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Photopolymerized silver-containing conducting polymer films. Part I. An electronic conductivity and cyclic voltammetric investigation

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Abstract A photopolymerization process that simultaneously deposits electronically conducting polymer films and incorporates nanophase silver grains within the films, the silver grains having been formed in situ on irradiating cast, photopolymerizable formulations containing silver salts, was developed. Polymer films produced from formulations containing large organic anions were very flexible and strongly adherent to substrates. Polypyrrole films containing silver grains were characterized electronically on measuring their electronic conductivities and electrochemically on recording their cyclic voltammetric profiles. Conductivities were affected by the chemical identity and concentration of components added to photopolymerizable formulations. The best photopolymerized films had a conductivity of the order of 1 S cm^{-1}. Electronically conducting films derived from formulations consisting of a monomer, an electron acceptor/"dopant," and a photoinitiator were electrochemically active. They possessed long-term stability under extended electrode potential cycling conditions, acceptable charge storage capacity, and the ability to oxidize or reduce redox couples in solution.

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Introduction

Technological advances in the aerospace, telecommunications, and electronics industries are placing increasing demands for the development of novel organic-based materials having unique combinations of physical, chemical, and mechanical properties [1, 2]. Improvements sought over conventional materials include high electronic conductivity, improved optical properties, increased stability, enhanced flexibility, and low-cost thin and thick film fabrication processes [3–5]. The discovery of intrinsically electronically conducting organic polymers about 30 years ago that have the potential to combine the electronic and optical properties of semiconductors (and metals) with the simplified processing procedures and attractive mechanical characteristics of conventional polymers [6, 7] has led to the emergence of these materials in applications previously reserved for traditional inorganic-based electronic conductors [8, 9]. The most well-known conducting polymers in this class include polyacetylene, polypyrrole, polythiophene, and polyaniline, which display electronic conductivities, in the oxidized state, as high as 10^3 to 10^5 S cm^{-1} [10]. However, the heterocyclic-based conducting polymers, polypyrrole and polyaniline, are the most attractive from an applications perspective because of their chemical and thermal stabilities, ease of preparation, and the ability to modify their properties by utilizing either substituted derivatives of their monomers, copolymers, or the incorporation of various electrolyte anions [11].

A number of methods have been developed to prepare intrinsically electronically conducting polymers. These include electrochemical processes [12, 13], chemical syntheses [14, 15], and enzyme catalysis [16, 17]. However, only a few preliminary reports utilizing ultraviolet (UV) radiation for the deposition of such polymer films have appeared in the literature. TiO_2 powders were photoelectrochemically coated with polypyrrole layers on irradiating TiO_2 dispersions in an aqueous solution containing pyrrole, oxygen, and tetrabutylammonium tetrafluoroborate with UV light [18]. Photochemical deposition of polypyrrole on various substrates has been accomplished on transforming the excited state of a photosensitive Cu^{1+} complex into the corresponding Cu^{2+} complex, by reducing p-nitrobenzylbromide, and the resulting Cu^{2+} complex subsequently oxidizes pyrrole to polypyrrole [19]. The photochemical polymerization of powdery polypyrrole was achieved using a solution containing Ru $(bpy)_3^{2+}$ as a photosensitizer and $Co(NH_3)_5Cl^{2+}$ as a sacrificial oxidant [20]. The self-sensitized photopolymerization of pyrrole on various substrates by illumination with sunlight has also been reported [21].

Utilization of light as the energy source for polymerizing and cross-linking functional monomers and oligomers constitutes the basis for important commercial processes [22]. Applications for UV radiation-induced polymerization include microlithographic masks for computer chip generation, printing inks, reinforcement coatings for fiber optics, and in stereolithography [23]. The attractiveness of the method stems from: fast rates of polymerization, low energy consumption (compared to conventional surface coating technologies), reduced pollution, and excellent product quality. When UV radiation is used to produce an active initiator species in solution, a three-dimensional polymer network can be formed by a chain reaction on photopolymerizing a monomer [24–27]. However, since most monomers do not produce an initiator species in sufficiently high yield upon UV exposure, it is desirable to introduce a photoinitiator that will cause the photopolymerization process to start almost instantaneously. A suitable photoinitiator system must possess: high solubility in the monomer, high absorption in the emission range of the light source, excited states that have a short lifetime yielding reactive radicals or ionic species with the highest quantum yield, and it should not induce degradation of the polymer upon aging.

Since the formation of radical cations is well-known to take place on electrochemically forming polypyrrole from pyrrole monomers in solution [28], cationic photoinitiators are likely to be particularly useful. Thermally stable cationic photoinitiators of commercial significance are onium salts, e.g., triarylsulfonium and diaryliodonium, with complex anions [29, 30]. A key feature of these photoinitiators is the low nucleophilicity of the anions

which reduces termination processes and allows ambient temperature cationic polymerization to proceed. Besides their specificity, cationic-initiated photopolymerizations have the advantage of being insensitive to atmospheric oxygen.

Conducting polymers are most useful when fabricated as continuous films, and processes which maintain both flexibility and conductivity are aggressively sought after. The development of a photopolymerization process for the deposition of nanophase silver-containing, electronically conducting polymer films onto any solid substrate material, including nonconducting substrates, together with an electronic conductivity and cyclic voltammetric characterization of the films produced, are described in this paper. The process uses light of sufficient energy as the driving force to induce electron transfer from the monomer species in a cast solution film to a suitably energetic electron acceptor, preferably in the presence of a photoinitiator, both of which are also present in solution. Normally, the electron acceptor is a simple inorganic transition metal salt where the redox potential of the transition metal cation is sufficiently positive to oxidize not only the monomer in solution but also at least some of the monomer-derived moieties incorporated into the growing polymer chains in the polymer backbone. Anions of the salt also are incorporated as "dopants" into the growing positively charged polymer film to provide charge neutrality. A three-dimensional homogeneous oxidation process takes place on irradiating a cast photopolymerizable formulation in contrast to the two-dimensional heterogeneous electrochemical oxidative approach to the synthesis of electronically conducting polymer films.

Experimental equipment, procedures, and methods

Equipment for photopolymerization of conducting polymer films

Photopolymerizations were accomplished with UV light. Oriel UV illumination systems, models 66165 and 66002 with 200-Watt mercury–xenon arc lamps were used. A collimator with an $f/1.0$ condensing lens and an additional $f/19.7$ and 50 mm focal length lenses served to distribute the arc spot to less than a 1-cm diameter sized area. A 90° light beam reflector was employed to direct the light vertically downward onto a substrate. All the optical accessories were made of fused silica in order to pass high-energy UV as well as visible light. The irradiances at the surfaces of substrates on which conducting polymer films were photopolymerized were measured by using an Eppley radiometer, model PSP with a calibrated EMF of 9.38×10^{-6} V W^{-1} m^{-2}. Substrate surface temperatures

were measured by means of a Fe/constantan thermocouple probe. An illumination intensity of up to 2.5 W cm^{-2} and a temperature of 70 °C could be obtained with the light sources used.

