

PHOTOINDUCED CONVERSION OF POLYANILINE FROM AN INSULATING STATE TO A CONDUCTING STATE

Field of the invention

The present invention relates to a method of preparing electrically
5 conductive polymeric material by treatment with a viologen salt under UV-light
irradiation and to electrically conductive polymeric articles formed thereby.

Description of related art

In recent years electrically conductive polymers have been widely studied
because of their potential important commercial applications. Such polymers
10 include polypyrrole and its derivatives and polyaniline and its derivatives.

The aniline family of polymers is an example of one of the most widely
studied electroactive polymers because of the ease of synthesis and the unusual
nature of its electrical conductivity which can be varied over a wide range.
Polyaniline (PANI) in its insulating base form is readily soluble in N-
15 methylpyrrolidinone and can be cast into films or coated on different substrates.
The insulating form can be converted to the conductive form by the following
methods:

(1) Treatment with aqueous protonic acids

PANI in the emeraldine (50% oxidized) base state when treated with
20 protonic acids shows an increase in electrical conductivity. The resulting
conductivity is a strong function of the pH of the equilibrating solution. For
example, when aqueous HCl is used at pH greater than 4, the PANi remains as
the essentially insulating non-protonated form whereas at pH~0 (i.e. with 1 M
HCl), the conductivity increases by 10 orders of magnitude (J. C. Chiang and A.
25 G. MacDiarmid, *Synth. Met.* 13, 193 (1986)). In the latter case, the imine units of
the PANi are protonated to give a N⁺/N ratio of about 0.5. In this form of doping,
there is no change in the number of electrons in the PANi chains.

The electrical conductivity of the PANi treated with protonic acids depends not only on the pH of the equilibrating solution but also on the oxidation states of the PANi. For example, PANi in the leucoemeraldine (100% reduced) state shows only a small increase in conductivity when treated with protonic acids (J. C. Chiang and A. G. MacDiarmid, *Synth. Met.* 13, 193 (1986)).

(2) Charge transfer interaction with organic electron acceptors

PANi in the emeraldine base state can undergo charge transfer interaction with organic electron acceptors such as tetrachloro-o-benzoquinone and 2,3-dichloro-5,6-dicyano-p-benzoquinone in acetonitrile (S. H. Khor, K. G. Neoh and E. T. Kang, *J. Appl. Polym. Sci.* 40, 2015 (1990)). An increase in electrical conductivity is achieved and the magnitude of the conductivity is dependent on the type of organic acceptors and acceptor concentration. The charge transfer interaction of emeraldine base with the organic electron acceptor is analogous to that of protonation by HCl, with the hydrogen atoms in the latter replaced by the partially dehalogenated halobenzoquinone rings. The maximum conductivity achieved is at least an order of magnitude lower than that achievable in protonic acid doping of emeraldine base.

PANi in the leucoemeraldine state undergoes oxidation doping by organic electron acceptors in acetonitrile solution which involves first the oxidation of the amine nitrogen and also the formation of the imine structure through hydrogen transfer from the amine nitrogen to the acceptor. The so-produced imine nitrogen is then in turn doped by the acceptor, as described above for PANi in the emeraldine state (E. T. Kang, K. G. Neoh, T. C. Tan, S. H. Khor, and K. L. Tan, *Macromolecules.* 23, 2918 (1990)). The maximum electrical conductivity obtained is also about an order of magnitude lower than that obtained from protonic acid doping of emeraldine.

(3) Interaction with aqueous solutions of viologens

Applicants have recently shown that PANi base in the form of freestanding film, coating or powder can be converted to the doped state upon exposure to the

aqueous viologen solution under ambient conditions (Patent Application under review). The reactions involve the transfer of electrons from PANi to the viologen dications resulting in the formation of viologen cation radicals and the transfer of some of the halide ions initially associated with the viologen to the PANi. This form
5 of oxidative doping of PANi offers the advantage of the use of near-neutral aqueous medium rather than a strongly acidic medium or organic solvent as discussed in (1) and (2) respectively.

It would be a significant advance in the art if a method of preparing an electrically conductive polyaniline material could be provided which would function
10 irrespective of the oxidation state of the polyaniline. It would be a further significant advance in the art if a method could be provided which did not involve the use of acid or other aqueous media or organic solvents such as acetonitrile. It would be a still further advance in the art if the level of conductivity achieved would be enhanced and particularly if the conductivity path can be tailored by
15 selective treatment.

