# Photoinduced and Thermal-Activated Doping of Polyaniline

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The reaction of 50% oxidized polyaniline (emeraldine base, EB) with alkyl halide and viologen in the dry state was studied using X-ray photoelectron spectroscopy, UV−visible absorption spectroscopy, and sheet resistance measurements. To facilitate this study, a low-density polyethylene substrate was first surface graft copolymerized with vinylbenzyl chloride or viologen moieties. A coating of polyaniline (PANI) was then deposited on the top of the film. Under UV irradiation or heat treatment at 65 °C or higher, the PANI reacted with the vinylbenzyl chloride and/or viologen, resulting in its conversion from the insulating base state to the conducting state. The conversion was more readily achieved with viologen, and a significant portion of the imine nitrogen of PANI was converted to positively charged nitrogen. The photoinduced method was more effective than the thermal-activated process in achieving a conducting PANI film. The most conductive film was obtained by irradiating the PANI−viologen film for 30 min or more using a 1 kW Hg lamp, and the conductivity achievable was about 1 order of magnitude lower than that of the conventional acid-protonated PANI film.

## Introduction

After the first intrinsic electrically conducting organic polymer, doped polyacetylene, was reported in 1977,[1] great interest in “conducting polymers” was spurred. Polyaniline (PANI), one of the most well-known conductive polymers, has been extensively studied for its interesting properties and practical applications.[2,3] Highly electrically conducting PANI can be achieved by protonic acid doping and oxidative doping. Protonic acid doping can be accomplished by treating PANI in its 50% oxidative state (emeraldine base, EB) with aqueous protonic acids such as 1 M aqueous HCl and is accompanied by a 9−10 orders of magnitude increase in conductivity.[4] This process results in the protonation of the imine nitrogen sites to yield polysemiquinone radical cations with the delocalization of the polarons along the chain. Oxidative doping, on the other hand, is different from the protonic acid doping in that the number of electrons associated with the polymer backbone changes during the oxidative doping process, while the number of H atoms on the backbone remains constant.[4−8]

In addition to these more conventional doping methods, several other novel methods have been proposed recently. Concurrent doping of PANI during the N-alkylation process was reported by Zhao et al.[9] The alkylation reactions and oxidative doping of PANI with organic electron acceptors are usually carried out in organic solvents, which may be unfavorable for substrates susceptible to such solvents. The conversion of PANI from the insulating to conducting state in aqueous viologen solutions, which represent a milder environment, was recently reported.[10] These previous studies on the doping of PANI are carried out in a solution or “wet” environment. However, there is recent growing interest in radiation-induced doping of PANI in the dry solid state because of the potential for a wide range of applications, and photoinduced doping of PANI involving the generation of acid upon UV irradiation has been reported.[11−14]

In the present paper, we report how photoinduced and thermal-activated doping of PANI in the dry state can be achieved through reaction with alkyl chloride and

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viologen. The reactions were carried out on PANI coated on a low-density polyethylene (LDPE) substrate that was graft modified with vinylbenzyl chloride (VBC) and viologen. The effects of UV-irradiation intensity, temperature, and graft density of VBC and viologen were investigated. The films were characterized by UV−visible absorption spectroscopy, X-ray photoelectron spectroscopy (XPS), and sheet resistance (Rs) measurements. The use of thin films of PANI on the transparent LDPE substrate allows the use of UV−visible absorption spectroscopy for easy and rapid monitoring of the changes occurring in the PANI during the course of the reaction.

## Experimental Section

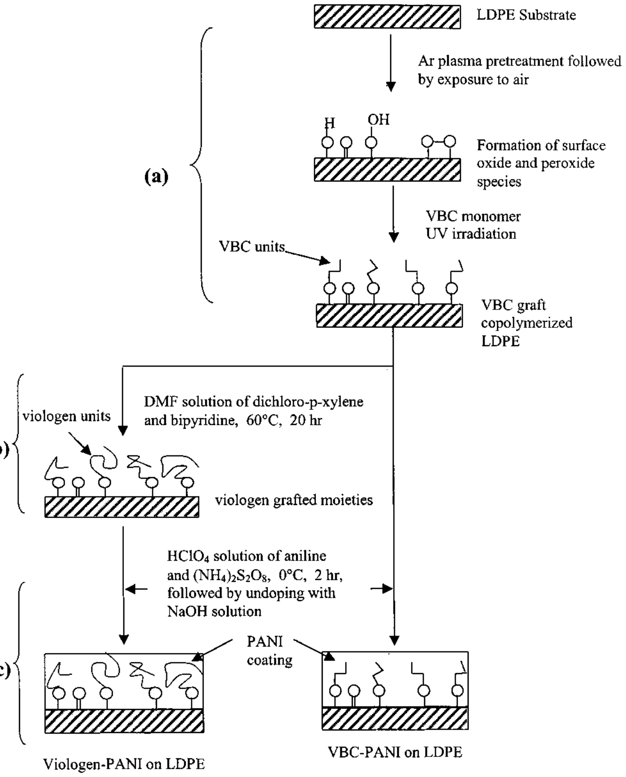
**Materials.** VBC (97%), dichloro-*p*-xylene, and 4,4′-bipyridine were obtained from Aldrich Chemical Co. The aniline monomer (99.5%), dimethylformamide (DMF), was obtained from Merck Chemical Co. The LDPE film (0.125 mm in thickness) was from Goodfellow Inc.