Approach used for photopolymerizing conducting polymer films

Polypyrrole (and polyaniline) films were prepared from their respective monomers, which were freshly distilled under vacuum prior to use. Conducting polymer films were photopolymerized on aluminum, gold, platinum, ceramic, glass, Teflon®, Mylar®, and polystyrene substrates exposed to ambient air atmosphere. Photopolymerized films were prepared from solutions containing pyrrole (and aniline) monomers, along with various additives (electron acceptors/"dopants," photoinitiators, and flexibilizers). The additives were dissolved in the pure monomer, so as to accelerate the polymerization process and to improve the quality of the resulting films. Electron acceptors/"dopants" used were silver nitrate (AgNO$_3$) and silver tosylate $\left[AgTs; Ts^- = CH_3(C_6H_4)SO_3^- \right]$ which were added in amounts of 0.01–8 mol% [moles electron acceptor/"dopant" per (moles of monomer+moles of electron acceptor/"dopant")]. The photoinitiators investigated included Irgacure 784 (a titanocene radical photoinitiator) and Irgacure 261 (a cationic ferrocenium photoinitiator) supplied by Ciba Geigy and Cryacure 6990 and Cryacure 6974 (triarylsulfonium PF$_6^-$ and SbF$_6^-$ salts, respectively) supplied by Union Carbide. The photoinitiators were added in amounts corresponding to 1–8 wt.% (w/w of monomer).

Components of photopolymerizable formulations were mixed in glass vials that excluded the penetration of light. Furthermore, the glass vials were sonicated to help with the dissolution and homogenization of the formulations. Since a slow (1–2 days) chemical polymerization of pyrrole takes place in the presence of Ag$^+$ cations, freshly prepared photopolymerizable formulations were made up immediately prior to carrying out a polymerization experiment. A thin layer of a formulation was then cast and evenly spread on the surface of a selected substrate (usually 1 or 4 cm^2 in area). The coated substrate was subsequently placed under the output of a UV lamp. Curing was performed under strictly controlled illumination conditions. After a few minutes of UV irradiation, the initially transparent cast films were transformed into soft black coatings. After a further few minutes of light exposure, films became hard; that is, they were cured. After completion of curing of the first coating, a second coating was applied and cured in a similar fashion. Multiple coating–curing cycles (up to ten layers in some cases) were carried out in order to produce relatively thick films. In order to improve the mechanical properties of supported conducting polymer films and free-standing films, additives, such as large anionic surfactants, e.g., dodecyl sulfate, sodium salt (DDS; Aldrich) and dodecylbenzene sulfonate, sodium salt (DDBS; Aldrich) were added to photopolymerizable formulations.

Electronic conductivity measurements of conducting polymer films

Electrical conductivities of photopolymerized polypyrrole films were measured by the standard four-point probe resistivity method [31]. Conductivity was measured at several different locations on the surface of a conducting polymer film. An Alessi standard four-point probe apparatus was used which consisted of a contact probe station, model CPS-05, that provided a pressure-controlled contact of 40–70 g per tip (C4S-475S probe head) or 70–180 g per tip (C4S-645S probe head). Low contact resistance was achieved by using osmium tips of 127 μm radii. Spacing between the tips was 1.0 and 1.5 mm, respectively.

Thickness measurements of conducting polymer films

Photopolymerized polypyrrole films were removed from metal and glass substrates using a sharp scalpel. In some cases, films were peeled off by bending the metal substrates, which also provided an indication of the extent of adherence and flexibility of the films. For relatively thick films (20–250 μm), film thicknesses were measured by a digital micrometer (Mitutoyo, Japan) with an accuracy of ±2 μm. For thinner films, in the range 0.1–20 μm, film thicknesses were obtained from scanning electron micrographs (SEM) of film cross-sections.

Electrochemical apparatus and the recording of cyclic voltammetric profiles

Experiments were performed in either one- or three-compartment Pyrex® glass cells. Reference electrodes and counter electrodes used were silver/silver chloride and cylindrical platinum gauzes, respectively. PAR, models 273 and 173, potentiostats/galvanostats; PAR, model 175, universal programmer; Houston Instruments, model 2000; X–Y or Yokogawa, model 3025; two-pen X–Y recorders; and Fluke model 8050A digital multimeters were used as needed. Voltammetric scans of photopolymerized polypyrrole (and polyaniline) films were carried out in aqueous 0.5 M H$_2$SO$_4$ solutions at 25 °C. High purity chemicals and 18 MΩ water were used throughout this investigation. Normally, stable voltammetric profiles were obtained after approximately 10–15 min of cycling within the potential limits −0.3 and +0.55 V (Ag/AgCl) using a scan rate of 20 mV s^{-1}.

Results and discussion

Electronic conductivity of photopolymerized polypyrrole films

To determine what additives (photoinitiators and electron acceptors/"dopants") are necessary to bring about the successful photopolymerization of conducting polymer films, preliminary experiments were carried out involving the addition of each of these additives separately to neat pyrrole. The magnitude of the electronic conductivity of the resulting polymer films was selected as the primary parameter to be evaluated in determining a successful outcome for each photopolymerization event. When pyrrole alone or pyrrole in the presence of a photoinitiator, e.g., titanocene (Irgacure 784), was photopolymerized, transparent yellow polymer films were obtained, exhibiting insulating properties. Resistances of over 20 MΩ were measured for such films using an ohmeter. DC (or AC) measurements were not possible because the voltage needed to drive currents, even as small as 1 nA, exceeded the compliance voltage of the galvanostat PAR 273 (100 V).

Representative photographs of photopolymerized polypyrrole films on alumina and aluminum foil substrates are presented in Fig. 1. Large gold electrical contacts were vapor-deposited on both ends of alumina substrates prior to the photopolymerization of polypyrrole films (cf. Fig. 1a). Resistive photopolymerized polypyrrole films, obtained from formulations containing pyrrole alone or pyrrole in the presence of a photoinitiator, had a yellow–green coloration in the as-deposited state (Fig. 1c,d). Thin electropolymerized polypyrrole films in the reduced state display a similar coloration [9, 32]. Heating this neutral polypyrrole film in air partially oxidized the polymer giving rise to a more conducting material and correspondingly a darker coloration (cf. Fig. 1e,f). Polymer films possessing increasing electrical conductivities derived from formulations containing pyrrole, a photoinitiator, and with increasing amounts of silver nitrate displayed increasingly darker colorations. Films with the highest conductivity, 0.3 S cm^{-1}, had a dark bluish color, as exemplified by the polymer films shown in Fig. 1g,h. Photopolymerization of the first cast formulation layer in each case resulted in a completely covered substrate surface.

Choice and optimal concentration of electron acceptor

From preliminary studies, it was found that silver nitrate (AgNO$_3$), when used as the electron acceptor/"dopant" in the photopolymerization of pyrrole, is far superior to silver perchlorate (AgClO$_4$), silver nitrite (AgNO$_2$), and silver tetrafluoroborate (AgBF$_4$). In order to improve the mechanical properties of photopolymerized polypyrrole films, two
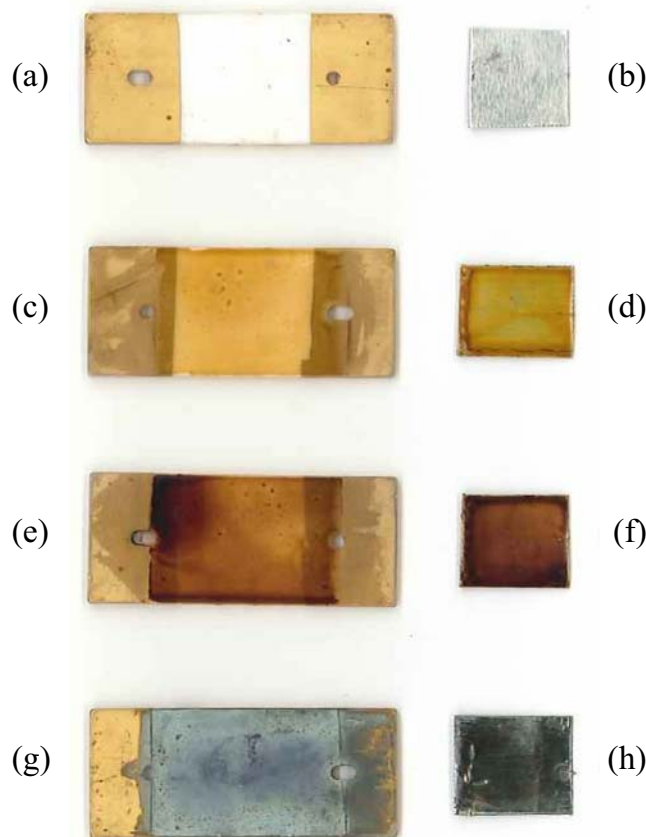