It is accordingly an object of the present invention to overcome, or at least alleviate, one or more of the difficulties and deficiencies related to the prior art.

Summary of the invention

Accordingly, in a first aspect of the present invention there is provided an
20 electrically conductive polymeric article including a polymeric material capable of exhibiting electrical conductivity;

the polymeric material being rendered electrically conductive by treatment with a source of electromagnetic radiation, e.g. UV or near UV irradiation, in the presence of a viologen salt.

25 It has surprisingly been found that the electrically conductive polymeric article formed according to this aspect of the present invention exhibits a high level of electrical conductivity. For example, electrically conductive polyaniline may be prepared with resistances (R_s) decreasing from approximately 10^{10} to approximately $10^5 \Omega/\text{sq}$ or below, irrespective of the oxidation state of the

polyaniline material. Polyaniline material may be in the leucoemeraldine (0% oxidation state) or emeraldine (50% oxidation state) states or in any oxidation state between these two states.

Further, it will be understood that a conductivity path may preferably be
5 constructed in a selected pattern dictated by the radiation treatment pattern.

Examples of polymeric materials capable of being rendered electrically conductive by treatment with a viologen salt include polymers derived from aromatic bases such as aniline and its derivatives and from heterocyclic bases such as pyrrole and its derivatives. Other polymers which may be used may be
10 selected from the group of substituted and unsubstituted polyanilines, polyparaphenylenvinyles, substituted and unsubstituted polythiophenes substituted and unsubstituted poly-p-phenylene sulfides, substituted polyfuranes, substituted polypyrroles, substituted polyselenophene, polyacetylines formed from soluble precursors, combinations thereof and blends thereof with other polymers.

15 Preferred polymeric materials for inclusion in the polymeric articles of the invention include polyaniline and its derivatives and polypyrrole and its derivatives. Polyaniline and polypyrrole are particularly preferred polymeric materials.

The electrically conductive polymeric article may be formed in any suitable manner and may take any suitable shape. The polymeric article may be in the
20 form of a film, e.g. a free standing film, a film coating, e.g. a thin film coating, or a powder.

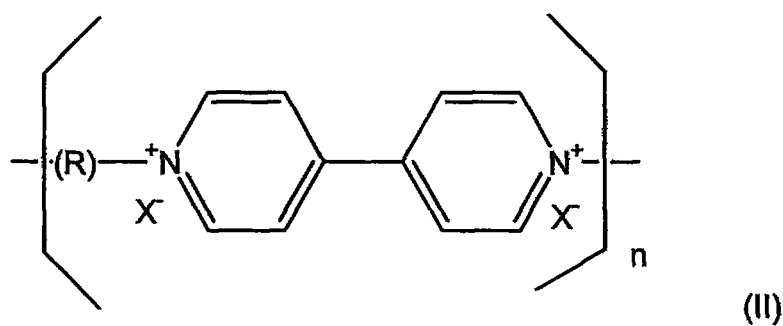
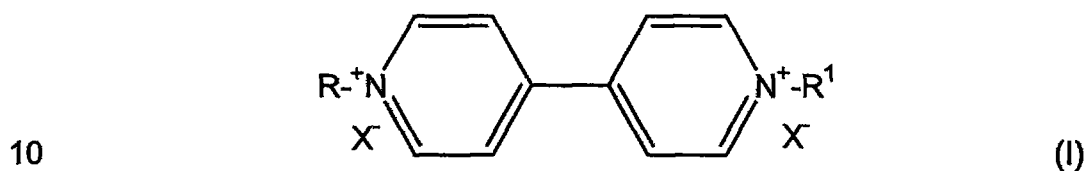
In a preferred aspect, the polymeric material may be deposited or supported on a suitable substrate. The substrate may be a fabric, polymeric matrix film or other construct. A polyethylene substrate, e.g. a low density
25 polyethylene (LDPE) substrate may be used.

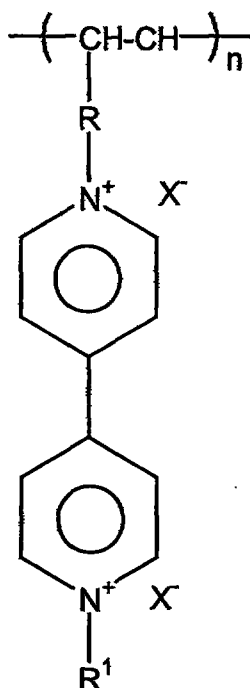
The viologen salt utilised as a dopant for the polymeric material may be of any suitable type. Viologen salts such as a dihalide salt of a viologen (1,1'-disubstituted 4,4'-bipyridinium) have been found to be particularly suitable.

