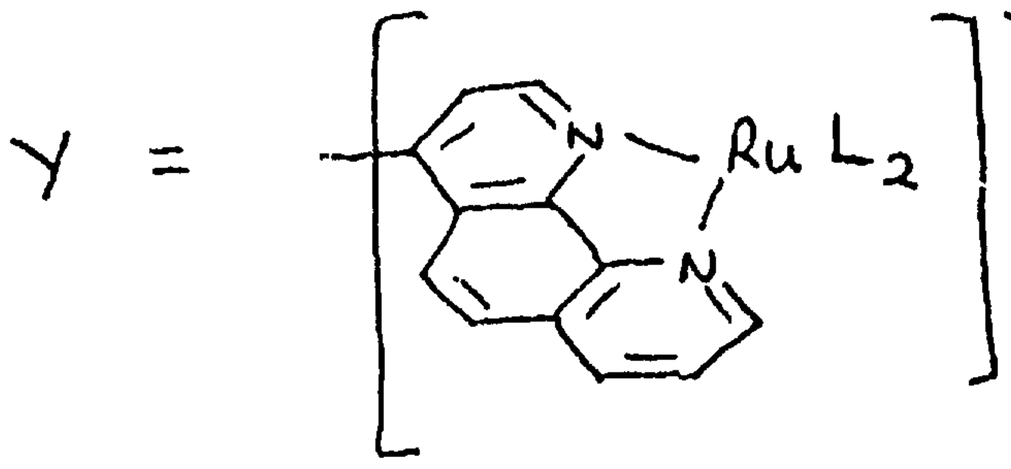
(4)

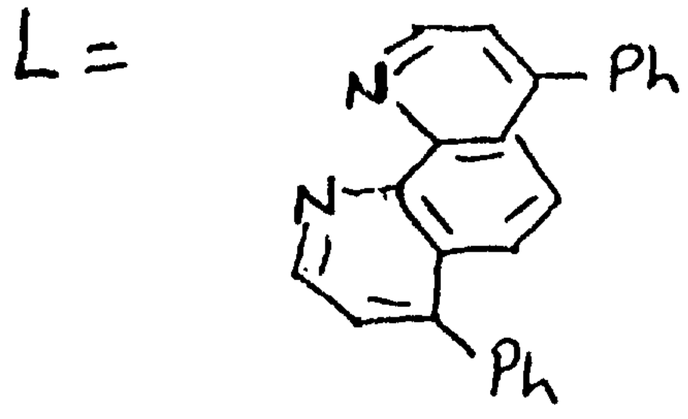


(3)

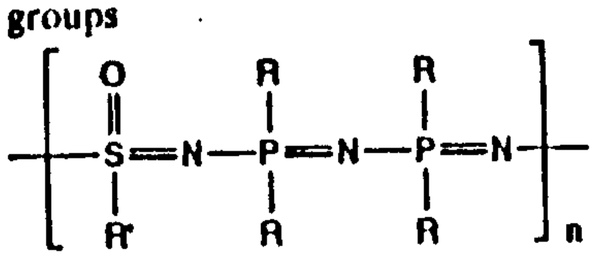
R^1 = NHBu

R^{II} = NH $CH_2CH_2CH_2CH_2OCH_2$— Y





Selected characterization data for poly(thionylphosphazenes) and halogen or aryloxy side groups

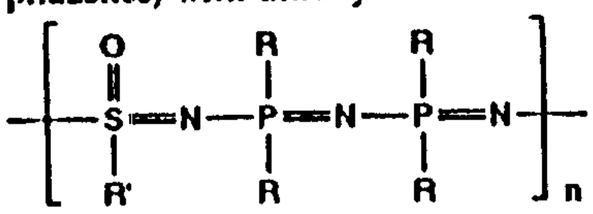


Structure	R'	R	GPC[a] $\bar{M}_w$	GPC[a] $\bar{M}_n$	^{31}P NMR[b] (ppm)	T_g (°C)
16	Cl	Cl	—	—	−10.0[c]	−46
18	F	Cl	—	—	−8.6[c]	−56
19	Cl	OPh	5.8×10^4	4.0×10^4	−21.5	10
19	Cl	OC_6H_4Ph-*p*	1.4×10^5	5.1×10^4	−20.9	55,
19	Cl	$OC_6H_4CMe_2Ph$-*p*	1.1×10^5	6.3×10^4	−21.0	43
19	Cl	$OC_6H_4Bu^t$*p*	4.3×10^4	3.7×10^4	−21.0	42
19	Cl	$OC_6H_4CF_3$-*m*	1.8×10^5	1.5×10^5	−21.0	−25
19	Cl	$OC_6H_4CF_3$-*p*	7.4×10^4	5.5×10^4	−21.5	18
20	F	OPh	3.8×10^4	2.5×10^4	−20.3	−15
20	F	OC_6H_4Ph-*p*	9.0×10^4	5.8×10^4	−19.5	48