Fig. 1 Uncoated (**a** and **b**) and photopolymerized polypyrrole film-coated (**c**–**h**) alumina and aluminum metal substrates, on using Irgacure-784, a titanocene radical photoinitiator: as-deposited photopolymerized polypyrrole films using only the photoinitiator (**c** and **d**); thermally treated photopolymerized polypyrrole films (170 °C in air for 12 h) using only the photoinitiator (**e** and **f**); as-deposited films on using photoinitiator and silver nitrate as electron acceptor (**g** and **h**)

silver-based electron acceptor/"dopant" salts were investigated more fully: AgNO$_3$ and AgTs. The incorporation of tosylate anions improves the mechanical properties of electropolymerized polypyrrole films [32]. Thus, these two salts were added separately to photopolymerizable formulations using pyrrole/electron acceptor/"dopant" molar ratios ranging from 100:1 to 4:1, the latter being close to the ratio of pyrrole monomer to "dopant" anion found for electropolymerized or chemically prepared polypyrrole.

The dependences of the electrical conductivity of photopolymerized polypyrrole films on the concentration of electron acceptors/"dopants" (AgNO$_3$ and AgTs) added to photopolymerizable formulations are presented in Fig. 2. Both curves exhibit a maximum conductivity value of approximately 0.1–0.3 S cm^{-1} at a pyrrole/salt molar ratio of about 8:1. For both silver salt-based electron acceptors/ "dopants," a steep decrease in conductivity occurred at
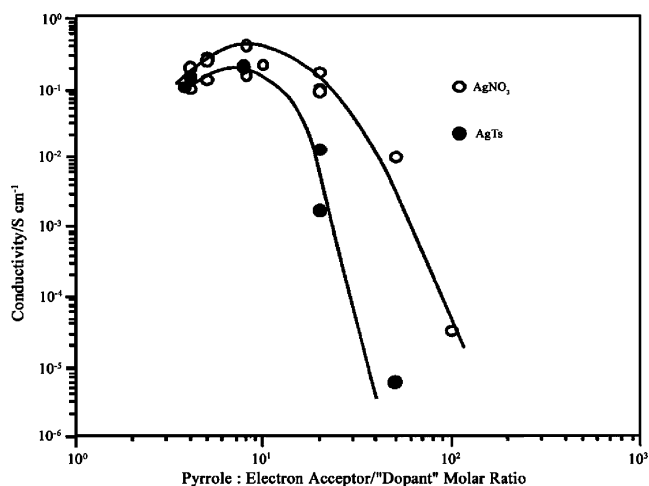
Fig. 2 Dependence of electronic conductivity on the chemical identity and concentration of "dopant" anions present in photo-polymerized polypyrrole films

molar ratios higher than 15:1. In the case of AgTs, at low added salt concentrations, the conductivities of polymer films were several orders of magnitude lower than those for polymer films photopolymerized using $AgNO_3$ as the electron acceptor/"dopant." This could be due to the fact that, although nitrate and tosylate anions are mobile within polypyrrole matrices, the nature of the interaction between nitrate anions and photopolymerized polypyrrole chains, together with the smaller effective ionic radius for nitrate, are likely to yield faster transport rates for this anion. This is indirectly supported by radiotracer studies of the strengths of interactions between polypyrrole and incorporated anions [33]. From the data presented in Fig. 2, it is clear that $AgNO_3$, when added to photopolymerizable formulations in amounts corresponding to 4–10 mol%, is the optimal choice of electron acceptor/"dopant." The maximum in the conductivity of photopolymerized poly-pyrrole films at pyrrole/salt molar ratios in this range for $AgNO_3$ (and AgTs) salts may be due to optimum solubility/viscosity effects for the formulations, providing efficient diffusion of the anions (NO_3^- or Ts^-) and cations (Ag^+) through the thin layers as they photopolymerize. The data shown in Fig. 2 were obtained from polymer films of different thicknesses. Although the thinner films were less brittle and less fragile, no improvement in mechanical properties was observed for photopolymerized films on utilizing AgTs as the electron acceptor/"dopant."

It should be pointed out that there is a significant directional influence on the measured conductivity of conducting polymer materials [34–36]. For electrochemically deposited polypyrrole films, the electrical conductivity in the transverse direction was found to be about three times less than in the longitudinal direction [34, 35], while for a polyaniline-poly(ethylene terephthalate) composite

film, the measured conductivity along the film was in the range of 0.1–0.2 S cm^{-1}, whereas, through the film, it was about 10^{-9} S cm^{-1} [36]. Furthermore, drying conducting polymer films can lower their electrical conductivity, as evidenced by the more than two orders of magnitude reduction in the electrical conductivity for polyaniline films that were dried at 105 °C for 24 h [37]. Drying causes the removal of water or moisture or solvent contained within polymer matrices. Electron diffraction studies of polypyrrole indicate that the polymer chains lie flat in the plane of the film, thus, this could also contribute to the anisotropic electrical conductivity in this material [38]. The conductivity of polypyrrole remains stable at temperatures less than 80 °C in the absence of oxygen and water [39]. In general, it has been observed that conducting polymers demonstrate temperature dependences of conductivity similar to that of conventional semiconductors [40].

Choice of photoinitiator

Ideally, the choice of photoinitiator is governed by the mechanism involved in the photopolymerization process. It is known that electropolymerization of pyrrole proceeds through the oxidation of the monomer leading to the formation of cation radicals, dimers, and ultimately, polymer chains that precipitate onto the electrode surface with the formation of cationic charges inside the polymer [41, 42]. On this basis, it might be expected that a cationic photoinitiation step would be involved in the photopolymerization process leading to the formation of polypyrrole films. To test this hypothesis, both radical (Irgacure 784) and cationic (Irgacure 261, Cyracure 6974, and Cyracure 6990) photoinitiators were used in order to gain further insight into the photopolymerization mechanism. The latter three photoinitiators have been developed for the absorption of light at very long wavelengths [up to 550 nm, though Cyracure 6974 and Cryacure 6990 (triarylsulfonium salts), do not absorb light so efficiently above 350 nm]. Absorption of long wavelength light is known to enhance the curing of thick films as well as the curing of pigmented coatings because absorptivity is usually weaker allowing light to penetrate further.

