

Imparting Conductivity and Chromic Behavior on Polyester Fibers by Means of Poly(3-methylthiophene) Nanocoating

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ABSTRACT: Poly(3-methylthiophene) (P3MT)-coated polyester fabric is a conductive textile with specific electrical and optical properties; for instance, color change under external stimulus (chromic behavior) was successfully prepared by chemical polymerization with continuous, speed stirring technique. To investigate the striking effect of some variable conditions of polymerization process, the effect of reaction time, temperature, and oxidant concentration on conductivity of the P3MT-coated fabric was studied. Scanning electron microscopy confirmed that the surface of fabric has entirely been coated with P3MT particles. The further characterizations were investigated using Fourier transform infrared spectroscopy to provide

evidence of forming particles onto the fabric, UV-vis absorption spectroscopy, electrical surface resistivity, and pressure dependence visible reflectance spectrophotometer measurements and X-ray diffraction analysis. The blue shift in wavelength of maximum absorption of about 95 nm to a longer wavelength from that observed in the reflectance spectra of coated polyester fabric; under high-pressure P3MT-coated polyester fabric demonstrated piezochromism. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3007–3012, 2012

Key words: poly(3-methyl thiophene); X-ray; UV-vis spectroscopy; fibers; piezochromism

INTRODUCTION

In the recent years, the coating of textile fabrics by conducting polymers (CPs) such as polyaniline,^{1–3} polypyrrole,^{3,4} and polythiophene⁵ was investigated as new smart composite textile.^{3,6} CPs have been widely researched because of their specific electrical and optical properties and potential applications in various fields such as chemicals, sensors, biosensors, antistatic coating and rechargeable batteries, electromagnetic interference shielding, dust and germ-free clothing, data transfer in clothing, and military applications like camouflage technology.^{3,7,8} The coating of various substrates with a layer of CPs is achieved by the use of few possible procedures.⁸ To prepare the conductive composite fabrics, many scientists have focused on *in situ* polymerization, because it is a relatively simple and easy method to control the conductivity by maintaining the high strength of the substrate fabric.² According to many researches,^{3,9,10} monomers such as aniline and pyrrole are polymerized from a solution of oxidant and

deposited on the surface of textile fabrics (nylon 6 or 66, cotton, polyester, wool, and nomex).

Polythiophenes have received more attention as a wide class of conjugated polymers due to their good environmental stability, easy processability, considerable electrical, and optical properties. Introducing side chain such as alkyl groups onto aromatic structure may have a strong influence on the electronic structure of the resulting polymers and may also lead to interesting optical properties that are not observed in the unsubstituted parent polymer. For instance, the striking color changing phenomena such as thermochromism, electrochromism, solvatochromism, and piezochromism have been reported in some polythiophene derivatives principally, poly(3-alkylthiophenes).^{5,7,11–13} Chromic phenomena in various regioregular and nonregioregular polythiophene derivatives have been investigated both in the solid state and in solution.¹⁴ In conjugated polymers, there is a strong correlation between the electronic structure and the backbone conformation, any twisting of the backbone conformation leading to a modification of the effective conjugation length associated with a shift of the absorption in the UV-vis range. On the basis of these results, it was believed that various external stimulus could perturb the side-chain organization of conjugated polymers specifically polyalkylthiophenes and, consequently, induce some chromic

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phenomena.^{13,14} To the best of the authors' knowledge, there is a lack of research work on studying chromic behavior of polythiophene-coated fabrics, leading to conduct the present study.

In the present work, the preparation of conductive poly(3-methylthiophene) (P3MT)-nanocoated polyester fabric by means of oxidative chemical polymerization is reported. After depositing P3MT on polyester fabric, the samples are investigated using scanning electron microscopy (SEM), optical and stereo microscope, Fourier transform infrared (FTIR) spectroscopy, surface resistance measurements, and UV-vis absorption spectroscopy. Also, piezochromic behavior of the samples is examined by visible reflective spectrophotometer and X-ray diffraction (XRD).

EXPERIMENTAL

Materials

3-Methylthiophene (3MT, Aldrich chemical co, %99+>), anhydrous ferric (III) chloride (FeCl_3), and chloroform (CHCl_3) (synthetic grade, Merck Co.) were used without further purification. Polyester fabric (plain weave, 250 g/m^2) was obtained from local supplier.

Chemical synthesis of poly(3-methylthiophene)

The poly(3-methylthiophene) (P3MT) was polymerized similar to Hotta's method.¹⁵ Polymerization reactions have been carried out in a rigorously deoxidized and dehydrated medium. At first, 0.018 mol anhydrous FeCl_3 was put into the three-necked round-bottomed flask under dry nitrogen atmosphere and remained at about 100°C under vigorous mechanical agitation. Then, the oxidant suspension in dry chloroform (30 mL) was prepared and stirred rigorously for 1 h. The solution of 3MT (0.006 mol) in chloroform (20 mL) was added dropwise into the oxidant suspension through the funnel under rigorous agitation. After all the thiophene monomer was added, the suspension was further stirred for about 8 h at room temperature to complete the reaction. The suspension was turned to blue immediately after adding the 3MT monomer and had a deeper color with time. After completing the reaction, the reactant solution (or suspension) was precipitated into methanol (50 mL). The resulting blue-black precipitate (an as-grown material) was collected by filtration. This precipitate turned dark red after being washed alternately with copious amount of methanol, acetone, and water.

