

## Chemical Vapor Deposition of Poly(3-alkylthiophene) Nanoparticles on Fabric: Chemical and Electrochemical Characterization

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**ABSTRACT:** Chemical vapor deposition of poly(3-methylthiophene) and poly(3-hexylthiophene) as conductive polymers on the surface of polyester fabrics was successfully obtained. Fourier transform infrared spectroscopy confirmed the formation of polymers on surface of fabrics (the fingerprint of polythiophenes,  $\nu$  600–1500  $\text{cm}^{-1}$ ). The uniformity of deposition and nanoparticles (average size of 60 nm) were proved with scanning electron microscopy. Electrochemical impedance spectroscopy showed that P3HT-coated samples offer higher conductivity in compared to P3MT-coated samples. The impedance modulus of P3HT-coated samples was lowered nine times to that of row materials and reached to  $\approx 8000 \Omega$ . The samples have also shown electrochromic properties under electrical current, changing its color from yellowish green at 0 V to dark green at +12 V for poly(3-hexylthiophene) samples and from brown at 0 V to red at +12 V for poly(3-methylthiophene)-coated fabrics ( $V = 0 \text{ V}$ ,  $\lambda = 450 \text{ nm}$ ;  $V = 12 \text{ V}$ ,  $\lambda = 650 \text{ nm}$ ). © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40673.

**KEYWORDS:** conducting polymers; nanoparticles; nanowires and nanocrystals; textiles

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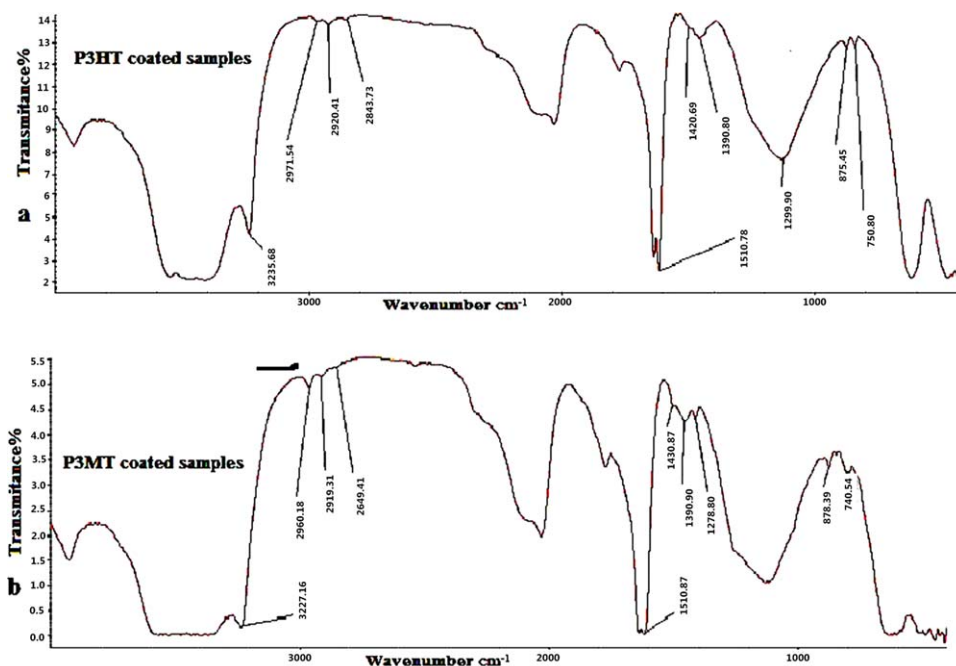
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### INTRODUCTION

Conducting polymers are processible and potentially useful for building inexpensive and flexible electronic devices. The possibility to have electronics in textiles is a growing research objective so that many commercially important applications have already been carried out.<sup>1–3</sup> Electronic and smart textiles have applications in military, medical, sports as well as the industrial textile areas.<sup>4–6</sup> Different methods of the synthesis of conducting polymers on the fabrics have been employed to produce conducting fabrics.<sup>7</sup> Lots of researches have been published concerning the production of polyaniline (Pani) or polythiophene (PT)-coated fabrics to produce conductive fabrics.<sup>8–13</sup> Polythiophenes (PTs) have been the subject of intensive research and are one of the most important classes of conjugated luminescent polymers.<sup>14</sup> Conducting polymers can be deposited on fabric surfaces chemically<sup>15</sup> or electrochemically.<sup>16</sup> Furthermore, poly(3-alkylthiophene) (P3AT) polymer is attractive because of its light weight, flexibility, and low cost fabrication. The chemical deposition is the most widely employed method. Chemical vapor deposition (CVD) of films and coatings involve the chemical reactions of gaseous reactants on or near the heated substrate surface. This atomistic deposition method can provide highly pure materials with structural control at atomic or nanometer scale level.<sup>17,18</sup> Among the P3ATs, poly(3-hexylthio-