Simple tests of thick film curing were performed by carrying out the simultaneous illumination of photopolymerizable formulations containing the photoinitiators identified above added at 3 wt.% to pyrrole/$AgNO_3$=8:1 solutions. In each case, exposure to UV light was brought about from the top of miniature glass vials (0.7 cm diameter and 1.1 cm height) containing the different formulations. The photopolymerization process was closely followed under low illumination conditions (corresponding to a substrate surface temperature of 30–32 °C), in order to determine the changes taking place. In all four vials, the

polymerization process went through different stages which affected the color of the bulk and/or surface layers of the formulations and the time at which solidification was achieved. From this simple experiment, it was observed that cationic photoinitiators exhibited faster curing rates than the radical photoinitiator. Especially, Irgacure 261 demonstrated the most effective curing as evidenced by a deeper and more homogeneous darkening and solidification of the entire formulation volume in the glass vial. The ferrocenium photoinitiator is more suitable for photopolymerization of pyrrole because it allows deeper light penetration through the black solidified surface layer.

The effect of photoinitiator concentration (Irgacure 261) on the curing time of photopolymerized polypyrrole films is shown in Fig. 3. Formulations containing increasing amounts of photoinitiator were applied to aluminum and glass substrates and were cured simultaneously. Curing time was determined by observing solidification and by the pencil hardness test. Increasing the amount of photoinitiator from 1 to 8 wt.% decreased the curing time by approximately a factor of 2. Increasing amounts of photoinitiator present in the films brought about a linear decrease in conductivity as shown in Fig. 4.

Influences of inner and outer surfaces of photopolymerized polypyrrole films on electronic conductivity

After curing, photopolymerized polypyrrole films were peeled off from their aluminum metal foil substrates and electrical conductivity was measured on both sides of the samples on at least five different locations. Conductivity measured at different locations should reflect uniformity (or lack thereof) of the prepared films. The conductivities for
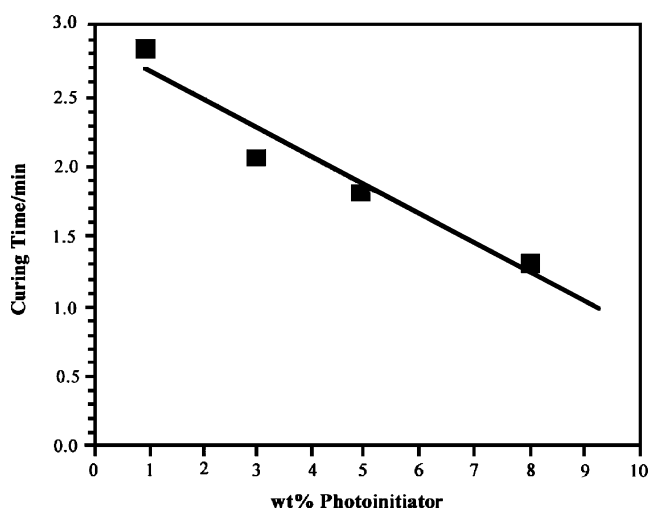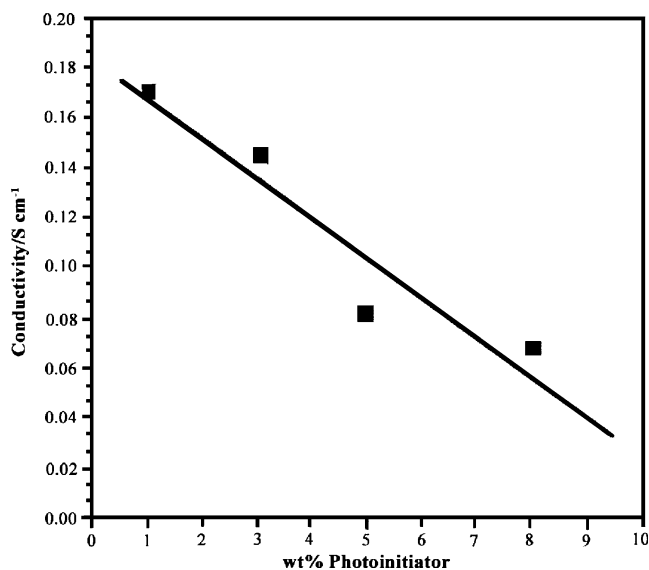
Fig. 4 Dependence of electronic conductivity on the concentration of photoinitiator (Irgacure 261) initially added to a pyrrole-based photopolymerizable formulation containing pyrrole/AgNO$_3$=8:1

photopolymerized samples containing 3 wt.% of Irgacure 261 and silver nitrate as the electron acceptor/"dopant" added in a molar ratio of pyrrole/silver nitrate=5:1 were within a narrow range of 0.15–0.3 S cm^{-1}. The outer surfaces of photopolymerized samples were smooth, uniform, and black. For comparison, the electronic conductivities of electropolymerized polypyrrole films prepared from aqueous sodium nitrate solutions at room temperature were in the range 4–30 S cm^{-1} [43]. Also, the conductivity at ambient temperature of a pressed disk (prepared under vacuum at 100 °C and 40,000 psi) of powdered polypyrrole synthesized chemically using Fe(NO$_3$)$_3$ was found to be 2.1 S cm^{-1} [44].

Improvement of mechanical properties of photopolymerized polypyrrole films

In general, polypyrrole films photopolymerized according to the procedure described above suffer from poor mechanical properties. The films lack flexibility, either as free-standing films or as substrate-supported coatings. To improve the mechanical properties of photopolymerized polypyrrole films, large amphiphilic (surfactant) organic anions were incorporated into polypyrrole matrices [32]. Organic anions chosen were those that are constituents of sodium dodecyl sulfate (DDS) and sodium dodecylbenzene sulfonate (DDBS) salts. They were added to the already optimized photopolymerizable formulation that yielded polypyrrole films having the highest conductivity, i.e., pyrrole/AgNO$_3$ ratio of 8:1 and 3 wt.% of Irgacure 261 photoinitiator. Amounts added to the optimized formulation are expressed as pyrrole/surfactant molar ratios. Polypyrrole

Fig. 3 Dependence of curing time on the concentration of photoinitiator (Irgacure 261) initially added to a pyrrole-based photopolymerizable formulation containing pyrrole/AgNO$_3$=8:1

films were photopolymerized using these formulations under different illumination conditions and on various substrates. A postcure thermal treatment at the highest lamp irradiance was applied after photocuring, since this is recommended by the manufacturer for completion of the curing process when Irgacure 261 is used as photoinitiator.

Photopolymerization over the whole surface area of a cast formulation on each substrate was followed by observing black solidifying zones smoothly spreading over the substrates. It was evident that these additives helped the diffusion of polymerizing components in the thin cast formulation layers. However, curing was generally slower than for formulations without surfactant additives. Photopolymerized polypyrrole films obtained showed a significant improvement in mechanical properties. They were very flexible compared to polypyrrole films that did not contain surfactant additives. It was possible to bend these polymer films, whether coated on an aluminum metal foil or on polystyrene sheets, through angles greater than 90° without breaking them. Also, surfactant additives greatly improved the adherence of polymer films to substrates. More importantly, polypyrrole films thus formulated retained good electronic conductivity. DDBS was less soluble in pyrrole and gave rise to polymer films having lower flexibility when compared to similar films with DDS as additive. Electronic conductivity and polymer film thickness data for DDS- and DDBS-containing photopolymerized polypyrrole films are presented in Table 1.

The flexibility and adherence of polypyrrole films containing DDS as an additive, photopolymerized on Mylar® and Teflon® substrates are visually demonstrated in Fig. 5. The excellent adherence to untreated Teflon® was unexpected.