**Sample Preparation.** The LDPE films were first washed in acetone in an ultrasonic bath for 1 h to get rid of surface impurities and then dried under a dynamic vacuum in a desiccator. The cleaned films, cut into strips of 2 cm × 4 cm, were treated by argon plasma for 60 s on both sides, using an Anatech SP100 plasma system. The plasma power applied was kept at 36 W. These plasma-treated films were exposed to air for 5−10 min before proceeding with the graft copolymerization experiments. This results in the formation of the surface oxide and peroxide groups, which were utilized for initiating the graft copolymerization of VBC onto the plasma-treated LDPE films.[15,16]

The graft copolymerization of VBC with LDPE was carried out as shown in part a of Scheme 1. A small amount of VBC monomer was placed on both surfaces of the argon plasma-pretreated LDPE film, and then the films were sandwiched between two pieces of quartz plate. This assembly was inserted into a Pyrex tube and then exposed to UV irradiation in a Riko rotary photochemical reactor (RH400-10W) at 24−28 °C for either 30 or 40 min to achieve different VBC graft concentrations. The graft-copolymerized films were extracted from the quartz plates after soaking in DMF in an ultrasonic bath for 1 h and then washed thoroughly with DMF to remove the VBC homopolymer.

The viologen moieties were introduced via the reaction of the VBC graft-copolymerized films with an equimolar mixture of dichloro-*p*-xylene and 4,4′-bipyridine (0.06 M of each) in DMF at 60 °C for 20 h (part b of Scheme 1), which is similar to the preparation of ionene-type viologen polymers.[17,18] The reacted films were washed with DMF followed by deionized water to remove unreacted reactants and homopolymers. The viologen-grafted films were finally dried under reduced pressure.

**Scheme 1**



The coating of PANI onto the viologen- and VBC-grafted LDPE films was accomplished by immersing the films into a mixture of 0.1 M aniline and 0.025 M $(NH_4)_2S_2O_8$ in 1 M $HClO_4$ for 2 h at 0 °C (part c of Scheme 1). The films were then washed with 0.01 M aniline in a 1 M $HClO_4$ solution for 1 h followed by dipping into 0.5 M NaOH for 1 h to obtain the EB-coated films.[4] Finally, these films were washed with deionized water and dried under reduced pressure to obtain the VBC−PANI and viologen−PANI films.

**Testing and Characterization.** The irradiation of the VBC−PANI and viologen−PANI films was performed at a temperature between 24 and 28 °C, using a 1 kW Hg lamp in the Riko rotary reactor. The samples were placed in a Pyrex tube and positioned 5 cm from the light source. For investigations on the effect of light intensity on the samples, optical density filters (from Ealing Corp.) were used to reduce the transmission by 50% and 90%, respectively. In the experiments on thermal-activated doping, the films were put into an oven maintained at three different temperatures: 45, 65, and 85 °C. The experiment was not conducted at temperatures higher than 85 °C because of the thermal limitations of the LDPE substrate. The sheet resistance was measured right after the films were taken out of the oven. The Rs values measured as described are about 10−25% higher than the corresponding values obtained after the films have been cooled to room temperature.

The UV−visible absorption spectra of the films were obtained using a Shimadzu UV-3101 PC scanning spectrometer, with pristine LDPE films as the reference. XPS analysis of the films was made on an AXIS HSi spectrometer (Kratos Analytical Ltd.) using the monochromatized Al Kα X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of

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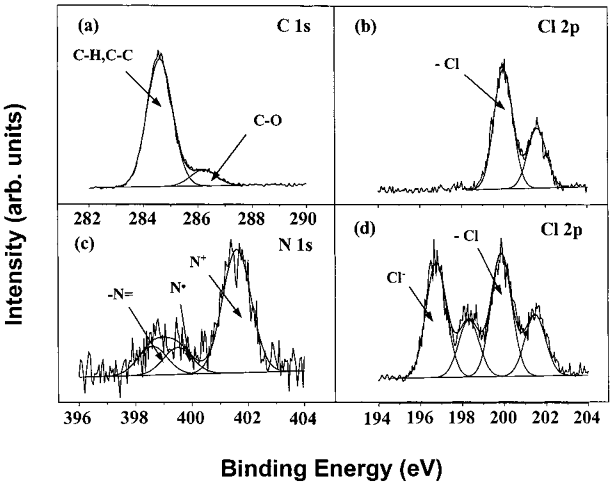


**Figure 1.** XPS: (a) C 1s and (b) Cl 2p core-level spectra of a VBC graft-copolymerized LDPE film (sample VBC-2); (c) N 1s and (d) Cl 2p core-level spectra of a viologen graft-modified LDPE film (sample Vio-2).

40 eV. The anode voltage was 15 kV and the anode current was 10 mA. The pressure in the analysis chamber was maintained at $5.0 \times 10^{-8}$ Torr or lower during each measurement. The films were mounted on the standard sample studs by means of double-sided adhesive tape. The core-level signals were obtained at a photoelectron takeoff angle of 90° (with respect to the sample surface). All binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.6 eV. In the peak synthesis, the line width (full width at half-maximum or fwhm) of the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak area ratios, after correction with the experimentally determined sensitivity factors, and were reliable to ±5%. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries. Sheet resistances of the films were measured using the standard two-probe method [conductivity = 1/(Rs × thickness of the film)].[19] The reported value is the average of 2 or more measurements, and for the more conductive samples (Rs $< 10^5$ Ω/sq), the relative error ranges from 10% to 50%.

