



STABILITY ENHANCEMENT OF ELECTROACTIVE POLYMERS VIA SURFACE GRAFT COPOLYMERIZATION OF HYDROPHOBIC MONOMERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method for enhancing the stability of electroactive polymers in water. The process calls for thermally or UV light induced graft copolymerization of the electroactive polymer's surface with a hydrophobic monomer with or without the presence of a photoinitiator. Upon immersion in water, the process of undoping of the modified electroactive polymers with concomitant loss of counterions and decrease in electrical conductivity is retarded.

2. Description of Related Art

Electroactive polymers such as polyaniline and polypyrrole have high conductivity and are relatively easy to synthesize. However, these polymers upon immersion in water readily undergo undoping when the counterions migrate out of the polymer matrix. The undoping of the polymers results in the electrical conductivity decreasing by a few orders of magnitude. Various methods have been employed to immobilize the counterions in the polymer matrix. These methods and some of the related drawbacks are summarized below:

(i) Treatment with fuming sulfuric acid

In this method, polyaniline and polypyrrole are treated with ~30% fuming sulfuric acid which results in sulfonic acid ($-\text{SO}_3^-$) groups being substituted into the aniline or pyrrole rings (J. Yue, Z.H. Wang, K.R. Cromack, A.J. Epstein and A.G. MacDiarmid, *J Am Chem. Soc.*, 113, 2,665 (1991); E.T. Kang, K.G. Neoh, Y.L. Woo and K.L. Tan, *Polym. Commun.* 32, 412 (1991)). The immobilized groups serve as counterions in the polymer matrix. Such self-doped polymers are less conductive than the externally doped polymers (about an order of magnitude less conductive). The polymer is synthesized as a powder and can be cast as films on substrates but the films lack mechanical strength.

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(ii) Copolymerization of aniline and metanilic acid

The oxidative copolymerization of aniline and metanilic acid can be achieved in aqueous acid solutions (K.G. Neoh, E.T. Kang and K.L. Tan, Synth. Met. 60, 13 (1993)). The use of a 1:1 ratio of aniline and metanilic acid in the reaction mixture results in about 20% of the aniline rings having the covalently bonded $-\text{SO}_3^-$ groups. These groups together with the external counterions (from the acid solution) account for a protonation level (anion/N ratio) of close to 0.5. This polymer's electrical conductivity is an order of magnitude lower than that of externally protonated polyaniline. It has been verified that water treatment for 20h has no effect on the immobilized $-\text{SO}_3^-$ groups but almost all the external counterions are lost, and the conductivity decreases drastically.

(iii) Use of organic and polymeric anions

Polyaniline salt films cast from salt solutions when treated with water retain anions better if organic anions such as sulfosalicylic acid rather than the smaller inorganic acid anions are used (K.G. Neoh, M.Y. Pun, E.T. Kang and K.L. Tan, Synth. Met. 73, 209 (1995)). Such as-cast salt films are substantially weaker mechanically than the base films after reprotonation but the latter lose the anions readily upon immersion in water. It can be expected that polymeric anions incorporated into the conducting polymer matrix would not be easily lost when the polymer is immersed in water. However there are other problems. Doped polyaniline films prepared by blending polyaniline and poly (acrylic acid) in NMP have the problem of nonuniform and inefficient doping (S.A. Chen and H.T. Lee, Macromolecules 28, 2858 (1995)). The synthesis of polyaniline in polymeric acids lead largely to soluble products (K.G. Neoh, E.T. Kang and K.L. Tan, J. Phys. Chem. 101, 726 (1997)). The electrochemical synthesis of polypyrrole in polymeric acid results in substantially lower doping level and conductivity compared to the case when non-polymeric acid is used. The polymeric anions do not seem to be fully incorporated within the polypyrrole matrix (R. Yang, K. Naoi, D.F. Evans and W.H. Smyrl, Langmuir 7, 556 (1991), K.G. Neoh, E.T. Kang and K.L. Tan, J. Phys. Chem. 101, 726 (1997)).

The present invention uses an approach entirely different from the methods described

above to enhance the stability of electroactive polymer films in water. The present method involves the modification of the surface of films to incorporate hydrophobic groups via graft copolymerization of the appropriate monomers. A review of the literature yields no similar cases. Other patents related to the stability enhancement of electroactive polymers are summarized below:

US Patent 4499007 discloses a method of stabilizing iodine-doped, conductive polyacetylene in a deaerated aqueous solution by introducing a source of chloride ions into the solution to provide a chloride ion concentration of $> 0.5M$.