Electrochemical characterization of photopolymerized polypyrrole films

The magnitude of the current density in the cyclic voltammetric profile obtained from a yellow-colored photopolymerized film, prepared on photopolymerizing a formulation consisting of pyrrole and a photoinitiator (titanocene) only, was very low (cf. solid curve in Fig. 6a). The polymer film formed was electrochemically inactive compared to the well-known behavior of polypyrrole. This is not surprising, since transparent, yellow-colored, chemically prepared polypyrrole films have been found to be electronically insulating [9, 32]. Also, the film dissolved slowly in the H_2SO_4 solution when subjected to electrode potential cycling. On dissolving silver nitrate in pyrrole, a black polymer film characteristic of conducting polypyrrole was formed after curing under UV light. On subjecting this film to electrode potential cycling in aqueous 0.5 M H_2SO_4 for a period of 20 min, a stable voltammetric profile (cf. dashed curve in Fig. 6a) was obtained showing broad redox peaks characteristic of polypyrrole films. On keeping the amount of silver nitrate constant, various amounts of titanocene photoinitiator were added to photopolymerizable formulations. The photoinitiator had no effect on the electrochemical response of photopolymerized films; however, it shortened the cure times.

Nature of anodic/cathodic peaks in cyclic voltammograms

For freshly used photopolymerized polypyrrole films prepared using silver nitrate as electron acceptor/"dopant," the shape of the voltammetric profile characteristic of polypyrrole gradually developed with increasing number of electrode potential cycles (cf. Fig. 6b). Change and evolution of cyclic voltammetric profiles recorded for polypyrrole-coated platinum electrodes in monomer-free solutions were considered to be due either to solid state reactions and ion movement during charging and discharging or the as-prepared polymer films were much less charged than they could be [45]. The first, second, third, 20th, and 120th voltammetric scans are presented in Fig. 6b. In the initial three scans, a pair of quasireversible peaks centered at approximately 0.43 V (Ag/AgCl) can be seen. The current densities associated with both the anodic and cathodic peaks decreased in magnitude with cycle number and were absent for the longer scans. For this pair of peaks, the anodic peak is associated with electrochemically enhanced dissolution of silver metal grains incorporated into the polypyrrole polymer matrix to give Ag^+ cations in acid solution. The reversible potential for the Ag/Ag^+ redox couple in aqueous solutions under standard conditions is approximately 0.57 V (Ag/AgCl). The shift to the more cathodic value of approximately 0.43 V (Ag/AgCl) for the photopolymerized polypyrrole is partly due to

Table 1 Conductivity of photopolymerized polypyrrole films containing large organic anions (pyrrole/AgNO$_3$=8:1; pyrrole/surfactant=15:1; photoinitiator: 3 wt.% Irgacure 261; curing time: fast, 1.9 W cm^{-2} with a thermal postcure at 2.3 W cm^{-2})

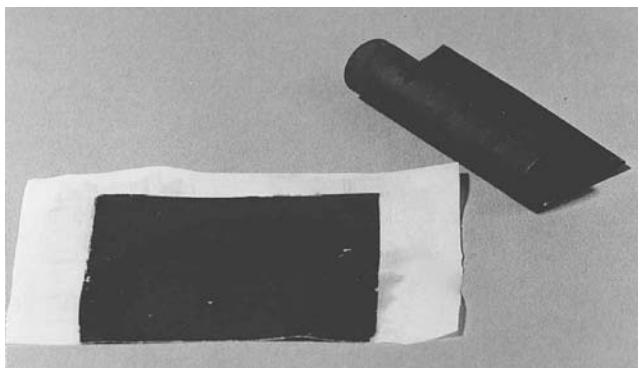| Additive	DDS		DDBS	
Substrate material	Conductivity (S cm^{-1})	Thickness (μm)	Conductivity (S cm^{-1})	Thickness (μm)
Free-standing	0.51	61	0.59	75
Polystyrene	0.48	39	0.32	62
Polymer film appearance	Smooth, black, curing time=1.3 min/layer, very flexible		Smooth, black, curing time=2 min/layer, flexible	

Fig. 5 Flexibility and adherence of photopolymerized polypyrrole films (derived from a photopolymerizable pyrrole-based formulation containing pyrrole/silver nitrate=8:1, pyrrole/DDS=20:1, and 3 wt.% Irgacure 261) on Teflon® 4.5×5.0 cm and on Mylar® 5.0×5.5 cm—polypyrrole film on Teflon® was approximately 40 μm thick and had an electronic conductivity of 0.34 S cm^{-1} while the polypyrrole film on Mylar® was approximately 20 μm thick and had an electronic conductivity of 0.27 S cm^{-1}

the nature of the interactions (electronic in particular) between the surfaces of the silver grains and the electronically conducting polypyrrole chains.

The cathodic peak is associated with the deposition of silver metal on the underlying platinum metal substrate through pores and voids in the polypyrrole film. Evidence in support of this is provided by a cyclic voltammetric investigation of a 2.9-μm thick poly(o-phenylenediamine) electronically conducting polymer film on gold where oxidation/reduction peaks characteristic of monolayer gold oxide formation and removal were observed in addition to and well separated from the charge storage peaks for the thick overlaying polymer film [46]. As in the present investigation, the polymer film was not degraded or destroyed. It was concluded that the polymer chains were anchored to the surface of the gold substrate at a few random points or small islands. Also, compact polypyrrole-coated platinum electrodes were observed to evolve hydrogen gas when polarized at electrode potentials approaching −3.0 V (Ag/AgCl) in aqueous solutions,
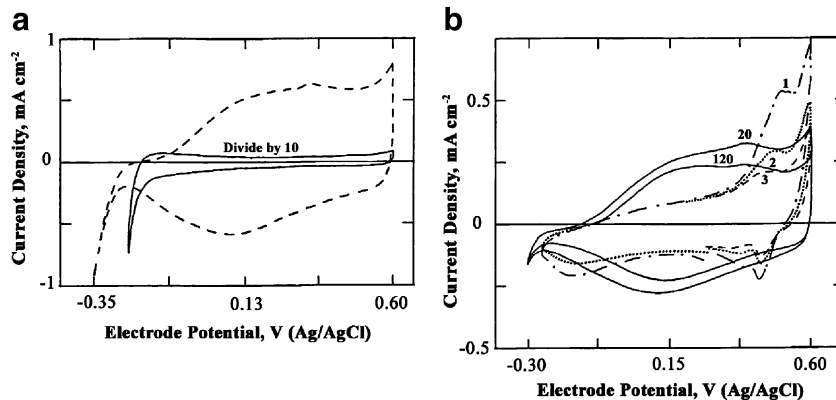
whereas free-standing polypyrrole films polarized at similar potentials gave rise to little or no hydrogen evolution [13], again demonstrating access of electrolyte solution to underlying conducting polymer film-covered metal substrates. Thus, the surface of the platinum substrate is most likely not fully passivated by the photopolymerized, hydrophilic polypyrrole film, and Ag$^+$-containing aqueous acid solution is able to penetrate to the platinum surface where deposition of silver can take place.

A SEM of the fracture surface of a photopolymerized polypyrrole film approximately 9 μm thick is presented in Fig. 7. In this case, the photopolymerized polymer film was made using a photopolymerizable formulation having a pyrrole/silver nitrate molar ratio of 8:0.192. The photopolymerized film is very porous, open-structured, and contains extensive voids, allowing ready access of acid solution to locations deep within the matrix of the polymer. The silver grains, although not easily recognized in this micrograph, are clearly shown to be uniformly distributed throughout polymer matrices in part II of this series of papers. Formation of the voids and porosity is primarily due to the volatilization of unreacted pyrrole monomers through the growing polymer film as it was being cured, since the formulation used was electron acceptor (silver cation) and "dopant" (nitrate anion) limited. Furthermore, as shown on electrochemically synthesizing polyaniline, incorporation of BF_4^-, ClO_4^-, and CF_3COO^- anions gave rise to more compact structures, while HSO_4^-, NO_3^-, or Cl^- anions yielded more open structures [47]. Also, in accordance with theoretical predictions [48], the densities of deposited conducting polymer films decrease with distance from the surfaces of the underlying substrates [49] (cf. Fig. 7).