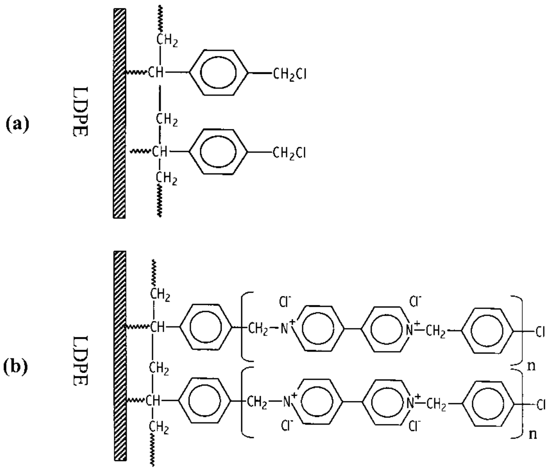
## Results and Discussion

**LDPE Graft-Modified with VBC and Viologen.** After the pristine LDPE film was graft-copolymerized with VBC, it becomes less transparent. After the introduction of the viologen moieties onto the VBC-grafted film, the film becomes pale yellow. The success of surface graft copolymerization of VBC and viologen on the LDPE substrates is ascertained by XPS analysis as shown in Figure 1. The C 1s core-level spectra of these films (Figure 1a) show a dominant peak at 284.6 eV representing the C−H bonds and a smaller peak at a BE of 286.2 eV attributed to C−O.[20] For the VBC graft-copolymerized LDPE film, the Cl 2p core-level spectrum (Figure 1b) shows a spin−orbit split doublet (Cl $2p_{3/2}$ and Cl $2p_{1/2}$) with peaks at 200.2 and 201.7 eV attributable to covalent Cl.[20−22] A representation of the VBC-surface graft-copolymerized LDPE is shown in part a of Chart 1. Based on the XPS analysis, the VBC graft copolymer density defined as moles of VBC per mole of LDPE repeat unit can be calculated as follows:

$$\frac{M_{\mathrm{VBC}}}{M_{\mathrm{Ethylene}}} = \frac{\text{peak area of Cl 2p}}{(\text{peak area of total C 1s} - 9 \times \text{peak area of Cl 2p})/2}$$

where the peak areas have been corrected with the appropriate sensitivity factors and the stoichiometric factors of 9 and 2 are introduced to account for the nine C atoms per VBC unit and two C atoms per repeating units of the LDPE substrate. The graft concentration as calculated above is used as a basis for comparing the results obtained under different conditions.

**Chart 1**



For viologen-grafted films, a N 1s signal was observed, indicating the existence of the pyridine rings. An idealized situation in which all of the VBC units have reacted with the bipyridine and dichloro-*p*-xylene to form the viologen moieties is shown in part b of Chart 1. The N 1s core-level spectra of the viologen-grafted films can be deconvoluted into three peaks with BEs at 398.6, 399.5, and 401.7 eV (Figure 1c). The first peak at 398.6 eV suggests the presence of unreacted imine nitrogen of the pyridine rings.[23] The peak at 399.5 eV is attributed to the viologen radical cation formed during X-ray excitation in the analysis chamber, and the peak at the highest BE is attributed to the positively charged nitrogen of the diquaternized bipyridine molecules.[24] The corresponding Cl 2p core-level spectra of the viologen-grafted films are resolved into two-spin−orbit split doublets with BEs for the Cl $2p_{3/2}$ peaks at 197.1 and 200.1 eV (Figure 1d) attributable to ionic ($Cl^-$) and

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**Table 1. Surface Compositions of VBC Graft-Copolymerized and Viologen Graft-Modified LDPE Films**

| sample | | synthesis condition | surface composition[a] | | | | VBC grafting density |
|---|---|---|---|---|---|---|---|
| | | | $Cl_T/C$ | $-Cl/Cl_T$ | N/C | $Cl_T/N$ | |
| VBC graft-copolymerized LDPE film | VBC-1 | Ar plasma pretreatment for 60 s, UV-induced graft copolymerization for 30 min | 0.013 | 1.0 | | | 0.03 |
| | VBC-2 | Ar plasma pretreatment for 60 s, UV-induced graft copolymerization for 40 min | 0.056 | 1.0 | | | 0.21 |
| viologen graft-modified LDPE film | Vio-1 | sample VBC-1 treated with a DMF solution of equimolar dichloro-*p*-xylene and bipyridine at 60 °C for 20 h | 0.018 | 0.68 | 0.017 | 1.02 | 0.03 |
| | Vio-2 | sample VBC-2 treated with a DMF solution of equimolar dichloro-*p*-xylene and bipyridine at 60 °C for 20 h | 0.047 | 0.52 | 0.046 | 1.01 | 0.21 |

[a] As determined from XPS analysis. $Cl_T$ denotes total Cl species while −Cl denotes covalently bonded Cl.

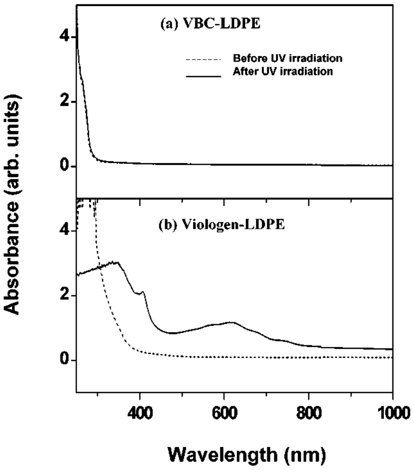

**Figure 2.** UV−visible absorption spectra of (a) sample VBC-2 and (b) sample Vio-2 before irradiation and after irradiation for 30 min.

covalent (−Cl) chlorine species, respectively.[20−22] The amount of viologen grafted on the LDPE surface can be qualitatively inferred from the [N]/[C] ratio and the ratio of the covalent Cl ([−Cl]/[$Cl_T$]) of the films. A high [N]/[C] ratio would indicate that a large number of the bipyridine units was successfully introduced, whereas a high [−Cl]/[$Cl_T$] ratio would imply that a number of VBC graft copolymer units did not react with the bipyridine units, although some dichloro-*p*-xylene serving as end groups would also contribute to the covalent chlorine species (please refer to part b of Chart 1).