phene) (P3HT) and poly(3-methylthiophene) (P3MT) are most widely used because of their low cost and superb properties. P3HT thin film has many potential uses in applications such as biosensors, wet ability switch devices, flexible electronic displays, microchips, electrochromic windows, and radiation screens.<sup>19–24</sup> P3HT and P3MT are usually synthesized in powder form by chemical oxidative polymerization, electrochemical polymerization, Grignard poly condensation, oxidative coupling.<sup>25–27</sup> However, there is poor surface morphology of fabricated P3HT films which is achieved by a wet-coating process.<sup>27,28</sup> It is reported<sup>29–31</sup> that CVD method can produce a thin, homogeny and coherent layers of polymer at the nanoscale on the surface of the substrates. Film formation on the surface of fabric is achieved without any changes on polymeric structure of substrates even at different polymerization situation.

In this study, CVD of P3MT and P3HT on the surface of fabrics which was not reported before is investigated. The coated samples are investigated by using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and electrochemical impedance spectroscopy (EIS). Chemical characterization of the coatings is determined by differential scanning calorimetry (DSC). Then, two types of P3AT coatings, P3HT- and P3MT-coated samples, are comprised and finally the electrochromic behavior of the coated samples are characterized



**Figure 1.** FTIR spectra of polyester coated fabrics by a) P3HT and b) P3MT nanoparticles CVD method. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

using stereomicroscope and visible reflective spectrophotometer to record color changing of the coated fabrics under electrical current.

## EXPERIMENTAL

### Materials

3-Hexylthiophene (3HT) and 3-methylthiophene (3MT) monomers were purchased from Aldrich chemical Co. Anhydrous ferric (III) chloride ( $\text{FeCl}_3$ ) (as oxidant), anhydrous methyl alcohol (MeOH) and anhydrous ethyl alcohol (EtOH) (as solvents) were purchased from Merck Co. that is used without any purification.

### Methods

The iron (III) solution chloride which is a mixture of MeOH and EtOH at a 1 : 1 ratio with 5 wt %  $\text{FeCl}_3$  is prepared and sonicated for 10 min at  $40^\circ\text{C}$ . The fabrics were submerged into the solution bath for about 2 h and the samples color change to yellow, and then samples were placed in the CVD chamber containing 3HT and 3MT monomers to evaporate and fill therein under a nitrogen purge.<sup>31,32</sup> The coating process is lasted for 2 h at  $60^\circ\text{C}$ . The coated fabrics washed with distilled water to eliminate iron (III) remaining on the substrate and dried in room temperature.

### Characterization

**Electrical and Electrochemical Measurements.** The surface resistance of coated fabrics by P3AT nanoparticles via CVD method was determined by two-probe technique. The Autolab N302 potentiostat/galvanostat was employed to perform EIS analysis in the  $10^5$ – $10^{-2}$  Hz frequency range, the amplitude of the sinusoidal voltage was  $\pm 10$  mV and Measurements were carried out in a two-electrode arrangement. Two types of configuration were employed to carry out the measurements. In the first one, the sample was located between two round copper electrodes ( $A = 1.5 \text{ cm}^2$ ) and in the second configuration, two

rectangular copper electrodes ( $0.5 \text{ cm} \times 1.5 \text{ cm}$ ) separated by 1.5 cm and pressed on the fabric sample. The measured area of the fabric with this configuration was a square of 1.5 cm so the measured impedance modulus ( $\Omega$ ) was equal to the surface resistivity ( $\Omega/\text{cm}^2$ ).

**FTIR Measurements.** FTIR spectra of the coated samples were obtained on a Nicolet magna-IR 560 Infrared spectrometer (USA) in the range  $500$ – $4000 \text{ cm}^{-1}$  using KBr pellets to provide information about the chemical bond of P3AT on the surface of polyester fabrics.