[a] in THF using polystyrene standards; [b] in THF; in CH_2Cl_2.

Table 1

Selected characterization data for poly[(amino)thionylphosphazenes] and poly(thionylphosphazenes) with alkoxy substituents



Polymer	R'	R	GPC[a] $\bar{M}_w$	GPC[a] $\bar{M}_n$	^{31}P NMR[b] (ppm)	T_g (°C)
21	10% Cl 90% NHMe	NHMe	—	—	5.0 (br)	—
21	50% Cl 50% NHBu^n	NHBu^n	1.4×10^5	6.7×10^4	2.1, 2.4	−17
21	50% Cl 50% $NHCH_2CH{=}CH_2$	$NHCH_2CH{=}CH_2$	7.1×10^4	2.9×10^4	0.1, 0.2	−40
21	20% Cl 80% NHC_6H_5	NHC_6H_5	1.3×10^5	7.4×10^4	−18.6	101
23	Cl	40% OCH_2CF_3 60% OC_6H_4Ph-*p*	1.2×10^5	7.7×10^4	−14 (br), −17 (br), −21	25
23	Cl	25% OBu^n 75% $OC_6H_4CF_3$-*m*	1.3×10^5	9.5×10^4	−19.7 (br), −21.6	−14
23	Cl	25% $OCH_2CH{=}CH_2$ 75% $OC_6H_4CF_3$-*m*	7.9×10^4	4.6×10^4	−19.0 (br), −19.5 (br), −21.5	−18

[a] In THF using polystyrene standards; [b] in THF.

Table 2

Scheme I



1

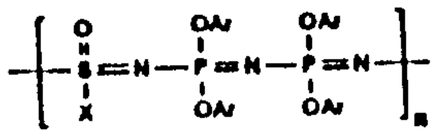
1a: X = Cl
1b: X = F

1a: 165°C
1b: 180°C

2

2a: X = Cl
2b: X = F

Na[OAr]



3a - 6a: X = Cl
3b, 4b: X = F

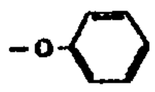
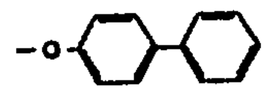
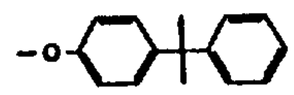
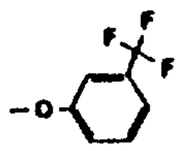
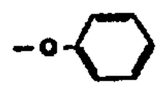
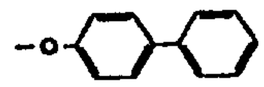
	X	OAr
3a	Cl	
4a	Cl	
5a	Cl	
6a	Cl	
3b	F	
4b	F	

Table 3

Analytical and Glass Transition Data for Polymers 2a–6a and 2b–4b

polymers	GPC M_w, M_n	elem anal. calc/found		T_g, °C
2a				−46
2b				−56
3a	5.8×10^4, 4.0×10^4	C	51.48/51.70	10
		H	3.60/3.61	
		N	7.50/7.46	
		Cl	6.33/5.68	
4a	1.4×10^5, 5.1×10^4	C	66.70/66.38	55
		H	4.20/4.28	
		N	4.86/4.80	
		Cl	4.10/3.78	
5a	1.1×10^5, 6.3×10^4	C	69.80/67.47	43
		H	5.86/4.79	
		N	4.07/3.56	
		Cl	3.43/3.78	
6a	1.8×10^5, 1.5×10^5	C	40.43/40.26	−25
		H	1.94/2.03	
		N	5.05/5.00	
		Cl	4.26/5.09	
3b	3.8×10^4, 2.5×10^4	C	53.04/52.77	−15
		H	3.70/3.77	
		N	7.73/7.66	
		F	3.49/3.49	
4b	9.0×10^4, 5.8×10^4	C	68.00/67.40	48
		H	3.81/4.48	
		N	4.96/4.99	

Table 4

CLAIMS

1. A polymer material formed from a polymeric material having a backbone containing nitrogen and one or more of sulfur and phosphorous, said polymer material further comprising at least one side chain, wherein either said at least one side chain or said backbone bears a phosphorescent dye agent.