The surface compositions of the VBC graft-copolymerized and viologen graft-modified LDPE films as determined from the XPS analysis are summarized in Table 1. It can be seen from this table that an increase in the UV-induced graft copolymerization time of VBC from 30 to 40 min results in a very substantial increase in the VBC graft density. The higher VBC graft density, in turn, results in more viologen moieties being grafted in step b of Scheme 1. This is evidenced by the higher [N]/[C] ratio and lower [−Cl]/[$Cl_T$] ratio in sample Vio-2 compared to sample Vio-1 (Table 1).

Figure 2 shows the UV−visible spectrum of a VBC graft-copolymerized LDPE film (sample VBC-2) and a viologen graft-modified LDPE film (sample Vio-2) before and after irradiation for 30 min. From Figure 2a, it can be seen that there is no detectable difference between the spectra of the VBC graft-copolymerized LDPE film before and after irradiation. However, for a viologen-grafted film (sample Vio-2), the film turns blue after UV irradiation in an evacuated quartz cell and a peak is observed at around 610 nm, as shown in Figure 2b. This peak is due to the highly colored radical cation produced by the transfer of one electron from the counteranion ($Cl^-$) to viologen dication during photoirradiation.[25] However, bleaching of the color is very fast once the film is exposed to air, and the film will return to the dication state. The sheet resistances of the viologen graft-copolymerized film before and after irradiation were similar at about $2.7 \times 10^7$ Ω/sq, while the VBC graft-copolymerized film remains insulating ($>10^{10}$ Ω/sq) before and after irradiation. These results will be compared to those of the VBC−PANI film and viologen−PANI film below.

**Photoinduced Doping of PANI Films.** The VBC−PANI film and viologen−PANI film were blue in color, as expected of PANI in the insulating EB state which was coated on the film surface. Upon exposure of these films to the irradiation from the 1 kW Hg lamp, the color of these films changed to green, and this gives the first indication of the conversion of the PANI from the insulating base state to the conducting salt state. The UV−visible absorption spectra of these films before and after irradiation are illustrated in Figure 3a,b. The absorption spectra of EB films before irradiation is expected to show two absorption peaks at around 325 and 620 nm, which are due to $\pi-\pi^*$ transition of the benzenoid rings and exciton absorption of the quinoid rings, respectively.[26] For the VBC−PANI and viologen−PANI films, the band in the 325 nm region would be associated with EB and either VBC or viologen.[27,28] As can be seen from Figure 3 ($t = 0$ curves), the absorbance in the 325 nm region is higher for the viologen−PANI film than for the VBC−PANI film, consistent with the larger number of benzene rings in the former. The exciton peak is clearly seen in both spectra. Upon irradiation, there is a decrease in the exciton absorption peak intensity and the appearance of new bands at 430 nm and beyond 800 nm. These two new bands are due to the formation of the polaron/bipolaron structure and are characteristic of doped and conductive PANI.[28,29] When parts a and b of Figure 3 are compared, it is evident that the photoinduced doping of the viologen−PANI film is more rapid than that observable with the VBC−PANI film.

The XPS N 1s and Cl 2p core-level spectra of the VBC−PANI and viologen−PANI films before and after

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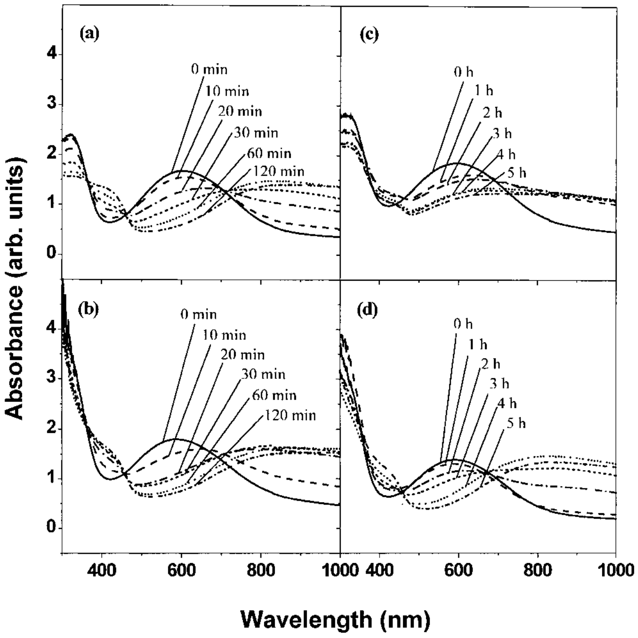

**Figure 3.** UV–visible absorption spectra of (a) VBC–PANI film (film VBC-2A) and (b) viologen–PANI film (film Vio-2A), after irradiation in air for various periods of time, (c) VBC–PANI film (film VBC-2A), and (d) viologen–PANI film (film Vio-2A), after thermal treatment at 85 °C for various periods of time.

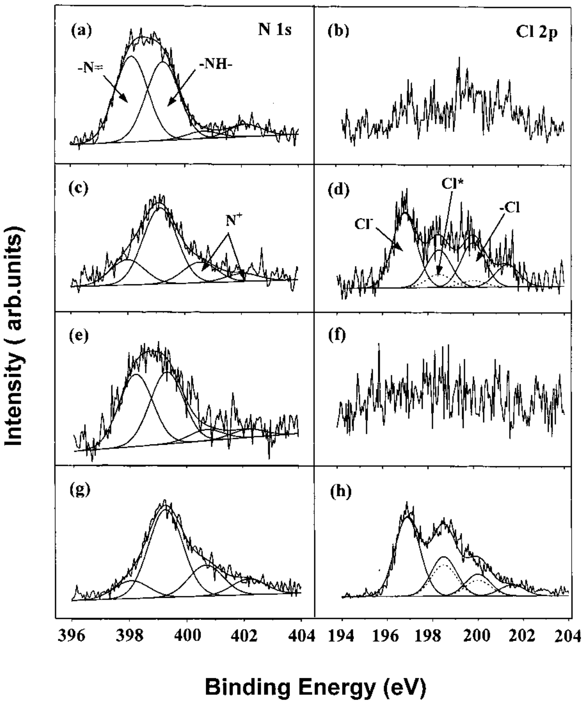

**Figure 4.** N 1s and Cl 2p core-level spectra of (a and b) VBC–PANI film before irradiation (film VBC-2A), (c and d) VBC–PANI film after irradiation in air for 2 h (film VBC-2B), (e and f) viologen–PANI film before irradiation (film Vio-2A), and (g and h) viologen–PANI film after irradiation in air for 2 h (film Vio-2B).