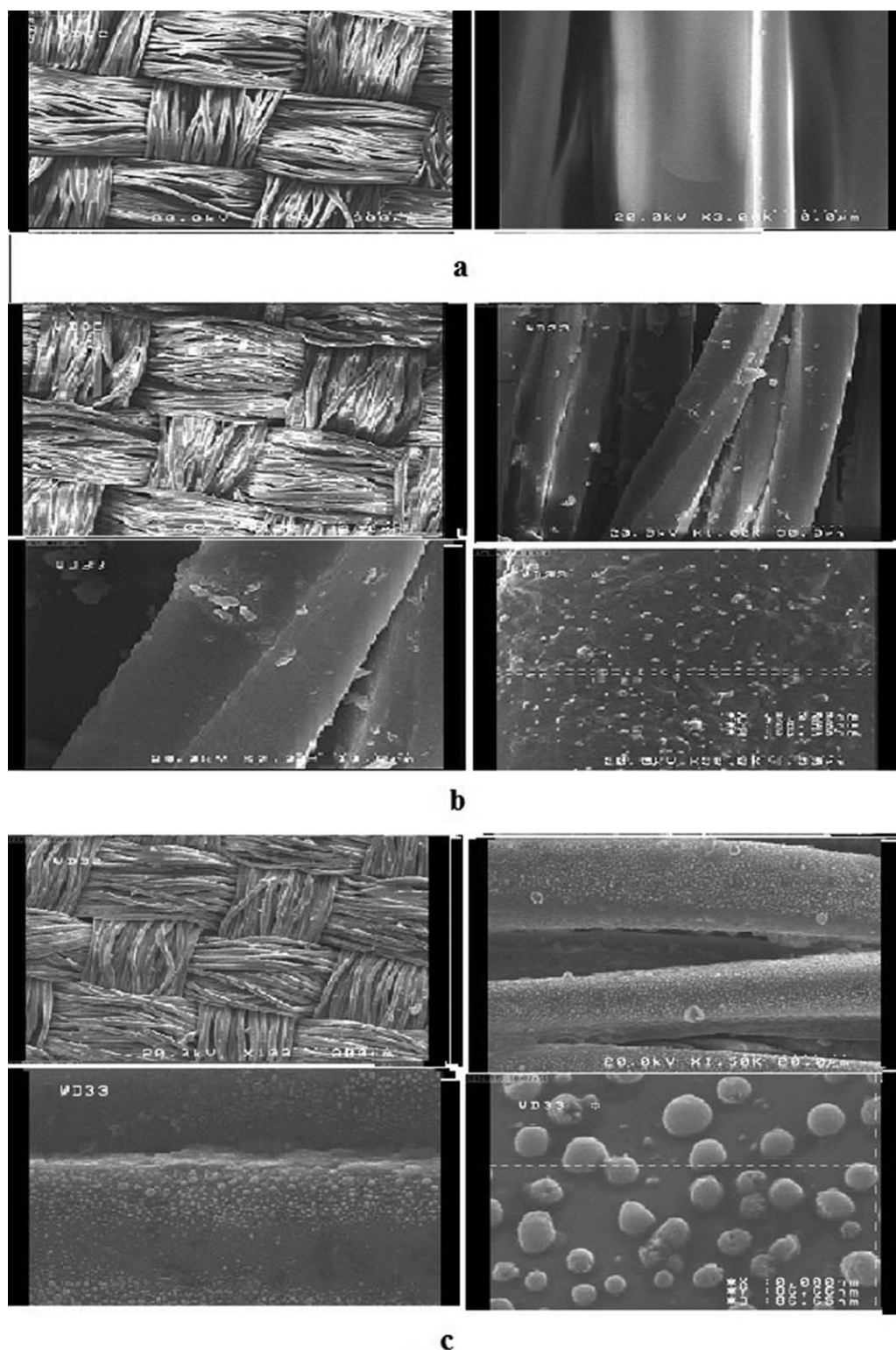
**Surface Morphology Characterization.** Surface morphology was studied by XL30, SEM (Philips Co., Poland) to characterize nanoparticles size and the uniformity of coating area on the surface of samples

**Differential Scanning Calorimetric Characterization.** To study thermal properties of coated polyester fabrics, differential scanning calorimeter (ALBAHR 302, Germany) was used. The size of samples was 3–4 mg. The samples were placed on aluminum pans and then were heated to  $300^\circ\text{C}$  at a heating and cooling rate of  $10^\circ\text{C}/\text{min}$ . The DSC was calibrated with indium before each set of experiments results.

## RESULTS AND DISCUSSION

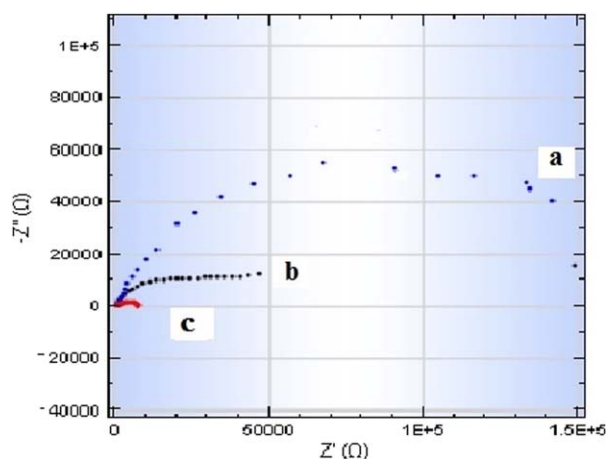
### FTIR Spectroscopy

Figure 1 shows the FTIR spectra of polyester fabrics coated by P3AT nanoparticles by CVD method. The spectra of P3AT powders were done to assign the different contributions of P3AT that may appear in the spectra of P3AT-coated fabrics. As can be displayed in Figure 1, both spectra are identical and present the same bands. The fingerprint of PT is at  $600$ – $1500 \text{ cm}^{-1}$ . The different P3AT bands observed were:



