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J. Colloid Interface Sci., 144(1), 27-35, (1991)

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(54) Abstract Title

Polymer coatings for metal oxides

(57) Thiophene in the liquid phase is polymerised by being held in contact with a film or substrate of ferric oxide. Other monomers which undergo oxidative polymerisation may be used, and other oxide films may be substituted for ferric oxide provided their redox potential is sufficiently positive to cause polymerisation of said monomer. The oxide film may be on a substrate of the related metal, i.e. iron or steel for ferric oxide. The polymer layer thus formed is useful for corrosion protection, and may be electrically conductive.

POLYMERISATION METHOD

The present invention relates to a method of polymerisation of a monomer, and provides a method for the preparation of thin polymer films on a substrate.

Japanese Patent Application No. 87-266714 (Toyota Jidosha KK) discloses the formation of a highly conductive polymer film on a copper sheet which has a solid peroxide layer formed thereon, by exposure to the vapour of a monomer capable of undergoing oxidative polymerisation, such as pyrrole, thiophene or aniline. The solid peroxide layer is produced by treatment with hydrogen peroxide, a dialkyl peroxide, or ozone, for example, and is not a conventional oxide. Thus, this method requires a separate oxidising agent to produce a surface layer or film, and the latter is neither copper nor a conventional copper oxide such as may normally occur on the surface of the sheet under atmospheric conditions.

In a presentation at the European Conference on Surface Science, Lille, France in September 1995, it was disclosed that the (0001) face of a crystal of ferric oxide, Fe_2O_3, catalyses the polymerisation of thiophene from the vapour phase to form a polythiophene film with a thickness of about 30 Å. This film is stable up to 720°C and survives atmospheric exposure. Thiophene is an example of a monomer which is known to be polymerisable by electrochemical or chemical oxidation, and is conveniently used as a "model" monomer for studying this type of polymerisation, and for predicting the properties of related monomers.

It has now been found that the oxide crystal can be replaced by a thin film of oxide, for example on the surface of the parent metal, and that polymerisation on the oxide film or substrate can occur from liquid monomer under conditions of temperature and pressure at or close to ambient. The latter aspect may be of considerable commercial interest, insofar as it considerably simplifies the production of these polymer films.

It is also believed that the oxides of other metals, such as cupric oxide CuO, will have a similar (catalytic) polymerising ability, provided the redox potential thereof is appropriately high for the monomer in question. Thus, the Cu^{2+} - Cu^{+} redox potential of 0.16eV has been found sufficient to polymerise thiophene in zeolite channels.

In a first aspect, the present invention provides a method of polymerising a monomer of the type capable of undergoing oxidative polymerisation, comprising the step of exposing said monomer in the liquid phase to a film or substrate formed of a metal oxide, said metal oxide having a redox potential sufficiently positive to cause polymerisation of said monomer.

Preferably, the metal oxide is selected from ferric oxide and cupric oxide. Thus in a particular form of the first aspect of the invention there is provided a method of polymerising a monomer of the type capable of undergoing oxidative polymerisation, comprising the step of exposing said monomer in the liquid phase to a film or substrate formed of ferric oxide.

In a preferred method, the metal oxide is in the form of a film on a substrate of different material.

In a second aspect, the invention provides a method of polymerising a monomer of the type capable of undergoing oxidative polymerisation, comprising the step of exposing said monomer to a film of a metal oxide film on a substrate of a different material, said metal oxide having a redox potential sufficiently positive to cause polymerisation of said monomer. Preferably the monomer is in the liquid phase.

Preferably, again, the metal oxide of the film is selected from ferric oxide and cupric oxide. Thus in a particular form of the second aspect of the invention there is provided a method of polymerising a monomer of the type capable of undergoing oxidative polymerisation, comprising the step of exposing said monomer in the liquid phase to a film of ferric oxide on a substrate of a different material.

A substrate, where required or provided, is preferably of the metal of the metal oxide film.

Monomers for use in the first or second aspects may be selected from thiophene and derivatives thereof, but the invention is not limited thereto. For example, it is believed that pyrrole and derivatives thereof, and other materials such as aniline and derivatives thereof could be used.

The formation of the polymer can be performed in the region of ambient temperature and pressure, for example at a temperature of between -10°C and +20°C, and at substantially atmospheric pressure. Naturally, where necessary, these conditions could be varied to ensure that the monomer is in the liquid phase for ease of handling.

The invention will now be described more particularly with reference to an embodiment thereof, and with reference to the prior art as presented at the Lille conference mentioned above.

<u>Prior art</u> An α-Fe_2O_3 crystal was cut and polished to within 0.5° of the (0001) plane as determined by Laue diffraction, cleaned by cycles of Ar bombardment, and annealed at about 1150°K in 10^{-4} mbar O_2 to produce a nominally stoichiometric, clean and ordered α-Fe_2O_3 surface as determined by low energy electron diffraction and Auger spectroscopy. Thiophene was dosed from the vapour above the room-temperature liquid, following several freeze-pump-thaw cycles to remove dissolved gases. The crystal at -120°K was exposed to thiophene vapour at low pressure to form a multilayer thereon.

Evidence that the thiophene formed a polymeric layer on annealing towards room temperature is threefold:

(a) The deposited multilayer was observed to remain as a film of average thickness 30±10Å after annealing to 720°K as calculated from the Fe 2p and S 2p XPS peak areas indicating formation of a surface species of increased thermal stability, in line with the properties of polythiophene.