irradiation are shown in Figure 4. The N 1s spectra of the VBC–PANI and viologen–PANI films before irradiation (film VBC-2A and Vio-2A as shown in parts a and e of Figure 4, respectively) have similar peak shapes, which can be curve fitted with two major components with BEs at about 398.2 and 399.4 eV. These peaks are assigned to the imine (–N=) and amine (–NH–) nitrogens of PANI, respectively.[30,31] The almost equal amounts of imine and amine nitrogen in the N 1s core-level spectrum of PANI-coated films before irradiation are consistent with the structure of EB. The smaller peaks at BEs greater than 400 eV can be attributed to the positively charged nitrogen on the PANI backbone possibly because of some surface oxidation. From Figure 4b,f, the chlorine signal of the VBC–PANI and viologen–PANI films was found to be insignificant before irradiation. This implies that the PANI coating is thicker than about 7.5 nm, which is regarded as the probing depth of the XPS technique in an organic matrix.[32] This corroborates the similarity of the spectra in Figure 4a,e with that of EB; i.e., the contribution from the viologen N is not significant in Figure 4e.

After irradiation of the VBC–PANI and viologen–PANI films for 2 h, there is an increase in the intensity of the Cl 2p signals as shown in Figure 4d,h. The Cl 2p core-level spectra of these irradiated films, VBC-2B and Vio-2B, can be deconvoluted into three-spin–orbit split doublets (Cl $2p_{3/2}$ and Cl $2p_{1/2}$), with the BE for the Cl $2p_{3/2}$ peaks at about 197.1, 198.6, and 200.2 eV.[20–22] The first component can be assigned to the ionic chlorine ($Cl^-$) and the third to the covalent chlorine (–Cl), while the second is assigned to the intermediate chloride species, Cl*, which has been widely observed.[33–36] This intermediate chloride species is associated with anionic chloride species resulting from the charge-transfer interactions between the halogen and the metal-like conducting state of the polymer chain.[37] In both cases, more than 50% of the chlorine exists as the ($Cl^-$ + Cl*) species. It has been reported earlier that PANI reacts with alkyl halide in organic solvents, resulting in N alkylation of the imine units.[9] This reaction can be classified as an aliphatic nucleophilic substitution, whereby the imine N is converted to $N^+$ and halide ions are formed in the process. It is postulated that a similar reaction takes place in the VBC–PANI film under irradiation. Because the imine nitrogen is preferentially attacked by alkyl halides, the chloride ions formed during the alkylation then serve as the counterions to the $N^+$ components of PANI, resulting in the doping of PANI.[37] A comparison of the N 1s core-level spectra of film VBC-2A (Figure 4a) and film VBC-2B (Figure 4c) shows a decrease in the proportion of imine N and a simultaneous increase in the proportion of positively charged nitrogen after irradiation, thus supporting this postulate. The increase in the Cl 2p signal observed after irradiation may be due to the greater electrostatic interaction between the $Cl^-$ anions and the positively charged PANI, resulting in the PANI coating "sinking in" and/or the migration of the $Cl^-$ anions from the inner

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**Table 2. Surface Compositions and Rs Values of VBC−PANI and Viologen−PANI Films**

| film | treatment conditions | $-N{=}/N$ | $-NH-/N$ | $N^+/N$ | $-Cl/Cl_T$ | $(Cl^- + Cl^*)/Cl_T$ | $Cl_T/N$ | $(Cl^- + Cl^*)/N^+$ | Rs (Ω/sq) |
|---|---|---|---|---|---|---|---|---|---|
| VBC−PANI Film (Sample VBC-2 Coated with PANI) | | | | | | | | | |
| VBC-2A | nil | 0.47 | 0.43 | 0.10 | | | | | $10^{10}$ |
| VBC-2B | after irradiation for 2 h | 0.19 | 0.59 | 0.22 | 0.34 | 0.66 | 0.18 | 0.54 | $2.4 \times 10^5$ |
| VBC-2C | after thermal treatment at 85 °C for 5 h | 0.17 | 0.67 | 0.16 | 0.74 | 0.26 | 0.43 | 0.70 | $1.7 \times 10^7$ |
| Viologen−PANI Film (Sample Vio-2 Coated with PANI) | | | | | | | | | |
| Vio-2A | nil | 0.44 | 0.44 | 0.12 | | | | | $10^{10}$ |
| Vio-2B | after irradiation for 2 h | 0.12 | 0.58 | 0.30 | 0.16 | 0.84 | 0.42 | 1.16 | $3.0 \times 10^4$ |
| Vio-2C | after thermal treatment at 85 °C for 5 h | 0.14 | 0.57 | 0.29 | 0.06 | 0.94 | 0.35 | 1.12 | $1.8 \times 10^5$ |

VBC graft copolymer layer toward the outer PANI layer. It should be noted that the ratio of $(Cl^- + Cl^*)/N^+$ is substantially less than 1 (Table 2). Because charge neutrality is expected to be maintained, it is postulated that a portion of $N^+$ is balanced by some negative oxygen species.