2. A polymer material as defined in claim 1 wherein said sulfur and phosphorus have side groups selected from the group consisting of oxygen, a halogen, methyl, a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group.

3. A polymer material as defined in claim 2 having a plurality of side chains at least one of said side chains bearing said phosphorescent dye agent.

4. A polymer material as defined in claim 3 wherein said sulfur has a first side group including oxygen.

5. A polymer material as defined in claim 4 wherein said sulfur has a second side group, said phosphorous has first and second side groups, the first and second side groups on phosphorus and the second side group on sulfur being either $NHBu^n$ or a group bearing said dye agent.

6. A polymer material as defined in claim 5 wherein at least one of the side groups on said phosphorous bears said dye agent.

7. A polymer material as defined in claim 6 wherein one of the side groups on said phosphorous bears said dye agent and the other side groups of said phosphor are the same as the second side group on said sulfur.

8. A polymer material as defined in claim 7 wherein said group bearing said dye agent includes a ruthenium substituent.

9. A polymer materials as defined in claim 8 wherein the group bearing said dye agent comprises a ruthenium phenanthroline complex.

10. A polymer material as defined in claim 8 wherein the group bearing said dye agent includes a heterocyclic group selected from the group comprising a substituted C_{3-20} cycloalkyl group, a substituted C_{6-20} aryl group and a substituted or unsubstituted C_{6-20} aralkyl group.

11. A phosphorescent oxygen sensor comprising a substrate having a surface, a polymer material as defined in claim 1 applied to said surface to form a coating.

12. A polymer material formed from a phosphorescent dye contained in a polymeric material of formula A, wherein:

E1, E2 and E3 are the same or are different and are selected from sulfur or phosphorus;

R1 to R6 are the same or different and are selected from the group comprising oxygen, a halogen, hydrogen, methyl a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or

branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group, and wherein at least one of R1 to R6 is a group bearing a phosphorescent dye agent.

13. A polymer material as defined in claim 12 wherein E1 is sulfur VI.

14. A polymer material as defined in claim 13 wherein E2 and E3 are each phosphorus.

15. A polymer material as defined in claim 14 wherein each of R2 to R6 includes an oxygen or a nitrogen substituent.

16. A polymer material as defined in claim 15 wherein each of R3 to R6 includes an aryloxy group or an alkamine group.

17. A polymer material as defined in claim 16 wherein R3 to R6 are each selected from the group consisting of $NHBu^n$, OBu^n, OC_6H_4, $OC_6H_4CF_3$-m, $OCH_2CH=CH_2$ and $OC_6H_4CF_3$-p, and the group bearing said dye agent.

18. A polymer material as defined in claim 17 wherein R2 is a halogen.

19. A polymer material as defined in claim 18 wherein R2 and R3 to R5 are the same and R6 is the group bearing said dye agent.

20. A polymer material as defined in claim 19 wherein R2 and R3 to R5 are each $NHBu^n$.

21. A polymer material as defined in claim 20 wherein said

group bearing said dye agent includes a ruthenium substituent.

22. A polymer materials as defined in claim 21 wherein the group bearing said dye agent is Ru(4,7-diphenylphen)$_3$

23. A polymer material as defined in claim 21 wherein the group bearing said dye agent includes a heterocyclic group selected from the group comprising a substituted C_{3-20} cycloalkyl group, a substituted C_{6-20} aryl group and a substituted or unsubstituted C_{6-20} aralkyl group.

24. A copolymeric material of the formula B wherein

E1, E2 and E3 are the same or are different and are selected from sulfur or phosphorus;

R1 to R6 are the same or different and are selected from the group comprising oxygen, a halogen, hydrogen, methyl a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group; and wherein at least one of R1 to R6 is a group bearing a phosphorescent dye agent.

R7 is selected from oxygen, nitrogen or from groups 15 and 16 of the periodic table of elements;

R8 is selected from the group comprising methyl, a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or

branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group.