With time, after a significant amount of the exposed incorporated silver metal grains accessible by the acid solution had dissolved, rearrangement of the polymer chains takes place. Multiple electrochemical oxidation/reduction cycles enables this rearrangement to occur as a result of a reorganization of the bonds in the polymer [47]. Because of this rearrangement, solution access to the underlying platinum metal substrate is hindered (or prevented), the silver redox

Fig. 6 Cyclic voltammograms recorded at a scan rate of 20 mV s^{-1} in 0.5 M sulfuric acid at 25 °C for photopolymerized polypyrrole films on platinum foil substrates—pyrrole/silver nitrate molar ratio of 8:0.192
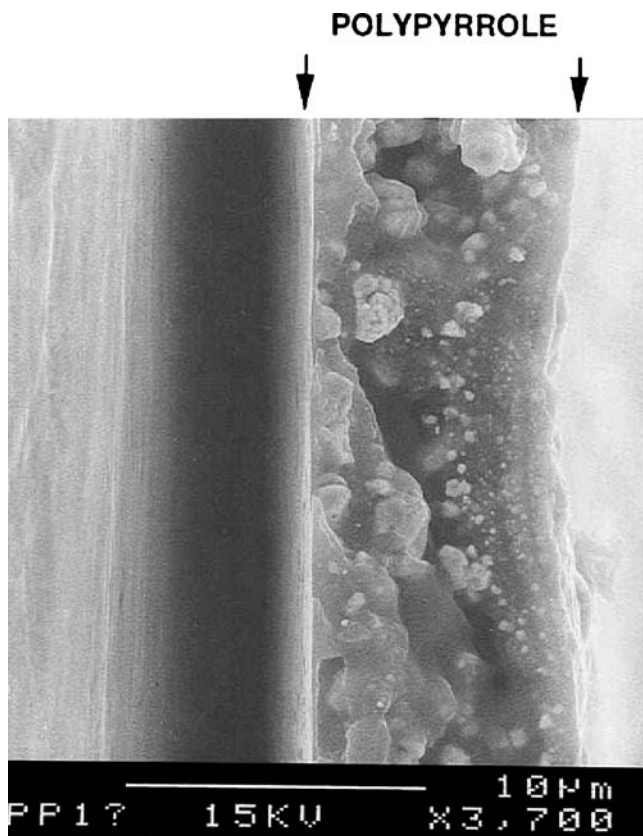
POLYPYRROLE

Fig. 7 SEM of the fracture surface of a photopolymerized polypyrrole film prepared using a pyrrole/silver nitrate molar ratio of 8:0.192 and Irgacure 784 as the photoinitiator
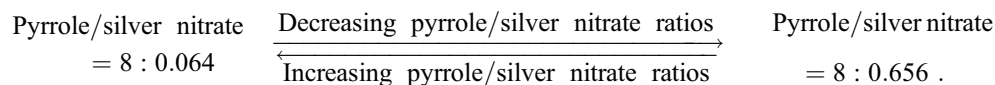
ruthenium metal. The maximum polymer film thickness investigated was 1.6 μm, and even then for lead, although deposition was observed, it occurred only as a slow process. It must be pointed out that the photopolymerized polypyrrole films used in this investigation were of the order of 10 μm in thickness, a factor of 6 greater.

An alternative explanation for the apparent disappearance of the silver redox process with electrode potential cycling, unrelated to the kinetics of the electrodeposition of silver on polypyrrole, involves the diffusion of silver cations away from the electrode surface into bulk solution with time resulting in an electrolyte-containing silver ions in a rather low concentration. Although likely to play a role, this effect may be of secondary importance only because of the role of very thick conducting polymer films on inhibiting or precluding the electrodeposition of metals [50].

Effect of pyrrole/silver nitrate molar ratio on charge storage capacity

Stable cyclic voltammetric profiles for photopolymerized polypyrrole films prepared using various $C_4H_4NH/AgNO_3$ molar ratios are presented in Fig. 8. As the molar ratio of pyrrole/silver nitrate decreased, background cathodic and anodic current densities increased for polymer films having the same apparent thickness based on the number of layers of each formulation applied to each platinum substrate and the composition of each formulation. Formulations having increasing pyrrole/silver nitrate molar ratios are increasingly electron acceptor (Ag^+) and "dopant" anion (NO_3^-) limited. Thus, two effects can be identified that are playing a role here. The first effect is that, for increasing pyrrole/silver nitrate molar ratios, the decreasing amount of Ag^+ cations present in formulations produces a decreasing amount of cation radicals yielding polypyrrole films that are actually thinner than for formulations having decreasing pyrrole/silver nitrate molar ratios. The second effect arises from the fact that, for increasing pyrrole/silver nitrate molar ratios, the conductivity of the polypyrrole films produced is decreasing (cf. Fig. 2) since, again, there is not enough available Ag^+ cations to oxidize but only a few of the pyrrole moieties incorporated into the growing polypyrrole chains to give a positively charged polymer backbone:

process no longer predominates, and the peaks characteristic of it are no longer visible. This demonstrates that the kinetics for the cathodic deposition of silver on the surface of polypyrrole is either very slow or the deposition reaction does not take place at all under the experimental conditions employed in this investigation. Support for these is provided by an account of the electrodeposition of a number of metals on electropolymerized polypyrrole films [50]. In all cases, even for very thin films, the primary influence of polypyrrole was to inhibit the initiation of metal deposition and the nucleation overpotential was increased by 50–300 mV. Also, electrodeposition of metals on polypyrrole was found to be very dependent on the thickness of the polymer films. In fact, for polymer films thicker than 30 nm, it was not possible to electrodeposit

$$\text{Pyrrole/silver nitrate} \quad \xrightarrow[\text{Increasing pyrrole/silver nitrate ratios}]{\text{Decreasing pyrrole/silver nitrate ratios}} \quad \text{Pyrrole/silver nitrate}$$
$$= 8 : 0.064 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = 8 : 0.656 \, .$$