In the case of the viologen−PANI film, a comparison of the N 1s core-level spectra before and after irradiation also shows a decrease in the proportion of imine N and a simultaneous increase in the proportion of positively charged nitrogens after irradiation as shown in Figure 4e,g and Table 2, again confirming the formation of charge carriers in the PANI coating of the irradiated film. It should be noted from Table 2 that there is also an increase in the proportion of amine groups after irradiation of the VBC−PANI and viologen−PANI films. This may be due to the reduction of some imine groups of the PANI to amine groups. In the case of the viologen−PANI film, a greater amount of viologen radical cations may also be detected because of the change in the arrangement of the PANI and viologen chains after irradiation as a result of electrostatic interactions as mentioned above. The XPS data are consistent with the UV−visible absorption spectra (Figure 3a,b), which show a decrease in the exciton peak due to the quinoid rings after irradiation.

The irradiation of the viologen−PANI film is expected to result in the initial reduction of the viologen whereby the viologen dications ($V^{2+}$) are converted to the viologen radical cations ($V^{\bullet+}$)[17,38] and Cl radicals. It is proposed that these reactive Cl radicals may extract electrons from the PANI, resulting in the formation of positive polarons and $Cl^-$ counterions. The decrease of the $-N{=}$ species and the corresponding increase in $N^+$ indicate the preferential interaction of the $-N{=}$ units with viologen under irradiation.

The conversion of films VBC-2A and Vio-2A from the base state to the doped state results in a decrease in their sheet resistance, Rs, as shown in Figure 5. Because the Rs values of the VBC graft-copolymerized LDPE film (sample VBC-2) and the viologen graft-modified LDPE film (sample Vio-2) do not change significantly upon irradiation as mentioned above, the decrease in Rs of films VBC-2A and Vio-2A after irradiation confirms that the doping of PANI resulted from the reaction of PANI with alkyl chloride and viologen, respectively. After 30 min of irradiation, the sheet resistance of film Vio-2A decreases sharply from $\sim 10^{10}$ to $5 \times 10^4$ Ω/sq, compared with film VBC-2A in which a Rs of $10^7$ Ω/sq is achieved during the same period of irradiation. The slower rate of conversion of the PANI from the insulating to conducting state in the VBC−PANI film as compared to the viologen−PANI film is consistent with the UV−visible absorption spectroscopy results in Figure 3a,b and the difference in the $N^+/N$ ratios [$N^+/N = 0.30$ for the viologen−PANI film (film Vio-2B) versus $N^+/N = 0.22$ for the VBC−PANI film (film VBC-2B)]. In Figure 3, the long absorption tail extending beyond 800 nm into the infrared region is attributed to the polaron band structure of the PANI as it undergoes doping.[28] As can be seen from Figure 3b, the highest degree of change in this region is during the first 20 min of irradiation, which also corresponds to the sharpest drop in Rs in film Vio-2A (Figure 5). After this initial period, the spectral changes in the region >800 nm for film Vio-2A are minimal, and the changes are essentially in the region <800 nm, which may reflect some changes in the electronic structure of the PANI that do not have a strong effect on Rs. It should also be recognized that the UV absorption spectroscopy technique is highly sensitive and the spectrum is representative of the structure of the entire film (surface and bulk), whereas the Rs measurement is more limited to the surface region. In the case of film VBC-2A, the polaron band structure and Rs continue to change substantially even after 30 min (Figures 3a and 5). The results presented above clearly show that the photoinduced doping of PANI is more effectively achieved with viologen than alkyl halide. The Rs value of $5 \times 10^4$ Ω/sq is about 1 order of magnitude higher than that obtained with a PANI (EB state) film protonated with 1 M $HClO_4$.[37]

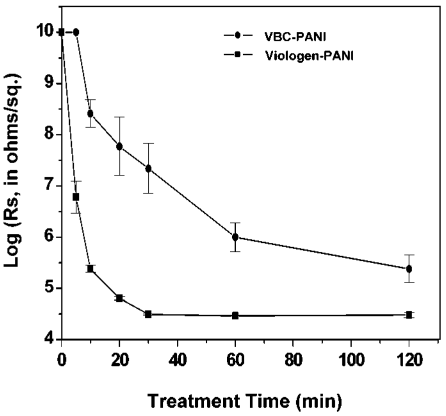

**Figure 5.** Sheet resistance (Rs) of VBC−PANI film (film VBC-2A) and viologen−PANI film (film Vio-2A) after irradiation in air for various periods of time.

**(i) Effect of UV Intensity.** The rate of decrease in Rs of the PANI films provides a convenient indication of the conversion of the PANI from the insulating EB state to the doped state. The effect of the UV intensity on this process is shown in Figure 6. When the light intensity was reduced by 90%, neither film Vio-2A nor film VBC-2A shows any sign of doping after 2 h of irradiation and the Rs of these films remains at about

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[38] Kamogawa, H.; Masui, T.; Amemiya, S. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 383.

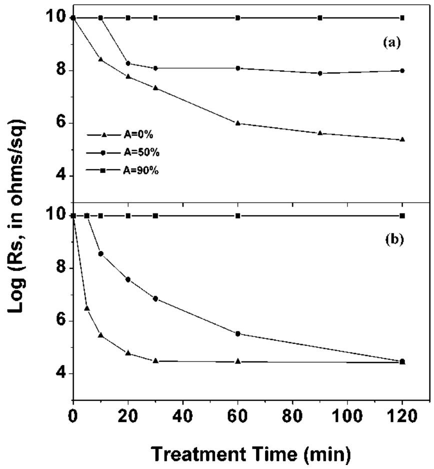

**Figure 6.** Sheet resistance (Rs) of (a) VBC−PANI film (film VBC-2A) and (b) viologen−PANI film (film Vio-2A) after exposure to irradiation of different intensities in air for various periods of time. *A* is the degree of attenuation of the irradiation.