US Patent 4692225 discloses a method of stabilizing electrically conductive polymers to hostile environment by encapsulating the conductive polymer with a suitable resin, preferably an epoxy resin.

US Patent 5456862 relates to compositions of thermally stable electrically conductive substituted and unsubstituted polyanilines and p-toluenesulfonic acid dopant, and to conductive articles formed from such compositions.

US Patent 5393610 discloses a method for stabilizing the shelf life conductivity of conductive coatings such as polypyrrole or nickel sulphide on a substrate such as fiberglass by incorporating in the conductive coating a polyphenol or a polysiloxane.

US Patent 5583169 relates to the stabilizations of non-conductive polyaniline in NMP solution against gelation by admixing the solutions with stabilizing additives selected from the group consisting of hindered amine light stabilizers, polymeric amines and dialkylamines.

US Patent 5716893 discloses a method of enhancing the stability of conductive polymer films deposited on a textile fabric substrate by the oxidative polymerization of a pyrrole compound in the presence of a dopant anion and a stabilizing agent. The stabilizing agent is selected from the groups consisting of benzophenone, dihydroxybenzophenone and tetrahydroxy benzophenone.

Japanese Patent JP2221851 discloses a method of improving the electrochemical properties

of conducting polymer chemical sensor by coating the polymer with a hydrophobic polymer via spin coating or by the use of adhesives. The thickness of the hydrophobic layer prepared by the spin coating method is 2 μ m. The type of adhesive
5 used and the thickness of the coating and adhesive layer are not specified.

SUMMARY OF THE INVENTION

The present invention relates to a method of enhancing the stability of electroactive polymer surfaces,
10 such as films, in the presence of water or mildly basic solution via surface graft polymerization with hydrophobic monomers. The preferred electroactive polymers include unsubstituted and substituted derivatives of polyaniline, polypyrrole and polythiophene in the form of free-standing
15 films, or composite films of unsubstituted and substituted derivatives of polypyrrole, polyaniline or polythiophene and nylon 6. The preferred method of surface modification is via thermally or near-UV-light induced surface graft copolymerization of the film surfaces with functional
20 monomers. For films which require pre-activation of the surfaces, the preferred methods are ozone or plasma treatment. The monomers for the surface graft copolymerization are selected from a family of vinyl monomers which readily undergo free-radical initiated
25 polymerization. More particularly, the said functional monomers are selected from the family of hydrophobic monomers such as but not limited to the styrene based monomers, pentafluorostyrene and styrene monomers.

Pursuant to the present invention, the surface
30 graft copolymerization is carried out by contacting the surfaces of the electroactive polymer films (pre-activated, if necessary) with the liquid hydrophobic monomer, and

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exposing the surfaces to heat or near-UV-light. The best advantages of the present invention are obtained when the near-UV-light induced surface graft copolymerization is carried out at temperatures higher than room temperature.

- 5 If necessary, a small amount of photoinitiator such as benzophenone may be added to the hydrophobic monomer. The objects and advantages of the present invention are achieved when the surface modification has resulted in a substantial density of the hydrophobic graft copolymer, as
- 10 manifested in a significant increase in the water contact angle of the grafted surface over that of the ungrafted surface. The hydrophobic graft layer's thickness is estimated to be less than 0.01 μ m.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Pursuant to the present invention, the first step of the process is to provide a sufficiently active surface on the electroactive polymers or composites for surface graft copolymerization. Surface pretreatment methods include treatment with plasma, ozone and corona discharge. These methods generate a surface coverage of peroxide and hydroxyl peroxy species which are subsequently decomposed thermally or by near-UV-light to initiate surface graft copolymerization reactions in the presence of the monomer. The choice of surface pretreatment method will be dependent on the film used. An example of a film which does not require surface activation prior to surface graft copolymerization is polyaniline salt film obtained by the reprotonation of polyaniline base film (cast from a solution of polyaniline base in N-methylpyrrolidinone). The preferred application and the best advantages of the present invention are obtained from electroactive polymers or composites in the form of sheets.