25. A copolymeric material as defined in claim 24 wherein E1 is sulfur VI and R1 is oxygen.

26. A copolymeric material as defined in claim 25 wherein E2 and E3 are each phosphorus.

27. A copolymeric material as defined in claim 26 wherein R7 is oxygen, nitrogen or sulfur.

28. A copolymeric material as defined in claim 27 wherein R3 to R6 are each selected from the group consisting of $NHBu^n$, OBu^n, OC_6H_4, $OC_6H_4CF_3$-m, $OCH_2CH=CH_2$ and $OC_6H_4CF_3$-p, and the group bearing said dye agent.

29. A polymeric material as defined in claim 28 wherein R2 is a halogen.

30. A polymeric material as defined in claim 29 wherein R2 and R3 to R5 are the same and R6 is the group bearing said dye agent.

31. A polymeric material as defined in claim 30 wherein R2 and R3 to R5 are each $NHBu^n$.

32. A polymer material as defined in claim 31 wherein said group bearing said dye agent includes a ruthenium substituent.

33. A polymer materials as defined in claim 32 wherein the group bearing said dye agent is Ru(4,7-diphenylphen)$_3$

34. A polymer material as defined in claim 32 wherein the group bearing said dye agent includes a heterocyclic group selected from the group comprising a substituted C_{3-20} cycloalkyl group, a substituted C_{6-20} aryl group and a substituted or unsubstituted C_{6-20} aralkyl group.

35. A method of forming a copolymeric material of the formula B, comprising the steps of:

providing a first polymeric block of the formula A, wherein:

E1, E2 and E3 are the same or are different and are selected from sulfur or phosphorus;

R1 to R6 are the same or different and is selected from the group comprising oxygen, a halogen, hydrogen, methyl a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group; and wherein at least one of R1 to R6 is a group bearing a phosphorescent dye agent.

carrying out a ring opening polymerization of an unsaturated heterocyclic group having at least one electron rich site therein to form a copolymeric material of formula B wherein:

R7 is selected from oxygen, nitrogen or from groups 15 and 16 of the periodic table of elements;

R8 is selected from the group comprising methyl, a substituted or unsubstituted C_{2-20} linear or branched alkyl group, a substituted or unsubstituted C_{2-20} linear or branched alkenyl group, a substituted or unsubstituted C_{2-20} linear or branched alkynyl group, a substituted or unsubstituted C_{6-20} aryl group, a substituted or unsubstituted C_{3-20} cycloalkyl group;

36. A method as defined in claim 35 wherein said ring opening polymerization step is carried out in the presence of said first polymeric block.

37. A method as defined in claim 36 wherein said unsaturated heterocyclic group is in the form of an unsaturated C_{3-5} cyclic group with an oxygen or nitrogen substituent therein.

38. A method as defined in claim 37 wherein said unsaturated heterocyclic group is tetrahydrofuran, ethylene oxide or propylene oxide.

39. A phosphorescent dye agent, comprising a phenanthroline complex which is reactive to form a polymer with said dye agent as a constituent thereof.

40. A dye agent as defined in claim 39 wherein said complex is a ruthenium phenanthroline complex.

41. A polymer material comprising the phosphorescent dye agent of claim 39 as a constituent thereof.

42. A coating composition comprising a polymer material, said polymer having a backbone and at least one side group with a phosphorescent dye agent as a constituent member of said

backbone or said side group, said polymer being capable of being applied as a coating.

43. A coating composition as defined in claim 42 wherein said polymer material is in a solvent mixture.

44. A coating composition as defined in claim 43 wherein said solvent mixture is homogeneous.

45. A method of forming a phosphorescent dye agent, comprising the steps of:

providing a phenanthroline complex with a dye agent as a constituent thereof; and

forming a reactive site on said complex which is reactive to form a polymer.