**Figure 2.** SEM photographs (a) raw polyester (100 $\times$ , 30,000 $\times$ ), (b) polyester fabrics coated by P3MT nanoparticles (100 $\times$ , 1000 $\times$ , 3000 $\times$ , 30,000 $\times$ ) (c) polyester fabrics coated by P3HT nanoparticles (100 $\times$ , 1000 $\times$ , 3000 $\times$ , 30,000 $\times$ ) (average size of nanoparticles 50 nm).

- The band centered at 820  $\text{cm}^{-1}$  correspond to stretching of C—H bond out of plane deformation, 2,3,5-substituted thiophene that confirms the formation of P3ATas a coating on the surface of fabrics.
- The band at 1378  $\text{cm}^{-1}$  originated from C—H bending of aliphatic CH<sub>3</sub> and CH<sub>2</sub> stretching vibration.
- The peaks centered at 1456 and 1510  $\text{cm}^{-1}$  belong to C=C asymmetric and symmetric stretching vibration modes of thiophene ring.



**Figure 3.** EIS analysis of (a) raw polyester (b) polyester fabrics coated by P3MT nanoparticles (c) polyester fabrics coated by P3HT nanoparticles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

- Several low intensity peaks in the range of 2800–3100  $\text{cm}^{-1}$  assigned to aliphatic and aromatic C–H stretching vibrations.
- The band centered at 3054  $\text{cm}^{-1}$  refer to C–H stretching vibration of aromatic rings originated from C–H stretching vibration

The peaks present in the spectrum of P3HT [Figure 1(a)] and P3MT [Figure 1(b)] obviously indicate the formation of P3AT layer on the surface of polyester fabrics and the sharp peak observed in 1510  $\text{cm}^{-1}$  refers to high regularity obtained from CVD method of polymerization.<sup>33</sup>

#### Scanning Electron Microscopy Characterization

Figure 2 shows the micrographs of the conductive fabrics coated by P3AT nanoparticles. The original polyester sample [that is shown in Figure 2(a)] shows a very smooth surface. Figure 2(b) shows the SEM images of conductive fabrics coated by P3MT nanoparticles in different magnification that shows the deposition of nanoparticles in average size of 50 nm and quite smooth with low grain size of coating on the surface of fabrics. In Figure 2(c), the P3HT nanoparticles-coated samples that are in average size of (60 nm) and a very thin homogenous layer on

the surface of the polyester fabrics can be observed and the higher conductivity is resulted because of the well smooth layer formation of nanoparticles that is effective factor on the surface resistivity. It may be concluded that the coating using CVD method is an effective method to produce conductive fabrics in comparison with the other way of polymerization and coating process.<sup>32</sup>

#### Electrical and Electrochemical Measurements

**EIS Analysis.** Figure 3 shows the Nyquist diagrams for the samples of PES [Figure 3(a)], PES-P3MT [Figure 3(b)] and PES-P3HT [Figure 3(c)]. Figure 3(a) shows the diagram for raw polyester with high surface resistance that is completely reduced in second and third diagram. When the sample of polyester was coated with P3HT nanoparticles by CVD method the value of the impedance modulus lowered more than nine orders of magnitude (a value of approximately 8000  $\Omega$  was obtained). This indicates that the samples acted as a resistor (conducting material) with different resistances that were previously indicated and polyester changed its behavior from an insulating material to a conductor one after P3AT nanoparticles deposition.

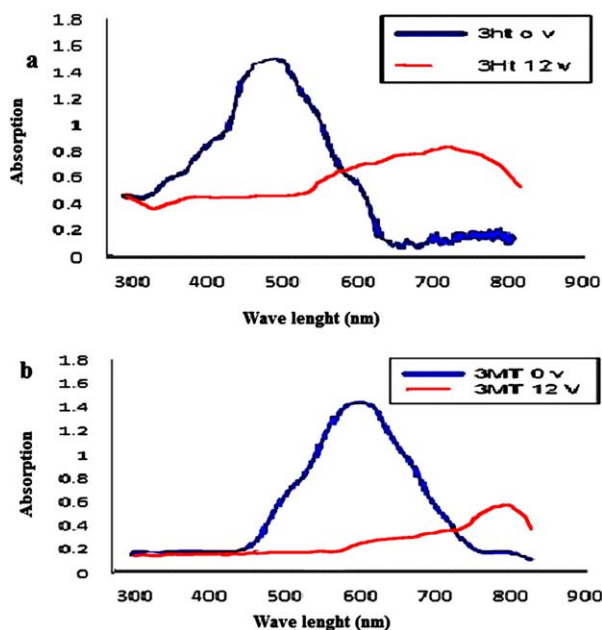
**Electrical Study of Surface Resistivity.** The conductivity of the polyester fabrics coated by P3HT and P3MT nanoparticles via CVD method for 2 h at the temperature of 65°C was measured by digital conductivity meter. To discuss the coating process of poly (3-alkylthiophene) nanoparticles on the surface of fabrics, the polymerization process was studied in three condition of oxidant: monomer ratio (1 : 1, 1 : 3, 1 : 5) and their surface resistance were determined. It can be observed that at higher ratio as the film layer is continuous and the gap distance between the nanoparticles is lower (about 60 nm) in comparison with the other oxidant: monomer ratio (about 100 nm). Also from SEM images, it can be concluded that in 1 : 5 oxidant: monomer ratio the layer of coated nanoparticles are continuous and it is about 300 nm and the higher conductivity is resulted.