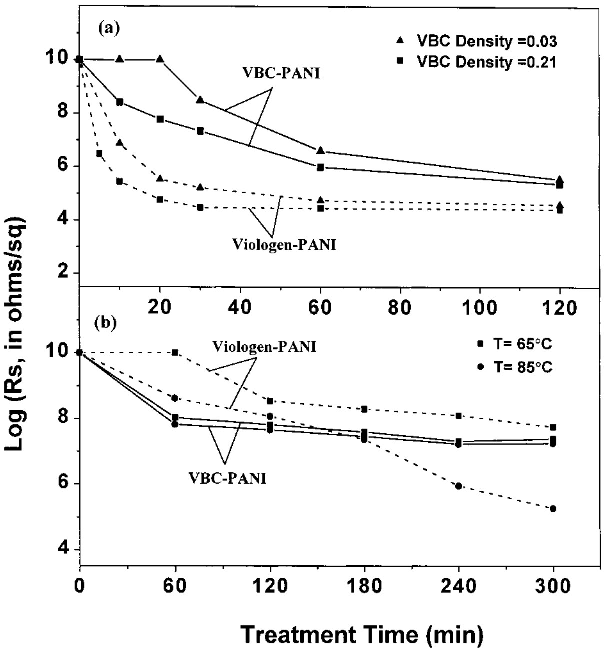

**Figure 7.** Comparison of the sheet resistance (Rs) of (a) VBC−PANI film (films VBC-1A and -2A) and viologen−PANI film (films Vio-1A and -2A), of different VBC graft densities after irradiation in air for various periods of time, and of (b) VBC−PANI film (film VBC-2A) and viologen−PANI film (film Vio-2A), after thermal treatment at 65 and 85 °C for various periods of time.

$10^{10}$ Ω/sq. With 50% attenuation of the light intensity, the Rs of film VBC-2A decreases to only 3 × $10^8$ Ω/sq after 20 min of irradiation and no further reduction was observed. In contrast, the Rs of film Vio-2A shows a steady decrease, and after 2 h of irradiation, the Rs is similar to that achievable within 30 min without attenuation of the light intensity. Thus, Figure 6 shows that the intensity of the UV irradiation is an important factor in determining the extent of conversion of PANI from the insulating to conducting state, especially in the reaction with VBC.

**(ii) Effect of VBC Graft Density.** The VBC graft density can be varied by changing the UV irradiation time in the Riko UV reactor in part a of Scheme 1. The VBC graft density increases substantially when the time of UV irradiation is increased from 30 to 40 min (Table 1). A higher VBC graft density also allows for more viologen moieties to be grafted, as indicated by the higher [N]/[C] ratio in Table 1. A comparison of the Rs of these two sets of films (films VBC-1A and -2A and films Vio-1A and -2A) upon irradiation is given in Figure 7a. As can be seen from this figure, the VBC density has a larger effect on the Rs of the VBC−PANI film as compared to those of the viologen−PANI film, especially in the initial stages of irradiation. After 2 h of irradiation, the Rs values obtained are very similar even though the VBC graft density differs by a factor of 7. This indicates that even at a graft density of 0.03 a sufficient number of VBC groups are available to achieve alkylation of the thin PANI layer. Similarly, the number of viologen moieties grafted at a VBC graft density of 0.03 is also sufficient to achieve the doping of PANI. This relative insensitivity of the PANI doping process to the number of VBC and viologen groups is probably due to the interaction of the PANI with the VBC and viologen groups being confined to the interfacial region only. The results presented were obtained with thin PANI films. If the PANI layer is significantly thicker, the effectiveness of the photoinduced doping method would be diminished for two reasons. First, the confinement of the VBC and viologen groups to the interfacial region may restrict the doping process to this region, and the surface of the PANI film may not achieve a similar conductivity level. Second, a thicker PANI layer may significantly attenuate the intensity of the irradiation, and as shown in Figure 6, the intensity of the irradiation is an important factor in determining the level of conductivity achieved.

**Thermal-Activated Doping of PANI Films.** Films VBC-2A and Vio-2A exhibit no visual change after thermal treatment for 5 h at 45 °C. These films remain in the insulating state with an Rs of about $10^{10}$ Ω/sq. However, after heating to 65 °C, film VBC-2A turns green after 2 h and a decrease in Rs is observed, as shown in Figure 7b. From this figure, it is obvious that increasing the temperature to 85 °C does not significantly change the rate of decrease of Rs and the value achieved after 4 h (about 3 × $10^7$ Ω/sq). From Figure 7b it can be seen that the viologen−PANI film is more sensitive to temperature as compared to the VBC−PANI film. At 65 °C, film Vio-2A attains a conductivity level similar to that of film VBC-2A after 5 h. However, with an increase in temperature to 85 °C, film Vio-2A becomes 2 orders of magnitude more conductive than the latter. The differences in Rs for the VBC and viologen graft-modified film as presented in Figure 7b are consistent with the UV−visible absorption spectroscopy results shown in Figure 3c,d. In the first 2 h, the doping of the VBC−PANI film proceeds at a faster rate than that of the viologen−PANI film, as reflected by the lower Rs and higher degree of change in the UV−visible absorption spectra of the former. However, after 5 h the characteristics of a doped PANI state are more evident in the viologen−PANI film (Figure 3d) as shown by the disappearance of the exciton band and the higher intensity of the absorption tail in the near-IR region.