The substituents on the bipyridinium molecule may be selected from alkyl or aryl groups. The alkyl groups may be substituted or unsubstituted C1 to C4 alkyl groups. The alkyl groups may be straight or branched chains. Substituents for the alkyl groups may be selected from a wide range of substituents including

5 halogen, phenyl and substituted phenyl. Phenylmethyl (benzyl) groups are the preferred alkyl substituents. The aryl groups may be substituted or unsubstituted aryl or heteroaryl.

Viologen salts may be provided as free compounds, shown below as I, or in the form of polymers, shown below as II and III,





(III)

where:

R and R^1 are independently chosen from alkyl or aryl groups as indicated above;

- 5 X^- is an anion, preferably a halide ion; and
 n is an integer greater than or equal to 2.

In a preferred aspect of the present invention the polymeric material may be directly treated with a viologen salt in the presence of UV-irradiation to render it electrically conductive.

- 10 Accordingly, in a preferred aspect of the present invention there is provided a method for preparing an electrically conductive polymeric article, which method includes

providing

- a polymeric material capable of exhibiting electrical conductivity; and
 15 a viologen salt

placing the polymeric material and viologen salt in contact to form
 a pre-doped material; and

subjecting the pre-doped material to a source of electromagnetic radiation, e.g. UV or near UV irradiation to render the polymeric material electrically

conductive.

Although not wishing to be bound by theory it is believed that when the polymeric material is treated with a viologen salt, and subjected to electromagnetic radiation, the polymeric material undergoes oxidative doping and the halide anions are incorporated into the polymer. The method may be conducted under ambient conditions or above, e.g. at or above room temperature in the presence of air. Preferably the method is conducted at a temperature of 0° to approximately 80°C in the presence of air. Thus the use of protonic acids or aqueous or organic solvents may be avoided.

Applicants have surprisingly discovered that utilising the method of the present invention the resistance of the polymeric material, R_s , is reduced by approximately 3 to 6 orders of magnitude within a period of 3 hours or less, preferably within a period of 1 hour or less. The R_s of the areas that are not subjected to UV or near-UV irradiation will not decrease.

The rate of the reaction is dependent on the ease of the reduction of the viologen salt, e.g. a viologen dihalide, and the transfer of the anions to the polymeric material to form a doped and conductive form of the polymeric material.

The preferred method involves the exposure of the polymer-viologen compositions in the form of thin film coatings to UV-irradiation at ambient conditions. Under such conditions, the increase in conductivity can be rapidly achieved. The rate of the reaction is dependent on the ease of the reduction of the viologen dication and the transfer of the anion to the polymer. This is in turn affected by the intensity of the irradiation, the type and amount of viologen salt used and the manner in which the PANi and viologen are in contact. Preferably the reactions are carried out by the UV-irradiation of a composition of polymer and viologen salt which are in close contact. The reactions preferably result in a substantial degree of oxidative doping of the polymer. The polymer-viologen composition may be in the form of blends or thin film coatings on substrates

The reactions may continue for a time sufficient to permit a substantial

degree of oxidative doping of the polymeric material to be achieved.

Preferably the rate of conversion of the polymeric material to a conducting state is varied by varying one or more of the type and concentration of the viologen salt, temperature and intensity and wavelength of UV irradiation and
5 period of exposure to UV irradiation.

The viologen salt may be selected from any suitable materials as discussed above. A viologen dihalide is preferred. The viologen salt may be monomeric or polymeric in nature. A mixture of viologen salts may be used.

Preferably, the 1,1'-substituent(s) of the viologen molecule(s) is (are)
10 selected from alkyl or benzyl groups, or a mixture thereof.

The method of contacting the surface(s) of the polymeric material with the viologen salt may vary widely, depending on the state of the polymeric material and the method selected for the reactions.

In one embodiment, the viologen salt is deposited on a suitable substrate.

15 More preferably, the viologen salt is grafted onto a suitable substrate utilising a heat and/or UV-induced treatment.

The viologen salt may, in a further preferred embodiment, be grafted onto a suitable substrate utilising a heat and/or UV-induced treatment.

In one embodiment, the viologen is then partially or substantially completely
20 coated with the polymeric material.

Preferably, a polymeric coating or film of the polymeric material is formed in situ.

Alternatively, a coating of the polymeric material is deposited on a suitable substrate.