Table I shows surface resistance of the samples. As the data shows, by increasing molar ratio (monomer : oxidant ratio) (1 : 1, 1 : 3, 1 : 5) surface resistivity is decreased that is because of formation the thicker layer of nanoparticles on the surface of fabrics. The decreasing of (MeOH :  $\text{FeCl}_3$ ) molar ratio increases

**Table I.** The Surface Resistance of Samples in Various Amount of Oxidant Concentration

Samples (S)	Time (h)	Temperature (°C)	Molar ratio (monomer : oxidant)	Molar ratio (MeOH : $\text{FeCl}_3$ )	Surface resistivity ( $\text{M}\Omega/\text{cm}^2$ ) S : P3HT	Surface resistivity ( $\text{M}\Omega/\text{cm}^2$ ) S : P3MT
S <sub>1</sub>	2	65	1 : 1	1 : 1	0.051	0.068
S <sub>2</sub>	2	65	3 : 1	1 : 1	0.040	0.052
S <sub>3</sub>	2	65	5 : 1	1 : 1	0.037	0.041
S <sub>4</sub>	2	65	1 : 1	1 : 5	0.071	0.082
S <sub>5</sub>	2	65	3 : 1	1 : 5	0.068	0.073
S <sub>6</sub>	2	65	5 : 1	1 : 5	0.063	0.070
S <sub>7</sub>	2	65	1 : 1	1 : 10	0.085	0.092
S <sub>8</sub>	2	65	3 : 1	1 : 10	0.075	0.087
S <sub>9</sub>	2	65	5 : 1	1 : 10	0.073	0.076





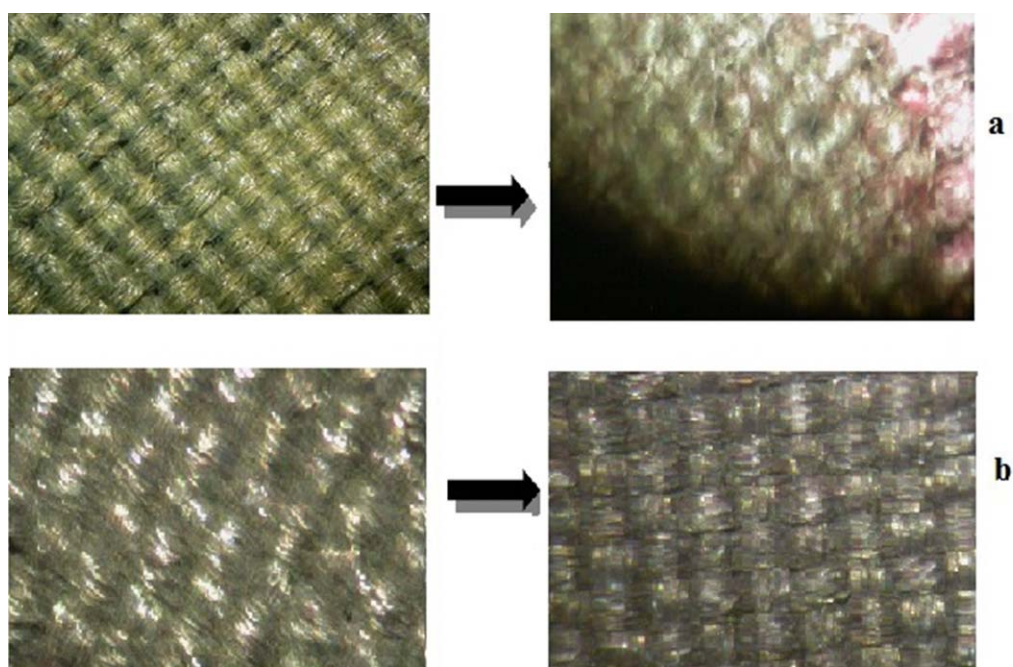
**Figure 4.** Diffuse reflectance spectroscopy analysis (a) polyester fabrics coated by P3HT nanoparticles (b) polyester fabrics coated by P3MT nanoparticles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

conductivity of coated samples is because of completed polymerization process done as oxidant ratio is increased. The P3HT nanoparticles-coated samples shows better conductivity results in comparison with P3MT nanoparticles-coated fabrics. The degree of crystallinity and the mobility values were increased as the alkyl chain length increased. The crystal structure of the polymers was composed of stacked layers con-

structed by a side-by-side arrangement of alkyl chains and in-plane  $\pi$ - $\pi$  stacking.<sup>34</sup>