The monomers for graft copolymerization used in this invention are selected from the family of hydrophobic monomers containing vinyl groups. The surfaces of the electroactive polymers/composites are rendered hydrophobic through graft copolymerization with the hydrophobic monomers. The method of contacting the surface of the electroactive polymers/ composites with the hydrophobic monomers may vary widely. One simple and preferred method involves placing the liquid hydrophobic monomer on the surfaces of the electroactive polymer/composite films and sandwiching the films between two pieces of quartz plates. A suitable amount of hydrophobic monomer must be provided to ensure complete coverage of the surfaces of the electroactive film/composite. The surface graft copolymerization reactions may be induced thermally or by using near-UV light irradiation. The best advantages of the present invention are obtained when the near-UV light induced surface graft copolymerization is carried out between 50°C to 70°C for a period of 10 min to 30 min. A small amount of photoinitiator such as benzophenone (2 wt% to 5 wt% of hydrophobic monomer) may be added to the hydrophobic monomer prior to placement of the mixture on the surface of the electroactive polymers/composites for UV-light induced graft copolymerization.

After the completion of the graft copolymerization, the electroactive polymer/composite is subjected to prolonged washing with chloroform to remove the

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unreacted monomer and homopolymer. The thickness of the hydrophobic graft layer is estimated (from the XPS results) to be less than 0.01 μ m.

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

Polyaniline was synthesized via the oxidative polymerization of aniline using ammonium persulfate in HCl (A.G. MacDiarmid et al. Synth. Met. 69, 285 (1987)). The polyaniline powder was undoped using excess 0.5M NaOH and the polyaniline base powder was dissolved in N-methyl pyrrolidinone (NMP). Free-standing films of 10-20 μ m was cast from the polyaniline in NMP solution. The base films were reprotonated by 1M HClO₄ for 24h. The resulting salt films were electrically conductive with a resistivity of the order of 10³ Ω /sq.

Surface graft copolymerization of pentafluorostyrene (PFS) on the polyaniline salt film was carried out as follows: PFS monomer was dropped onto the polyaniline film surfaces until complete coverage was ensured. The film was sandwiched between two quartz plates and exposed to near-UV light irradiation. Light irradiation on all surfaces was carried for 20min while the plates were heated with hot air at 60°C. The grafted film was then washed with copious amounts of chloroform to remove any unreacted monomer and homopolymer, and then dried under dynamic vacuum. The water contact angle of the film increased from about 25° before grafting to about 80° after surface graft copolymerization with PFS. The grafting density determined from XPS analysis and expressed as the number of moles of PFS per monomer unit of polyaniline is 1.0.

The stability enhancement of the polyaniline film after graft copolymerization with PFS is readily illustrated by comparing the electrical resistivity and anion concentration of

the ungrafted and PFS-grafted films after prolonged immersion in water. The results are as follows:

Immersion Time in Water	Ungrafted Film		Grafted Film	
	Resistivity Ω/sq	ClO_4^-/N	Resistivity Ω/sq	ClO_4^-/N
0	2×10^3	0.45	2×10^4	0.42
1h	8×10^6	0.32	5×10^4	0.40
24h	1×10^7	0.27	8×10^4	0.39

Thus, even though the conductivity of the film decreased by 1 order of magnitude after the grafting process, the grafted film's conductivity decreased by less than 1 order of magnitude after 24h immersion in water compared to the 4 orders of magnitude decrease observed for the ungrafted films. The decrease in conductivity is due to the migration of the anions (ClO_4^- anions) out of the film into the water as seen from the decrease in the ClO_4^-/N ratio in Table 1. The ClO_4^-/N mole ratio given is the bulk ratio and the ratio in the surface region of the film is expected to be significantly lower, giving rise to the observed large decrease in conductivity of the ungrafted film.

EXAMPLE 2

Free standing polyaniline salt films obtained via the reprotonation of the base films by HClO_4 were prepared according to the procedure in Example 1. Surface graft copolymerization of styrene was carried out using 2 wt% of benzophenone in styrene according to the procedure in Example 1. The water contact angle and surface resistivity of the grafted film were similar to those obtained after graft copolymerization with PFS (described in Example 1). The resistivity increase of the grafted film after 24h in water was less than 1 order of magnitude compared to 4 orders of magnitude for the ungrafted film after similar treatment in water.