The viologen salt may then be deposited on the polymer coated substrate.

In a particularly preferred form, the method further includes providing

- 5 a vinyl alkyl halide grafted low density polyethylene film substrate;
- an alkyl halide; and
- 4,4'-bipyridine;

contacting the grafted film substrate with the 4,4'-bipyridine for a time sufficient to permit reaction therebetween;

- 10 and subsequently contacting the modified grafted film substrate with the alkyl halide for a time sufficient to permit the formation of a viologen grafted film.

The method may further include the preliminary step of providing

- 15 a low density polyethylene film substrate;
- a solution of aniline or pyrrole;
- ammonium persulfate; and
- a vinyl alkyl halide

immersing the polyethylene film substrate into the solution of aniline or pyrrole and ammonium persulfate for a period sufficient to form a polymeric coating on the substrate,

- 20 contacting the coated substrate with the vinyl alkyl halide,
- subjecting the mixture to UV or near UV irradiation for a time sufficient to form a vinyl alkyl halide grafted substrate.

- One simple and preferred method involves the grafting of vinyl alkyl (or substituted alkyl) halides onto argon plasma pretreated LDPE (low density polyethylene) films, reacting the films with 4,4'-bipyridine followed by a second alkyl (or substituted alkyl) halide to form viologen moieties, and finally coating a thin polyaniline film onto the viologen grafted surfaces. Preferred conditions for near UV-light induced solution grafting of the vinyl alkyl halides onto argon plasma pretreated LDPE films include a monomer concentration of between 5 vol % to 10 vol % using ethanol or propanol as solvent, and a reaction time of 1 to 2 hours. Another preferred method involves placing the monomer on the surfaces of the
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plasma-treated LDPE films, sandwiching the films between two pieces of quartz plates and exposing the assembly to near UV-irradiation for a period of 15 to 60 minutes at room temperature. The grafted films are subjected to prolonged washing with dimethyl-formamide (DMF) to remove unreacted monomer and homopolymer. The grafting of viologen onto the films via reaction of the films with excess 4,4'-bipyridine and further reaction with excess alkyl or benzyl halides is preferably carried out at between 40°C and 70°C for 10 h to 20 h each, using DMF as solvent. The viologen-grafted films are washed in DMF to remove unreacted reactants before they are immersed in a reacting mixture of aniline and oxidant for deposition of a thin PANi coating onto the substrate.

The polymer coated films in the base or insulating state (in the form of emeraldine or 50% oxidation state) may be exposed to near UV-irradiation between 20 min to 120 min in the presence of air. The rate of doping of the thin PANi films depends on the type and amount of viologen grafted onto the films, the ease of reduction of the viologen salt and intensity of the light source. The change of PANi thin film from the insulating base state (blue in colour) to the conductive state (green in colour) is visibly obvious, and is confirmed by sheet resistance (R_s) measurements and UV-visible absorption spectroscopy.

EXAMPLES

The following specific examples are provided to illustrate this invention and the manner in which it may be carried out. It will be understood, however, that the specific details given in each example have been selected for the purpose of illustration, and are not to be construed as being limitations on the scope of the invention.

EXAMPLE 1

Vinyl benzyl chloride grafted film was synthesized by immersing an argon plasma pretreated LDPE film into a degassed monomer solution of 5 vol % using ethanol as solvent, and exposing the setup to near UV-irradiation for 2h. The grafted film was subjected to prolonged washing with DMF before it was reacted

with 0.024M 4,4'-bipyridine in a water bath at 70°C for 20h, followed by 0.4M benzyl chloride, again in a water bath at 70°C for 20h. Both reaction steps were carried out using DMF as solvent. The film was washed with DMF after both reaction steps to remove unreacted reactants. The viologen grafted film was finally
 5 immersed into a reaction mixture containing 0.10M aniline and 0.025M ammonium persulfate in 0.5 M HClO₄ for 2 h. The green polyaniline (in the emeraldine state) was undoped in 0.5M NaOH for 1 h, washed in deionised water and pumped dry under reduced pressure. The base film was exposed to near UV-light emitted from a 1kW mercury lamp for 1 h. The sheet resistance of the film decreased from
 10 10¹⁰Ω/sq. (before irradiation) to 10⁵Ω/sq.(after irradiation). The change in Rs with respect to irradiation time is shown in Figure 1.