Photopolymerized polypyrrole films that are thicker and have higher electrical conductivities as a result of decreasing

pyrrole/silver nitrate molar ratios give rise to better utilization of charge storage capacities. At the lowest pyrrole/silver
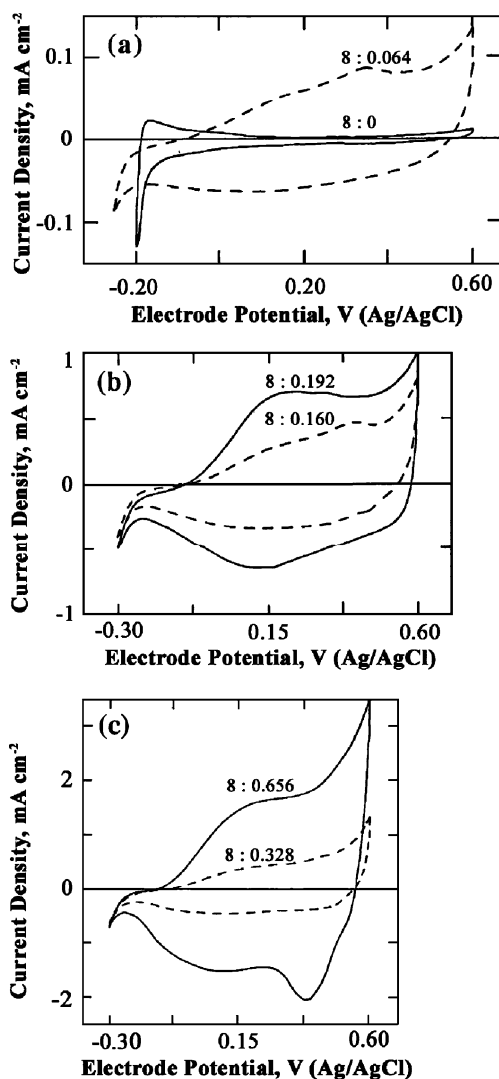
Fig. 8 Cyclic voltammograms recorded at a scan rate of 20 mV s^{-1} in 0.5 M sulfuric acid at 25 °C for photopolymerized polypyrrole films on platinum foil substrates—pyrrole/silver nitrate molar ratios are marked on the figures

nitrate molar ratio (8:0.656) (cf. Fig. 8c), the pair of peaks centered at approximately 0.42 V (Ag/AgCl) associated with the silver dissolution/deposition process is superimposed on the redox features characteristic of polypyrrole, even after undergoing extended electrode potential cycling. This demonstrates that the silver metal grains are an integral part of photopolymerized polypyrrole films. Evidently, for relatively thick photopolymerized polypyrrole films derived from formulations having low pyrrole/silver nitrate molar ratios and, hence, containing a relatively large amount of silver grains, long-term potential cycling is required even in strong aqueous acid solutions to dissolve nearly all of the silver out of the polymer matrices.

Effect of electrode potential cycling on charge storage capacity

In order to determine the stability and long-term electrochemical activity of photopolymerized polypyrrole films under conditions relevant to optoelectronic devices or batteries, a thick polymer film was subjected to long-term electrode potential cycling in 0.5 M H$_2$SO$_4$. Voltammetric profiles derived from a photopolymerized film are presented in Fig. 9. The letters a, b, c, d and e in the figure represent cycle numbers 93, 654, 1,589, 3,366, and 4,605, respectively. Loss of charge capacity on cycling the electrode potential may be due to the loss of some polymer particle/particle contact after silver metal dissolution takes place. Nonetheless, the profiles shown in Fig. 9 demonstrate reasonable stability and the potential suitability of this polymer material for a number of applications. Polypyrrole has been shown to have good oxidative stability in aqueous acid and neutral solutions [43].

The steady-state cyclic voltammetric profiles (cf. Figs. 6, 8, and 9) exhibit a combination of broad anodic and cathodic peaks with a plateau in the current densities at higher electrode potentials. Irreversible behavior between the main anodic and cathodic charge storage peaks is indicative of slow charge transport processes within the polymer films. This is to be expected since the photopolymerized polypyrrole films were thick (3–9 μm).

For applications including optoelectronic devices and batteries, both Coulombic capacity and the maximum number of charge/discharge cycles are important. The dependence of both charge and discharge capacity on the
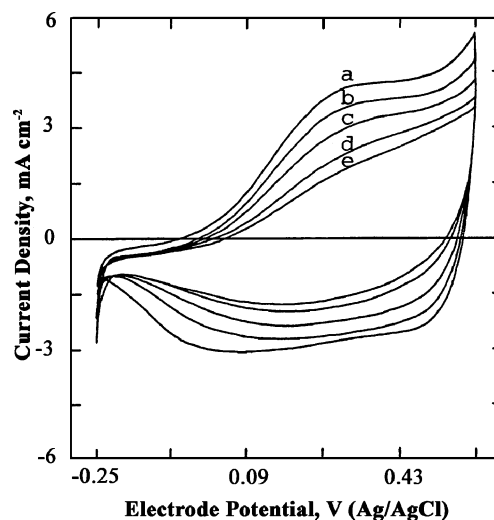

Fig. 9 Cyclic voltammograms recorded at a scan rate of 10 mV s^{-1} in 0.5 M sulfuric acid at 25 °C for a thick photopolymerized polypyrrole film on a platinum foil substrate—pyrrole/silver nitrate molar ratio of 8:0.656

cycle number for photopolymerized polypyrrole films prepared from formulations consisting of different pyrrole/electron acceptor/"dopant" molar ratios is shown in Fig. 10. More stable films were obtained at the higher concentrations of silver nitrate added to the formulations. Thus, acceptable stability for over 800 cycles (charge loss of only 10%) was obtained with films containing pyrrole/silver nitrate=4:1. Improved stability on cycling was obtained with films containing pyrrole/silver nitrate=5:1 and with dodecyl sulfate anions (DDS) added as flexibilizer (pyrrole/DDS=20:1). With this material after 1,000 cycles, only a small charge loss of about 15% occurred. Reasonable stability was retained after completing 3,000 cycles; 35% of the initial charge capacity was lost.

Electron transfer to and from an electrolyte-containing redox couple and electrochemical activity of photopolymerized polyaniline

The voltammetric response of photopolymerized polypyrrole films recorded in 0.5 M H_2SO_4 in the absence (solid curve) and in the presence (dashed curve) of 0.005 M quinone and hydroquinone are presented in Fig. 11. The pair of quasireversible peaks associated with the quinone/hydroquinone redox couple can be clearly seen, demonstrating that the surfaces of photopolymerized polypyrrole films are active electrochemically and capable of charge transfer to and from redox species in solution. Support for electrochemically active surfaces of intrinsically, electronically conducting polymers is provided by the fact that the rates for the electrochemical oxidation of hydroquinone and the reduction of quinone on polyaniline-coated gold
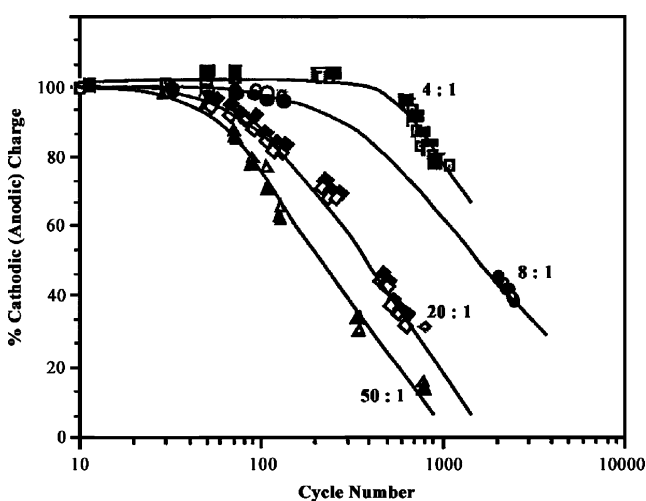

Fig. 11 Cyclic voltammograms recorded at a scan rate of 20 mV s^{-1} in 0.5 M sulfuric acid at 25 °C for a photopolymerized polypyrrole film on a platinum foil substrate in the absence (*solid curve*) and in the presence (*dashed curve*) of 5×10^{-3} M quinone and hydroquinone in the aqueous acid solution

electrodes at selected electrode potentials were significantly higher than the corresponding rates for a bare gold electrode in an aqueous 0.5 M H_2SO_4 solution [51]. Under these conditions, retardation of the rates of electron transfer on gold is due to the presence of a submonolayer gold oxide (or hydroxide) on its surface. For electronically conducting polymer films, there are no surface electrochemical processes taking place that inhibit electron transfer rates to redox couples in solution.