EXAMPLE 3

Polyaniline-nylon 6 composite films were synthesized in the following manner: Nylon 6 films were soaked in aniline for 1h and then wiped dry and transferred to 2M HCl

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containing 0.25M $(\text{NH}_4)_2\text{S}_2\text{O}_8$. After 10 min the film was removed, soaked in water followed by 2M HCl for 30 min each and pumped dry under dynamic vacuum. The film was transparent and green (which is the characteristic color of conductive polyaniline salt). Surface graft copolymerization with PFS with 2 wt% benzophenone was carried out as described in Example 1.

The UV-visible spectrum of the PFS grafted polyaniline-nylon 6 composite after 24h immersion in water is similar to that of the pristine film. On the other hand, the UV-visible spectra of the ungrafted polyaniline-nylon 6 composite after 24h immersion in water shows the characteristics of undoped and nonconductive polyaniline base.

EXAMPLE 4

Free-standing polypyrrole films were synthesized electrochemically (J.H. Lee and J.J. Chung, Synth. Met. 53,245 (1991)). Surface graft copolymerization with PFS was carried out as described in Example 1. After surface grafting with PFS, the water contact angle increases from 36° to 92°. After 24h immersion in water, the anion ($-\text{SO}_3^-$)/N molar ratio decreases by 5% compared to a decrease of 36% observed when as-synthesised polypyrrole films are subjected to the same treatment in water.

EXAMPLE 5

Surface graft copolymerization of PFS with polyaniline salt film was carried out as described in Example 1. The PFS grafted film was immersed in 0.001M NaOH for 1h. The conductivity of the film decreases by 2 orders of magnitude but is still 10 times higher than that of an ungrafted polyaniline salt film subject to the same treatment in 0.001M NaOH.

To those skilled in the art to which this invention relates, many changes in construction and widely different embodiments and applications of the invention will suggest themselves without departing from the spirit and scope of the invention. The disclosures and descriptions herein are purely illustrative and are not intended to be in any sense limiting.

CLAIMS:

1. A method of enhancing the stability of the surface of an electroactive polymer selected from the group consisting of unsubstituted and substituted derivatives of polyanilines, polypyrroles and polythiophenes for use in an aqueous environment, which method comprises graft copolymerization of one or more hydrophobic, vinyl group-containing monomers onto said surface, wherein the surface graft polymerization is induced thermally or via near-UV light irradiation or by a combination thereof.
2. A method according to claim 1, wherein the monomer is selected from styrene-based monomers, pentafluorostyrene and styrene monomers.
3. A method according to claim 1 or 2, wherein the surface of the polymer is preactivated prior to surface graft copolymerization.
4. A method according to claim 3, wherein the surface pretreatment is achieved with gas plasma, ozone or corona discharge.
5. A method according to any one of claims 1 to 4, wherein a photoinitiator is used during the UV-light induced graft copolymerization.
6. A method according to any one of claims 1 to 5, wherein the electroactive polymer is in the form of a composite.
7. A method according to claim 6 wherein the electroactive polymer is in the form of a composite with nylon 6.

8. A method according to any one of claims 1 to 7, wherein the electroactive polymer is doped by one or more dopants.

9. A method according to claim 8, wherein the said
5 dopants are inorganic or organic acids, acid derivatives or a combination thereof.

10. A method according to any one of claims 1 to 9, wherein the hydrophobic monomers for graft copolymerization is selected from vinyl monomers containing the appropriate
) 10 functional groups.

11. A method of modifying the surface of an object for stabilizing the surface for use in an aqueous environment consisting of an electroactive polymer selected from the group consisting of unsubstituted and substituted
15 derivatives of polyanilines, polypyrroles and polythiophenes, said method comprising graft copolymerization of one or more hydrophobic, vinyl group-containing monomers onto said surface, wherein the surface graft polymerization is induced thermally or via near-UV
20 light irradiation or by a combination thereof.

12. A method for stabilizing the surface of an electroactive polymer selected from the group consisting of unsubstituted and substituted derivatives of polyanilines, polypyrroles and polythiophenes for use in an aqueous
25 environment, comprising graft copolymerization of one or more hydrophobic vinyl group-containing monomers onto said surface, wherein the surface graft polymerization is induced thermally or via near-UV light irradiation or by a combination thereof.

30 13. An article comprising a non-electrically conductive portion and an electrically conductive portion

where stability enhancement in an aqueous environment is achieved using a method according to any one of claims 1 to 12.

14. An article with a surface modified according to
5 the method of any one of claims 1 to 12.