EXAMPLE 2

Vinyl benzyl chloride grafted film was synthesized as described in Example 1. The grafted film was reacted with an equimolar mixture of 4,4'-bipyridine and p-
 15 xylene dichloride (0.024M of each reactant), in a water bath at 70°C for 20h, using DMF as solvent. The film so obtained was washed with hot deionised water to remove the homopolymers and coated with polyaniline as described in Example 1. The sheet resistance of the film decreased from 10¹⁰Ω/sq. to 10⁴Ω/sq. upon exposure to near UV-irradiation for 30 min. The change in Rs with respect to time
 20 is shown in Figure 1. The change in UV-visible absorption spectrum from that of emeraldine base to that of the conductive salt is illustrated in Figure 2. Before irradiation, the spectrum shows two absorption bands in the 300nm region and at 615nm, the first band being characteristic of emeraldine base and viologen, while the second band is the exciton band of emeraldine base. After 20 min of near UV-
 25 irradiation, the 420nm band and the high intensity tail extending into the near IR region are characteristic of the polaron state of doped PANi.

EXAMPLE 3

A coating of polyaniline (emeraldine) on LDPE substrate was prepared by immersing a O₂ plasma pretreated LDPE film into a reaction mixture of 0.10M

aniline and 0.025M ammonium persulfate in 0.5M HClO_4 for 2 h. The green polyaniline coated film was undoped as described in Example 1. The film was then placed in a degassed solution of vinyl benzyl chloride (0.03 vol. % in ethanol) and exposed to near UV irradiation for 2h. The film so obtained was washed with a solvent mixture containing DMF and chloroform to remove the homopolymers as well as unreacted vinyl benzyl chloride. The grafted film was reacted with 4,4'-bipyridine and benzyl chloride as described in Example 1, and then dried under reduced pressure. The film has a R_s of $10^{10}\Omega/\text{sq.}$ before irradiation which subsequently decreased to $10^6\Omega/\text{sq.}$ upon exposure to near UV-irradiation for 70 min.

EXAMPLE 4

Vinyl benzyl chloride grafted films were synthesized by placing the monomer on both surfaces of an argon plasma pretreated LDPE film, sandwiching the film between two pieces of quartz plates, and exposing the assembly to near UV-irradiation for a period of 45 minutes at room temperature. The grafted film was reacted with 4,4'-bipyridine and benzyl chloride, and further coated with polyaniline (emeraldine state) as described in Example 1. The R_s of the film decreased from $10^{10}\Omega/\text{sq.}$ to $10^5\Omega/\text{sq.}$ upon exposure to near UV-light for 10 minutes.

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EXAMPLE 5

Polyaniline (emeraldine) was synthesized via the oxidative polymerization of aniline using ammonium persulfate in 0.5M H_2SO_4 (A.G. MacDiarmid et al. *Synth. Met.* 69, 285 (1987)). The polyaniline powder was undoped using excess 0.5M NaOH. The base powder was blended with 20 wt. % of monomeric benzyl viologen dichloride, and a freestanding film of approximately $10\mu\text{m}$ was cast using 10 wt. % of blend in N-methyl pyrrolidinone (NMP). The R_s of the film decreased from $10^{10}\Omega/\text{sq.}$ to $10^7\Omega/\text{sq.}$ upon irradiation with near UV-light for 2h.

EXAMPLE 6

Viologen grafted film was synthesized as described in Example 2. The film so obtained was immersed into a reaction mixture containing 0.08M pyrrole and 0.025M ammonium persulfate in 0.15M hydrochloric acid for 2h. The polypyrrole
5 film was undoped in 0.5M NaOH for 2h, washed with deionised water and pumped dry under reduced pressure. The R_s of the film decreased from $10^8 \Omega/\text{sq.}$ to $10^6 \Omega/\text{sq.}$ upon exposure to UV-irradiation for 75 min.

Finally, it is to be understood that various alterations, modifications and/or additions may be made without departing from the spirit of the present invention
10 as outlined herein.