To demonstrate the versatility of the new photopolymerization process, polyaniline films were also photopolymerized on platinum foil substrates, using silver nitrate as the electron acceptor/"dopant" in aniline solutions of a photoinitiator. The cyclic voltammetric response of a photopolymerized polyaniline film is shown in Fig. 12. Similar to that observed for photopolymerized polypyrrole films, the first cyclic voltammogram recorded for photopolymerized polyaniline showed a pair of reversible redox peaks located at approximately 0.45 V (Ag/AgCl). Again, these are attributed to the dissolution of silver metal grains contained in the polymer film and redeposition of silver metal from silver cations in solution on solution-accessible areas of the underlying platinum substrate. These peaks are in addition to the broad pair of peaks centered at approximately 0.20–

Fig. 10 Variation of charge capacity with cycle number for photopolymerized polypyrrole films derived from formulations containing different pyrrole/AgNO₃ molar ratios and 3 wt.% Irgacure 261 during long-term electrode potential cycling in 0.5 M H_2SO_4 solutions at 25 °C
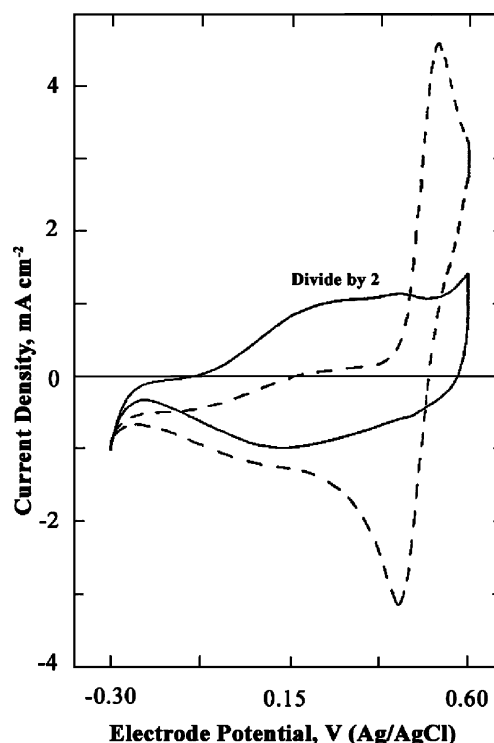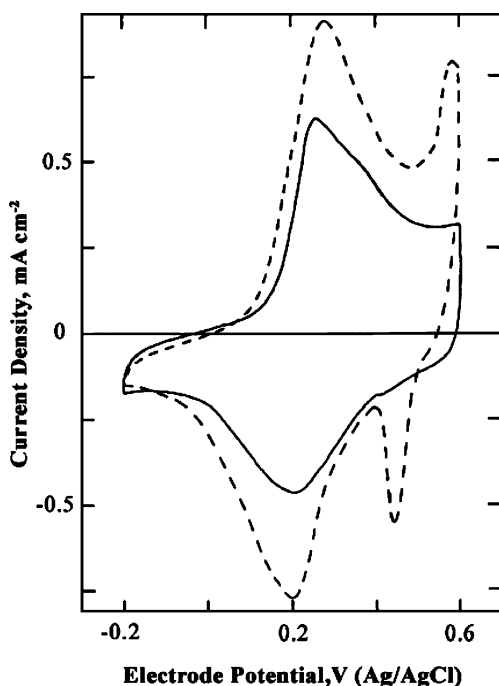
Fig. 12 Cyclic voltammograms recorded at a scan rate of 20 mV s^{-1} in 0.5 M sulfuric acid at 25 °C for a photopolymerized polyaniline film deposited on a platinum foil substrate: first cycle (*dashed curve*) and 15th cycle (*solid curve*)

0.25 V (Ag/AgCl) which are attributed to the redox behavior of polyaniline itself.

Cyclic voltammetric profiles of polyaniline recorded over a broad potential range [−0.15 to +1.0 V (Ag/AgCl)] in aqueous acid solutions display two anodic (oxidation) peaks and their corresponding cathodic (reduction) peaks [11]. The first pair of anodic/cathodic peaks at electrode potentials in the range of 0.20–0.25 V (Ag/AgCl) (cf. Fig. 12) corresponds to the oxidation/reduction of leucoemeraldine to the emeraldine form of polyaniline. The second pair of peaks is normally observed at electrode potentials in the range 0.75–0.825 V (Ag/AgCl) and has been attributed to the oxidation/reduction of emeraldine to the pernigraniline form of the polymer [11]. At the potentials of emeraldine stability, it has been noted that the polymer is protonated [52]. Clearly, the novel photopolymerization process has broad application for the preparation of electrochemically active, electronically conducting polymer materials containing silver grains.

Conclusions

Since the majority of commercial applications of intrinsically, electronically conducting polymers is likely to involve their use as thin or thick films deposited on conducting and nonconducting substrates, a photopolymerization process was developed that might satisfy this need.

It was demonstrated that UV light is sufficiently energetic to induce electron transfer from a pyrrole monomer species in a cast solution film to a suitably energetic electron acceptor, e.g., an Ag$^+$ cation of a salt such as silver nitrate, at fast rates in the presence (or absence) of a photoinitiator. An unexpected result of the process is the growth of silver metal grains having a broad size distribution as a result of the reduction of silver cations and the uniform distribution of the silver grains throughout photopolymerized conducting polymer matrices. Surprisingly, the nitrate anion-containing salt of silver proved to be much more effective than other anion salts of this element, e.g., nitrite, tetrafluoroborate, perchlorate, or tosylate. The developed process readily accommodates the addition of additives, such as surfactants, to photopolymerizable formulations. Silver-containing polypyrrole films incorporating the dodecyl sulfate anion as an additive had significantly improved mechanical properties; being very flexible and strongly adherent to underlying substrates, such as Mylar® and Teflon®. The excellent adherence to untreated Teflon® was unexpected.

Feasibility of the process was established by measuring electronic conductivities of various photopolymerized polymer films. The conductivities of the best films were about 1.0 S cm^{-1}. However, it is well-known that the conductivities of dry polymer films are affected by humidity and any vapor molecules present in the atmosphere that could interact electronically with the accessible surfaces of such films [33]. Polymer films obtained on photopolymerizing formulations containing pyrrole as a photoinitiator and silver nitrate as an electron acceptor/"dopant" anion were active electrochemically. They displayed voltammetric profiles characteristic of polypyrrole, a relatively slow loss of charge capacity on completing extended voltammetric cycling, and the capability of charge transfer to and from redox species in solution. It is suggested that these electronically conducting, black polymer films may find applications in optoelectronic devices, supercapacitors, and rechargeable batteries.

The initial voltammetric scans obtained from photopolymerized polypyrrole (and polyaniline) films containing a silver salt as electron acceptor/"dopant" anion displayed a pair of sharp redox peaks characteristic of the Ag/Ag$^+$ redox couple superimposed on the broad oxidation/reduction peaks characteristic of polypyrrole (and polyaniline). In the acid electrolyte used, it was shown that silver cations were leached from silver grains distributed uniformly throughout a porous, void-containing polymer matrix. However, in the dry state or in suitable aqueous and nonaqueous solutions, a random distribution of silver nanoparticles throughout porous (or nonporous) conducting polymer materials could give rise to application specific catalytic, optical, or sensing properties.

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