46. A method as defined in claim 45 wherein said complex is a ruthenium phenanthroline complex.

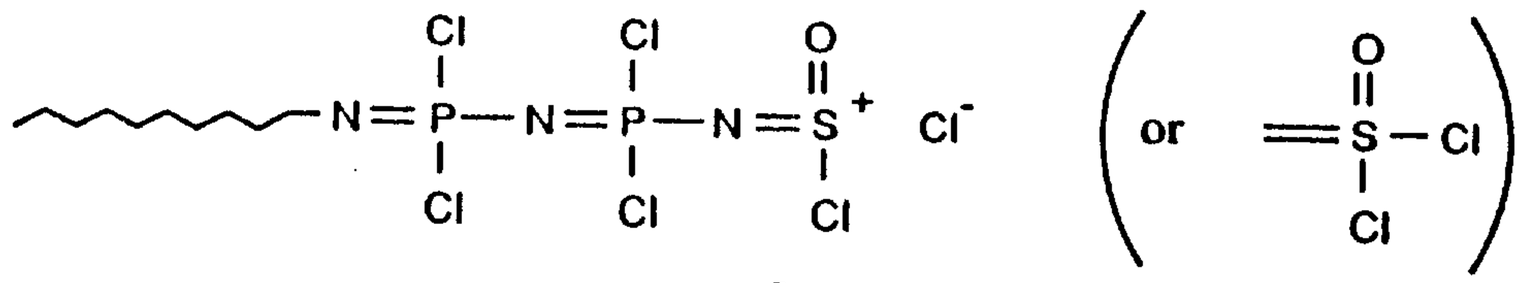
47. A method of forming a phosphorescent polymer material, comprising the steps of:

providing a phenanthroline complex with a dye agent as a constituent thereof;

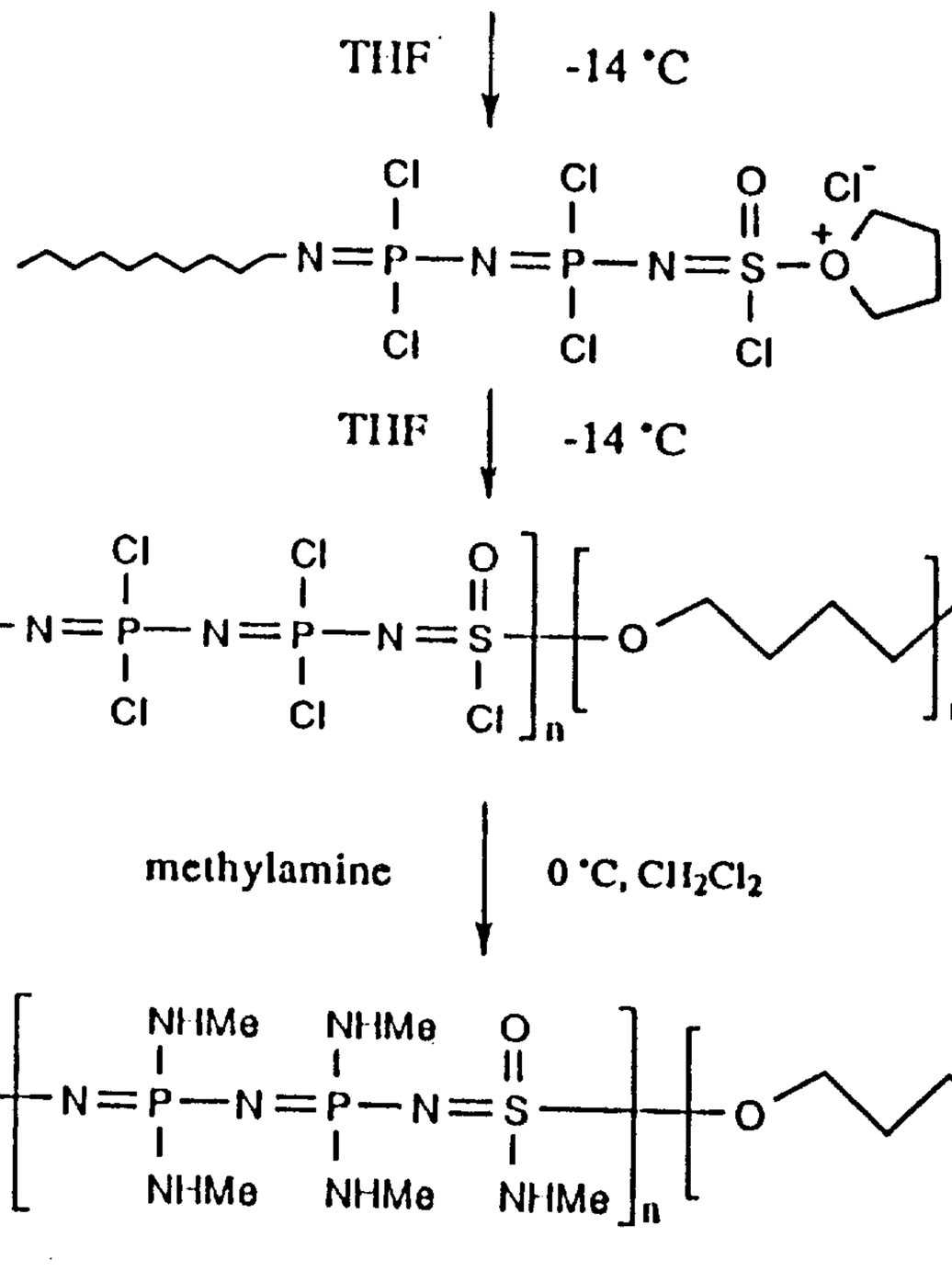
forming a reactive site on said complex; and