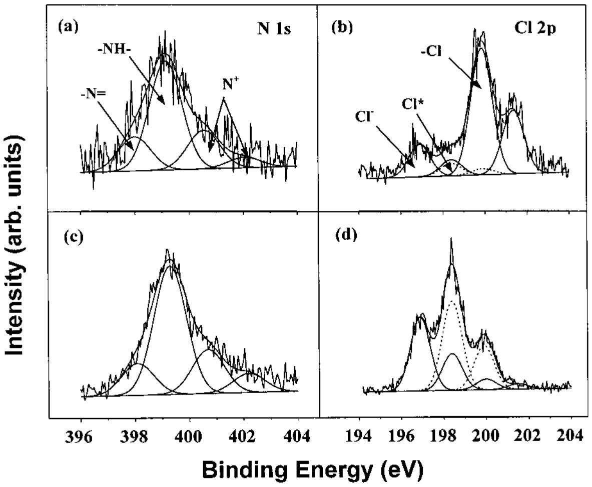

**Figure 8.** (a) N 1s and (b) Cl 2p core-level spectra of VBC−PANI film after thermal treatment at 85 °C for 2 h (film VBC-2C); (c) N 1s and (d) Cl 2p core-level spectra of viologen−PANI film after thermal treatment at 85 °C for 2 h (film Vio-2C).

The XPS N 1s and Cl 2p core-level spectra of the VBC−PANI and viologen−PANI films after thermal treatment at 85 °C for 5 h (films VBC-2C and Vio-2C, respectively) are shown in Figure 8. The N 1s and Cl 2p core-level spectra of these films before thermal treatment are similar to the spectra in Figure 4a,b,e,f. As described previously, before thermal treatment, the N 1s spectra are representative of the EB state with approximately equal proportions of −N= and −NH− components. After the thermal treatment at 85 °C, there is a substantial decrease in the proportion of imine units. At the same time, a high BE tail (>400 eV) appears, attributable to the formation of positively charged nitrogen ($N^+$). After 5 h treatment, the Cl 2p signals of both the VBC−PANI and viologen−PANI films increase in intensity. The appearance of the $Cl^-$ and Cl* peaks in the Cl 2p spectrum of films VBC-2C and Vio-2C provides an indication of the interaction of PANI with the VBC and viologen upon activation by thermal energy. It can be seen from Figure 8 and Table 2 that, in film Vio-2C, a large proportion of the Cl species exists as $Cl^-$ or Cl* and $N^+$ is closely balanced by the $Cl^-$ or Cl* species. In film VBC-2C, the bulk of the Cl species is covalently bonded Cl and the $(Cl^- + Cl^*)/N^+$ ratio is again substantially less than 1, similar to that observed with film VBC-2B. Hence, the possibility of negatively charged oxygen serving as counterions is again postulated.

The effect of temperature on the doping behavior of the VBC−PANI and viologen−PANI films may be attributed not only to the energy requirements of the two reactions but also to the possible change in the PANI morphology as the temperature increases. It has been reported that PANI (in the EB state) has two glass transition temperatures, ~70 and ~250 °C.[39] When the thermal treatment is at 65 °C, below the first glass transition temperature, the PANI chains are in a glassy state. When the treatment temperature is increased to 85 °C, the mobility of PANI chains increases. In the case of the VBC−PANI film, the fact that an increase in temperature from 65 to 85 °C has very little effect on the doping process indicates that the energy supplied is adequate to initiate the nucleophilic reaction and the morphological changes do not play a significant role. Previous work on N alkylation of PANI by alkyl halides in DMF showed that an increase in the temperature from 65 to 80 °C has an effect on Rs only in the initial stages of the reaction, and after 4 h, the Rs achieved at the two temperatures are very similar.[9] There is limited data available on the effect of temperature on the viologens. It has been reported that, above 180 °C, methyl viologen dication ($MV^{2+}$) can be reduced to the viologen radical cation ($MV^{+\bullet}$), with the electron coming from the oxidation of the chloride counterion.[40] For the viologen−PANI film, the reaction may also be initiated by the thermal reduction of the viologen dications to the radical cations, followed by the electron-transfer reaction with PANI. The increase in the mobility of the PANI chain may enhance the interaction of the PANI chains and the grafted pendant viologen moieties, as well as the transfer of the chlorine anions from the viologen to PANI. However, it should also be mentioned that, at 85 °C, the LDPE substrate undergoes softening and the possible rearrangement of the polymeric chains may affect the surface resistance and XPS measurements. On the other hand, the UV−visible absorption spectroscopy results would still give a representative indication of the changes in the state of the PANI.

The effect of different VBC densities on both VBC−PANI and viologen−PANI films at 85 °C was also carried out. The results show that VBC graft density in the range of 0.03−0.21 does not have a significant effect on the Rs in thermal-activated doping, similar to the observation for photoinduced doping (Figure 7a).

## Conclusion

The conversion of PANI from the EB state to the doped and conducting states was achieved by two new techniques: photoinduced doping and thermal-activated doping using VBC and viologen moieties. In both cases, the PANI is immobilized on a polymeric substrate which has been surface-graft-copolymerized with VBC and viologen moieties, and the doping process is carried out in a dry state. The photoinduced and thermal-activated doping of PANI with VBC is postulated to proceed via the attack of the alkyl halide on the imine N of PANI, with the halide ions formed during this alkylation process serving as the counterions to the $N^+$ of PANI. In the case of the viologen−PANI film, electron transfer from PANI to the viologen is assumed, resulting in the formation of positive polarons and $Cl^-$ counterions. The density of the grafted VBC and viologen does not play an important role in the doping of PANI under both UV irradiation and thermal treatment because the reactions are confined mainly to the interfacial region between PANI and the VBC or viologen. The thermal-activated doping proceeds at a substantial rate only at 65 °C or higher. A comparison of the two techniques indicates that the photoinduced method has two advantages over

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(39) Ding, L. L.; Wang, X. W.; Gregory, R. V. *Synth. Met.* **1999**, *104*, 73.

(40) Poizat, O.; Sourisseau, C.; Corset, J. *J. Mol. Struct.* **1986**, *143*, 203.

thermal-activated doping: the doping can be accomplished in a much shorter period of time and a more conductive film can be obtained in the former. Similarly, the viologen−PANI film can achieve a higher conductivity in a shorter period of time as compared to the VBC−PANI film with both techniques.

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