(b) NEXAFS and XPS spectroscopic data of the thermally annealed film fingerprint polythiophene formation. Features include shifts and absolute binding energies previously observed in experiments examining the difference between monomers, oligomers and polymers of thiophene. An absence of features at less than 284 and 162 eV binding energy in the C 1s and S 2p spectra of the annealed films respectively indicates that the thiophene rings remain intact and do not decompose, and the S/C stoichiometry as determined from the XPS peak areas remains at 0.26, very close to the value expected for thiophene and its polymer. Figures 1(a) and 1(b) show that the thermally annealed layer has S 2p and C 1s XPS shifts of 0.6 eV and 0.2 eV less than the unreacted thiophene.

(c) Figure 2 shows normal and grazing incidence S K-edge NEXAFS spectra of multilayer thiophene and films thereof successively thermally annealed to 143, 300 and 720°K. The relative invariance of the appearance of the spectra indicates that the annealed film contains thiophene rings with minimal structural modification, which is a specific feature of polythiophene. However, there is a broadening which is expected from a comparison between NEXAFS spectra of thiophene and an electrochemically grown polythiophene film. There is also a downward shift of about 0.6 eV in the leading resonance and, in contrast to the thiophene multilayer, there is no noticeable polarisation dependence.

Both the multilayer film annealed to 700°K and then cooling to room temperature, and one allowed to warm directly to room temperature, resulted in a polymer film of about 30Å thickness (by XPS). The relatively high vapour pressure of thiophene monomer would suggest that, had polymerisation not occurred, there would have been differing film thicknesses following the two treatments. A 24 hour exposure to atmospheric conditions did not alter the C 1s and S 2p XPS spectra, indicating that the product was stable to air and moisture.

Embodiment A piece of 0.14% C, 0.5% Mn sheet steel was polished to 500μ roughness, and suspended for 30 minutes in liquid thiophene monomer under ambient laboratory conditions. Characterisation of the resulting film by IR spectroscopy provided absorption bands consistent with the parent monomer (1494, 1454, 1230, 1100, 1052, 915 and 842 cm^{-1}), and polythiophene (1368, 788 and 730 cm^{-1}), as shown in Figure 3. The polythiophene bands at 788 and 730 cm^{-1} suggest a mixture of α-α' and α-ß' coupling of the monomeric units.

The polythiophene layer exhibited good corrosion resisting properties. The sample was immersed in a saturated sodium chloride solution at room temperature for 12 hours. The part of the sample covered with the polymer retained a metallic appearance and showed no visible sign of corrosion, whereas an untreated area was severely discoloured.

Polymer films are currently of great technological interest, for example in relation to electronic devices, sensors and protective coatings. Clearly, the present invention has a potential use in the corrosion protection of engineering steels and steel components, and of other components such as sensors.

Certain polymers, including polythiophenes and polypyrroles, also are electrically conductive when suitably doped. There thus exists the possibility that an electrically conductive substrate can be coated by the method of the invention while retaining surface conductivity. Where there is a substrate which is non-conductive, deposition of an electrically conductive polymer by the method of the invention will enable the production of electronic or electrical components, including sensors and conductive patterns or tracks.

CLAIMS

1. A method of polymerising a monomer of the type capable of undergoing oxidative polymerisation, comprising the step of exposing said monomer in the liquid phase to a film or substrate formed of a metal oxide, said metal oxide having a redox potential sufficiently positive to cause polymerisation of said monomer.

2. A method according to claim 1 wherein said metal oxide is selected from ferric oxide and cupric oxide.

3. A method according to claim 1 or claim 2 wherein said metal oxide is in the form of a film on a substrate of different material.

4. A method of polymerising a monomer of the type capable of undergoing oxidative polymerisation, comprising the step of exposing said monomer to a film of a metal oxide film on a substrate of a different material, said metal oxide having a redox potential sufficiently positive to cause polymerisation of said monomer.

5. A method according to claim 4 wherein the monomer is in the liquid phase.

6. A method according to any one of claims 3 to 5 wherein the substrate is of the metal of the metal oxide film.

7. A method according to any one of claims 3 to 6 wherein the substrate is electrically non-conductive.

8. A method of polymerising a monomer of the type capable of undergoing oxidative polymerisation, comprising the step of exposing said monomer in the liquid phase to a film or substrate of ferric oxide.

9. A method of polymerising a monomer of the type capable of undergoing oxidative polymerisation, comprising the step of exposing said monomer to a film of ferric oxide on a steel or iron substrate.

10. A method according to any preceding claim wherein the monomer is selected from pyrrole and derivatives thereof, and thiophene and derivatives thereof.

11. A method according to any preceding claim wherein the monomer is selected such as to provide an electrically conductive polymer.

12. A method according to any preceding claim, performed at a temperature of between -10°C and +20°C and at substantially atmospheric pressure.

13. A method of polymerisation according to claim 1 and substantially as herein described.

14. A component or substrate provided with a polymer coating prepared by a method according to any preceding claim.

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Claims searched:	1-14	**Date of search:**	21 May 1997

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): B2E

Int Cl (Ed.6): C08G 61/12

Other: Online: CAS-ONLINE, EDOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	J. Colloid Interface Sci., 144(1), 27-35, (1991) R. Partch *et al*, "Conducting polymer composites. I. Surface induced polymerisation of pyrrole on iron (III) and cerium (IV) oxide".	1-14

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.