reacting said complex with a monomer to form a polymer.

48. A method as defined in claim 47 wherein said complex is a ruthenium phenanthroline complex.



2a



Synthesis of Poly[(methylamino)thionylphosphazene]-b-Poly(tetrahydrofuran) Block Copolymer

Fig A

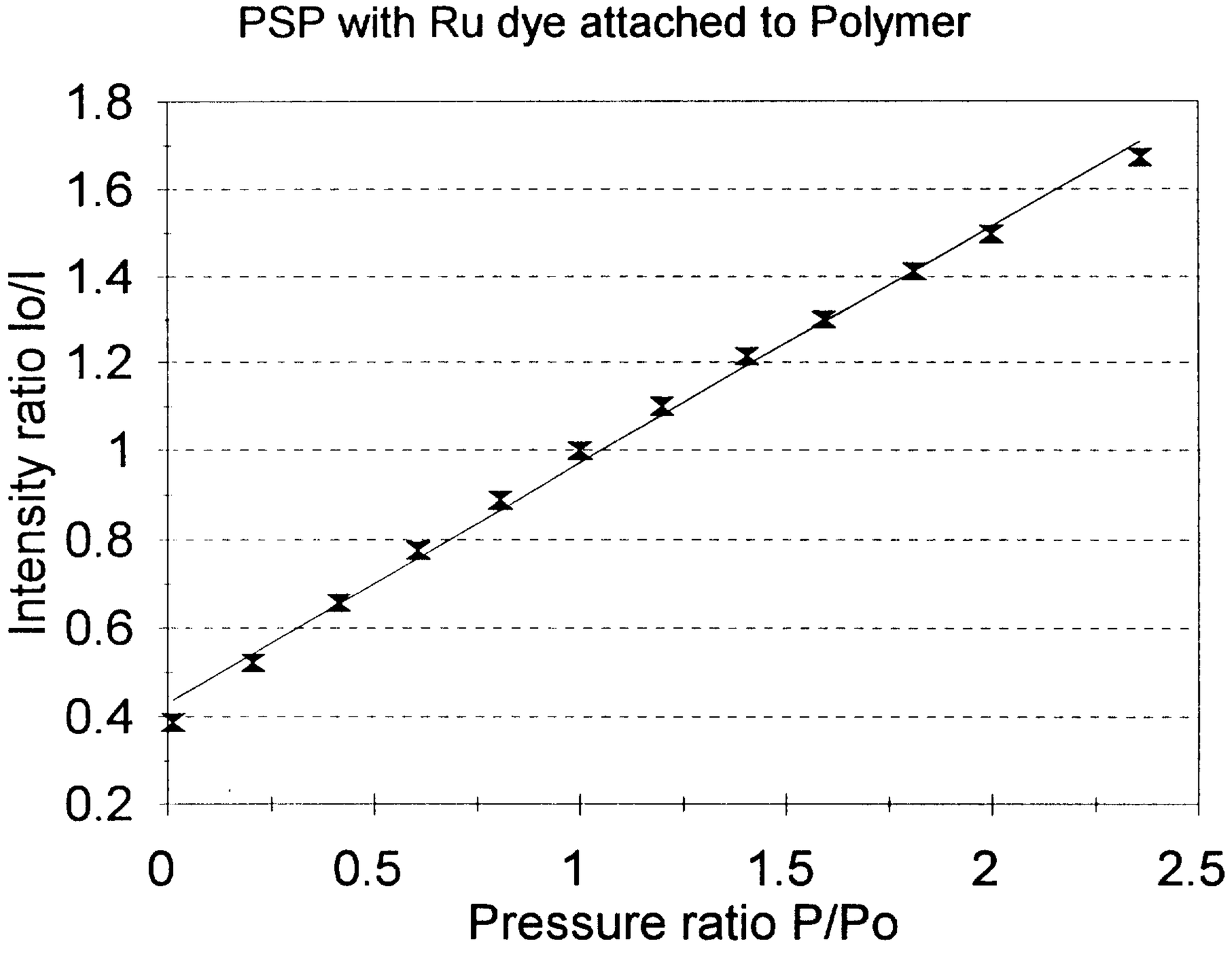

PSP with Ru dye attached to Polymer
Intensity ratio Io/I
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.5
1
1.5
2
2.5
Pressure ratio P/Po