**Diffuse Reflectance Spectroscopy Characterization.** Electrochromic properties of P3HT-coated polyester fabric under electrical current (0–12 V) is shown in Figure 4(a). DRS analysis by using  $\text{Ba}_2\text{SO}_4$  to calibrate feature peaks of the solid samples appear at 450 nm for fabrics coated by P3HT nanoparticles is shifted to the longer wavelength under electrical current to 700 nm (its color from green yellowish change at 0 V to dark green at +12 V), and because of formation of the layer of P3HT nanoparticles with electrochromic properties on the surface of fabrics under different applied electrical current. Figure 4(b) shows color change of polyester fabrics coated by P3MT nanoparticles, the original peak at 550 nm shifted to 750 nm (brown at 0 V and red at +12 V). So fabrics color changes occur and obviously it shows electrochromic properties of coated fabrics.

**Stereo Microscope and Reflectance Spectra Analysis.** Figure 5 compares coated samples color change properties as electrical current changed (0–12 V) by using Nikon Transformer XN, stereo microscope images. Fabrics with P3HT nanoparticles changes color from yellowish green to red and from dark green to dark red for (3-methylthiophene) coated fabrics [Figure 5(a,b)]. The changes in samples color, considerably confirms the formation of P3AT nanoparticles on the surface of polyester fabrics. Tables II and III show the values of reflectance spectra study,  $L^*$ ,  $a^*$ ,  $b^*$ , and  $h^\circ$  parameters of P3MT and P3HT nanoparticles-coated samples under different electrical current (0–12 V). The red shift of maximum wavelength from 450 nm (green color) to 700 nm (brown reddish) was investigated and changes in  $a^*$  and  $b^*$  values considerably confirms the color change of coated fabrics. Figure 6 shows the reflectance spectra of coated samples by P3HT [Figure 6(a)] and P3MT



**Figure 5.** Color change of P3HT- and P3MT-coated polyester fabric with CVD process, (a) (left) raw polyester fabric (right) P3HT- and (b) P3MT-coated polyester fabric, Stereo microscope. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table II.** The Changes of  $L^*a^*b^*$  Color System Parameters of P3MT Nanoparticles-Coated Polyester Under Electrical Current

$h^0$	$b^*$	$a^*$	$L^*$	%Reflectance	Wavelength (nm)	Applied electrical current (v)
84.61	10.08	0.95	27.37	2.5	620	0
79.26	6.84	1.05	34.95	6	630	2
76.29	5.77	1.09	38.83	8.47	640	4
67.78	5.58	1.07	39.68	8.78	650	6
52.20	5.05	1.21	41.60	10	660	8
43.93	4.85	1.26	42.68	11	670	10
34.73	4.45	1.48	42.86	11.90	680	12