CLAIMS

1. An electrically conductive polymeric article exhibiting enhanced conductivity including a polymeric material capable of exhibiting electrical conductivity;
5 the polymeric material being rendered electrically conductive by treatment with a source of electromagnetic radiation in the presence of a viologen salt.
2. An electrically conductive polymeric article wherein the source of electromagnetic radiation is a UV or near UV source.
3. An electrically conductive polymeric article according to Claim 2
10 wherein the polymeric material is chosen from polyaniline and its derivatives.
4. An electrically conductive polymeric article according to Claim 2 wherein the polymeric material is chosen from polypyrrole and its derivatives.
5. An electrically conductive polymeric article according to Claim 3 wherein the polymeric material is polyaniline.
- 15 6. An electrically conductive polymeric article according to Claim 4 wherein the polymeric material is polypyrrole.
7. An electrically conductive polymeric article according to Claim 5, wherein the polyaniline base material has an oxidation state between the leucoemeraldine (0% state) and the emeraldine (50% oxidation state).
- 20 8. An electrically conductive polymeric article according to Claim 1, herein the polymeric material is in the form of a film, film coating, or powder.
9. An electrically conductive polymeric article according to Claim 8, wherein the polymeric material is deposited on a suitable substrate.
10. An electrically conductive polymeric article according to Claim 1,
25 wherein the viologen salt is a viologen dihalide.



11. An electrically conductive polymeric article according to Claim 10, wherein the viologen dihalide may be in the monomeric or polymeric form.

12. An electrically conductive polymeric article according to Claim 5, wherein the resistance of the polymeric base material, R_s , is reduced by
5 approximately 3 to 6 orders of magnitude.

13. An electrically conductive polymeric article according to Claim 1, exhibiting a predetermined pattern of selectively non-electrically conductive sections and electrically conductive sections.

14. A method for preparing an electrically conductive polymeric article,
10 which method includes
providing
a polymeric material capable of exhibiting electrical conductivity; and
a viologen salt
placing the polymeric material and viologen salt in contact to form
15 a pre-doped material; and
subjecting the pre-doped material to a source of electromagnetic radiation
to render the polymeric material electrically conductive.

15. A method according to Claim 14, wherein the source of electromagnetic radiation is a UV or near UV source.

20 16. A method according to Claim 14, wherein the viologen salt is deposited on a suitable substrate.

17. A method according to Claim 16, wherein the viologen salt is grafted onto a suitable substrate utilising a heat and/or UV-induced treatment.

18. A method according to Claim 17, wherein the viologen salt is formed
25 in situ.

19. A method according to Claim 16, wherein a surface of the viologen-bearing substrate is partially or substantially completely coated with the polymeric



material.

20. A method according to Claim 14 wherein a polymeric coating or film of the polymeric material is formed in situ.

21. A method according to Claim 14 wherein a coating of the polymeric material is deposited on a suitable substrate.

22. A method according to Claim 14, wherein the viologen salt is deposited on the polymer coated substrate.

23. A method according to Claim 14, wherein the a mixture of viologen salts is used.

24. A method according to Claim 14 wherein the 1,1'-substituent(s) of the viologen molecule(s) is (are) selected from alkyl or benzyl groups, or a mixture thereof.

25. A method according to Claim 14 wherein the viologen salt is monomeric or polymeric in nature.

26. A method according to Claim 25, wherein the viologen salt is a viologen dihalide.

27. A method according to Claim 14 wherein the resistance of the polymeric material R_s is reduced by approximately 3 to 6 orders of magnitude within a period of 3 hours or less.

28. A method according to Claim 14, wherein the method is conducted at a temperature of 0°C to approximately 80°C in the presence of air.

29. A method according to Claim 14, wherein the rate of conversion of the polymeric material to a conducting state is varied by varying one or more of the type and concentration of the viologen salt, temperature and intensity and wavelength of UV irradiation and period of exposure to UV irradiation.



30. A method according to Claim 16, further including providing
- a vinyl alkyl halide grafted low density polyethylene film substrate;
 - an alkyl halide; and
 - 5 4,4'-bipyridine;
- contacting the grafted film substrate with the 4,4'-bipyridine for a time sufficient to permit reaction therebetween;
- and subsequently contacting the modified grafted film substrate with the alkyl halide for a time sufficient to permit the formation of a viologen grafted film.
- 10 31. A method according to Claim 30, further including the preliminary step of providing
- a low density polyethylene film substrate;
 - a solution of aniline or pyrrole;
 - 15 ammonium persulfate; and
 - a vinyl alkyl halide
- immersing the polyethylene film substrate into the solution of aniline or pyrrole and ammonium persulfate for a period sufficient to form a polymeric coating on the substrate,
- 20 contacting the coated substrate with the vinyl alkyl halide,
- subjecting the mixture to UV or near UV irradiation for a time sufficient to form a vinyl alkyl halide grafted substrate.
32. A method according to Claim 31 wherein the vinyl alkyl halide is vinyl benzyl halide.
- 25 33. An electrically conductive polymeric article whenever prepared according to the method according to Claim 14.