Fig. 1

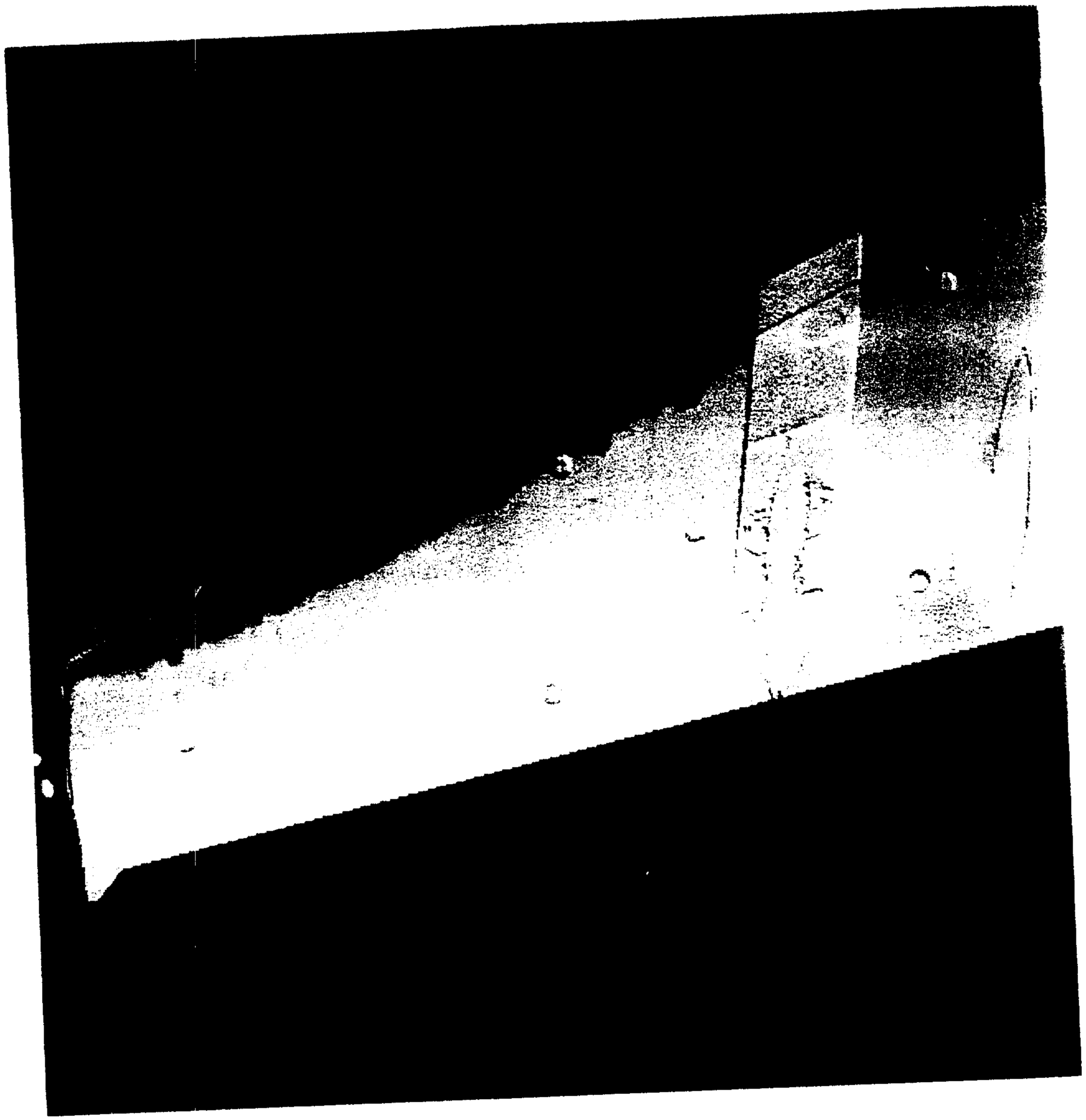


Fig. 2

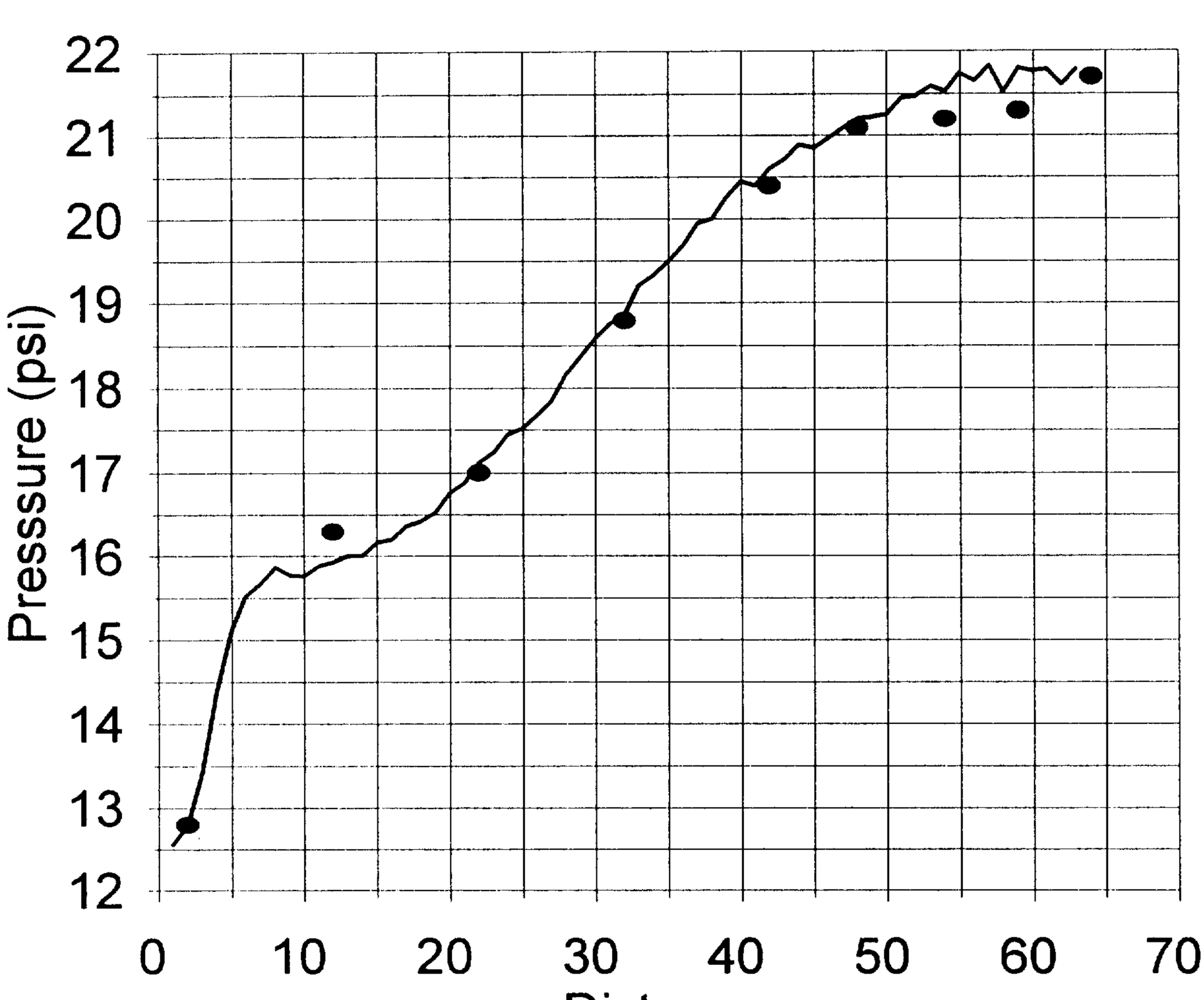

Pressure (psi)
22
21
20
19
18
17
16
15
14
13
12
0
10
20
30
40
50
60
70
Distance

Fig. 3.