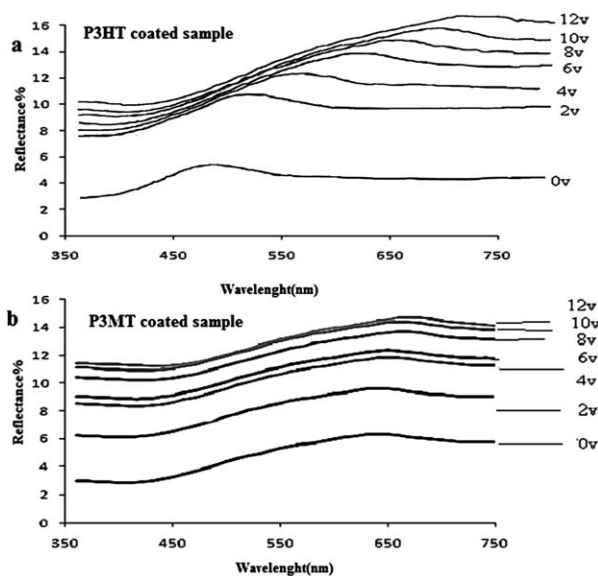
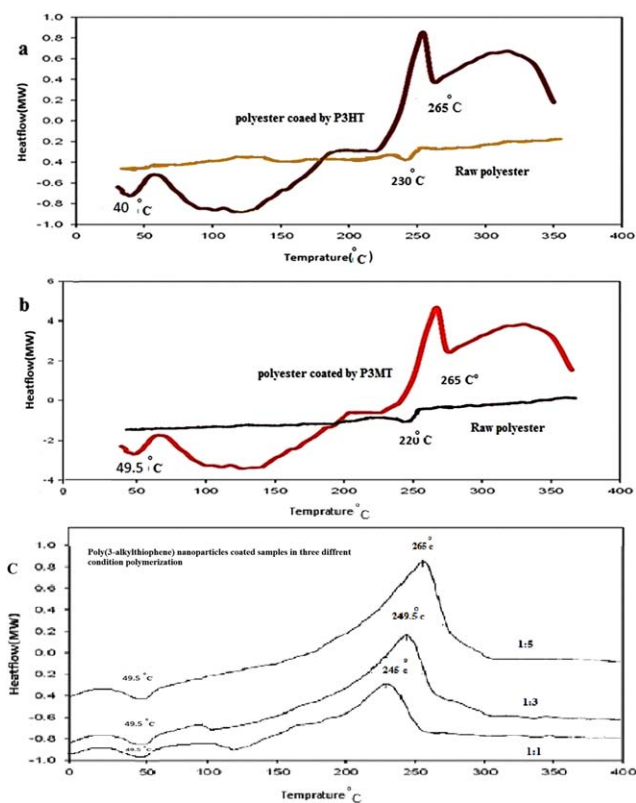
**Table III.** The Changes of  $L^*a^*b^*$  Color System Parameters of P3HT Nanoparticles-Coated Polyester Under Electrical Current

$h^0$	$b^*$	$a^*$	$L^*$	% Reflectance	Wavelength (nm)	Applied electrical current (v)
112.67	7.84	-7.316	26.83	2.30	490	0
95.14	5.02	-5.93	37.67	7.70	510	2
79.26	4.5	-2.36	38.10	8	530	4
68.51	3.38	0.34	38.67	8.30	550	6
52.24	1.52	2.24	38.72	9	570	8
47.82	0.72	4.07	38.77	9.70	590	10
33.82	0.12	4.50	40.45	10	610	12

[Figure 6(b)] nanoparticles, under electrical current (0–12v), wavelength shifted from 450 nm to 750 nm for P3HT-coated samples and from 550 nm to 700 nm for P3MT coated samples that shows electrochromic behavior of samples.

### Differential Scanning Calorimetry

DSC analysis of P3HT nanoparticles-coated polyester fabrics by CVD method in comparison with raw polyester is investigated. Figure 7(a) shows that the peak centered in 55°C attributed to the  $T_g$  of P3HT and the second peak belongs to polymer

**Figure 6.** Reflectance spectral graph of P3HT- and P3MT-coated polyester fabric under electrical current 0–12 V.**Figure 7.** DSC analysis of polyester fabric coated by (a) P3HT nanoparticles and polyester fabric coated by (b) P3MT nanoparticles oppose raw polyester (c) poly(3-alkylthiophene)-coated samples in different polymerization process. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

melting points on the surface of fabrics ( $T_m$ ) at 255°C and for the P3MT nanoparticles-coated fabrics DSC thermogram [Figure 7(b)],  $T_g$  is at 45°C and melting point ( $T_m$ ) is appeared at 255°C, Figure 7(c) shows thermal properties difference between P3AT coated samples in three condition of polymerization process, as monomer : oxidant ratio (1 : 1,1 : 3,1 : 5) increases, the crystallinity increased and as a result,  $T_m$  was shifted to higher temperature. As the P3AT has the unique characteristic of side chain crystallinity, in the DSC thermogram of melt-quenched samples the melting point depends significantly on the number of carbon atoms in side chain. The results clearly indicate an increase in melting temperature for P3HT in comparison with P3MT coated fabrics. This evidence confirms formation of polymer as a coating on the fabrics surface and also change in melting point corresponds to coherent layer coated on the fabrics surface.

## CONCLUSIONS

Polyester Fabrics have been coated with P3AT nanoparticles via CVD method. Two kinds of P3MT and P3HT nanoparticles coating have been employed and the best conductivity results have been achieved with P3HT nanoparticles-coated samples in oxidant : monomer ratio of 1 : 5 for 2 h at 65°C in CVD chamber under nitrogen purge. SEM showed that thin homogeneous layers of nanoparticles at average size of 60 nm have been formed on the surface of the fabrics. P3HT coated samples showed color change from yellowish green to dark green under electrical current. In the case of P3MT-coated samples, the color change was brown to red. EIS analysis showed that P3HT-coated polyester in comparison with P3MT-coated polyester offered higher conductivity.

## REFERENCES

1. Tsekouras, G.; Ralph, S. F.; Price, W. E.; Wallace, G. G. *Fibers Polym.* **2004**, *5*, 1.
2. Gregory, R. V.; Kimbrell, W. C.; Kuhn, H. H. *Synth. Met.* **1989**, *28*, 823.
3. Molina, J.; Del Río, A. I.; Bonastre, J.; Cases, F. *Eur. Polym. J.* **2008**, *44*, 87.
4. Li, Z.; Yang, S. C.; Meng, H. F.; Chen, Y. S.; Yang, Y. Z.; Liu C. H.; Horng, S. F.; Hsu, C. S.; Chen, L. C.; Hu, J. P. *Appl. Phys. Lett.* **2004**, *84*, 53.
5. Lee, E.; Choi, S. *Chem. Eng. J.* **2005**, *21*, 23.
6. Meador, M.; Hardy, D.; Auping, V. J. *Appl. Polym. Sci.* **1997**, *63*, 821.
7. Gilbert, J.; Steijskal, R. G. *Pure Appl. Chem.* **2002**, *74*, 857.
8. Dhawan, S. K.; Singh, N.; Venkatachalam, S. *Synth. Met.* **2002**, *125*, 89.
9. Dhawan, S. K.; Singh, N.; Venkatachalam, S. *Synth. Met.* **2002**, *129*, 261.
10. Acqua, L.; Tonin, C. *Synth. Met.* **2006**, *156*, 379.
11. Martina, V.; Ionescu, K.; Pigani, L.; Terzi, F.; Ulrici, A.; Zanardi, C.; Seeber, R. *Chem. Res.* **2007**, *387*, 2101.
12. Molina, J.; Bonastre, J.; Cases, F. *Polym. Degrad. Stab.* **2010**, *95*, 2574.
13. Lee, T.; Chung, Y.; Kwon, O.; Park, J. *Adv. Funct. Mater.* **2007**, *17*, 390.
14. Jang, K.; Kim, D.; wan Lee, Y.; Nam, J. *Org. Electron.* **2010**, *11*, 1668.
15. Truong, T. L.; Luong, N.; Nam, J.; Lee, Y.; Choi, H.; Koo, J.; Nguyen, N. *Macromol. Res.* **2007**, *15*, 465.
16. Hirase, R.; Hasegawa, M.; Shirai, M. *J. Appl. Polym. Sci.* **2003**, *87*, 1073.
17. Acqua, L.; Tonin, C. *Synth. Met.* **2006**, *156*, 379.
18. Wayne, E.; Jones, Jr. *Synth. Met.* **2011**, *161*, 1159.
19. Tanase, C.; Meijer, E. J.; Blom, P. W. M.; Leeuw, D. *Phys. Rev. Lett.* **2003**, *91*, 216601.
20. Giovanna, B.; Alessandro, B.; Massimo, Z. *Macromol. Res.* **1994**, *27*, 3039.
21. Cullough, M.; Richard, D. *Adv. Mater.* **1998**, *10*, 93.
22. Siringhaus, H.; Tessler, N.; Friend, R. *Science* **1998**, *280*, 1741.
23. Hugger, S.; Thomann, R.; Heinzl, T.; Thurn-Albrecht, T. *Colloid. Polym. Sci.* **2004**, *282*, 932.
24. Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.
25. Yamamoto, T.; Sanechika, K.; Yamamoto, A. *Chin. J. Polym. Sci.* **1980**, *18*, 9.
26. Sugimoto, R.; Taketa, S.; Yoshino, K. *Chem. Exp.* **1986**, *1*, 635.
27. Dashti, M.; Mokhtari, J.; Nouri, M.; Shirini, F. *J. Appl. Polym. Sci.* **2012**, *124*, 3007.
28. Masa, S.; Susumu, T.; Kyoji, K. *Synth. Met.* **1987**, *18*, 229.
29. Kim, J.; Eungryul, K.; Youngsoon, W. *Synth. Met.* **2003**, *139*, 485.
30. Lock, J. P.; Lutkenhaus, J. L.; Zacharia, N. S.; Im, S. G.; Hammond, P.T.; Gleason, K. K. *Synth. Met.* **2007**, *157*, 894.
31. Verilhac, J.; Gilles, A.; Djurado, D.; Rieutord, F. *Synth. Met.* **2006**, *156*, 815.
32. Nam, J. D.; Jang, K. S. *Appl. Mater. Interfaces* **2009**, *1*, 1567.
33. Singh, R.; Kumar, J.; Singh, R.; Kant, R.; Chand, S.; Kumar, V. *Mater. Chem. Phys.* **2007**, *104*, 390.
34. Ji-Woong, B.; Eun-Ah, S.; Keum-Joo, L.; Youn-Kyung, L.; Chae-Ryong, H.; Sang-Hyun, J.; Woo-Gwang, J.; Jin-Yeol, K. *J. Nanosci. Nanotechnol.* **2012**, *12*, 1461.