Preparation of P3MT-nanocoated polyester fabric

In situ chemical polymerization process has been performed to obtain conductive polyester fabric with

a homogenous coating. At first, a small piece $4 \text{ cm} \times 4 \text{ cm}$ of polyester fabric was soaked in 3MT monomer for about 24 h. The samples were weighed before and after soaking to determine the amount of adsorbed monomer. Monomer uptake was 10% wt for 3MT. Ferric chloride suspension in chloroform was prepared in a three-necked round-bottomed flask under nitrogen atmosphere and stirred for about 1 h. The soaked piece of fabric was involved into the flask and remained for a specific time under continuous stirring. Polymerization on the fabric surface was carried out in a deoxidized and dehydrated medium, as the chemical and electrochemical synthesized polythiophene in such medium exhibit significantly improved conductivity. The coated fabric was then washed with copious amounts of acetone and distilled water to remove residual materials and dried in room temperature.¹⁶

Characterization

For the identification of deposited P3MT on the fabric surface, FTIR spectroscopy was used (Nicolet Magna-IR 560). The UV-vis absorption spectra of the polymer solution in chloroform were obtained on Cintra 10, UV-vis absorption spectroscopy. The surface electrical resistivity of conductive polyester fabric was measured employing the two point-probe technique using a digital multimeter. Surface morphology was studied by XL30, SEM (Philips Co., Poland).

Pressure dependence studies

A $1 \text{ cm} \times 1 \text{ cm}$ piece of samples was placed in an IR pellet press, and then a pressure of up to 700 MPa was applied.¹⁷ The color change of coated polyester was shown by Nikon Microphot-FXA, $20\times$ optical microscope and Nikon Transformer XN, stereo microscope images. The blue shift of P3MT-coated polyester reflectance spectra under high pressure was recorded using X-rite, color-Eye 7000A reflectance spectrophotometer. XRD study on the piezochromic behavior of the samples was done using an XRD measurement was performed on a Philips PW 1840 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. XRD patterns were recorded at 40 kV, 40 mA, and scan rate $0.02 \text{ } 2\theta/\text{s}$.

RESULTS AND DISCUSSION

FTIR spectroscopy

The structure of products was determined by the Fourier transform infrared (FTIR) spectra. In Figure 1, the FTIR spectra of the chemically synthesized P3MT powder and P3MT particles polymerized on

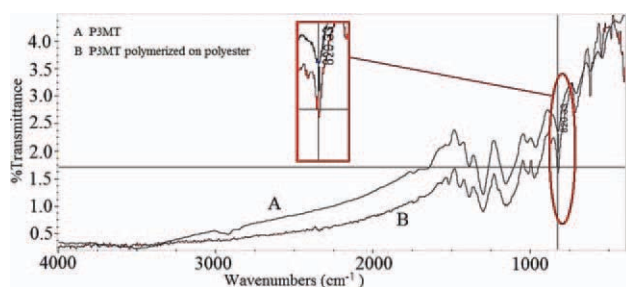


Figure 1 FTIR spectra of P3MT powder and P3MT powder on fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fabric measured on pressed pellets with KBr were presented. The P3MT spectrum was displayed several low intensity peaks in the range of 2800–3100 cm^{-1} that represent the aliphatic and aromatic C–H stretching vibrations. The fingerprint of PT is at 600–1500 cm^{-1} . A distinct peak at 820 cm^{-1} can be assigned to the C–H out-of-plane vibration of the 2,3,5-substituted thiophene, which is in agreement with other researchers finding,¹⁸ and other peaks in this region are attributed to the ring stretching mode, methyl deformation, and aromatic C–H deformation. The band at 690 cm^{-1} corresponds to monosubstituted thiophene ring vibrations.^{15,18,19} The spectrum related to P3MT-coated polyester in Figure 2 also displayed a distinct peak at nearly 820 cm^{-1} , which belongs to C–H out-of-plane vibration of the substituted thiophene, confirms the formation of polymer layer on the surface of polyester fabric.

The UV–vis absorption spectra

The UV–vis spectra of P3MT solution in chloroform was shown in Figure 3. Feature peaks of the solution appear at 220, 313, and 365 nm. The peak located at 220 nm is attributed to the π – π^* transition in the thiophene ring and its absorption is relatively strong. The 313 and 365 nm peaks are attributed to the π – π^* transition in the moiety.^{18,20–22}

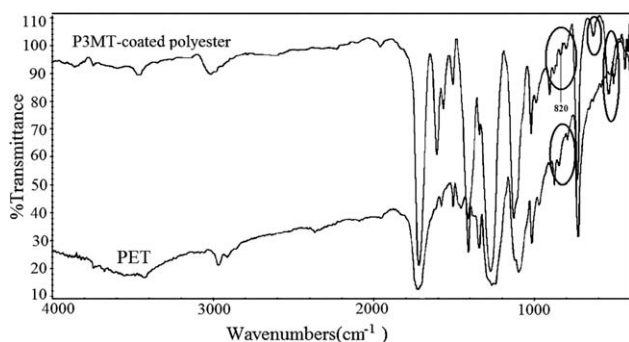


Figure 2 FTIR spectra of polyester fabric and P3MT-coated fabric.

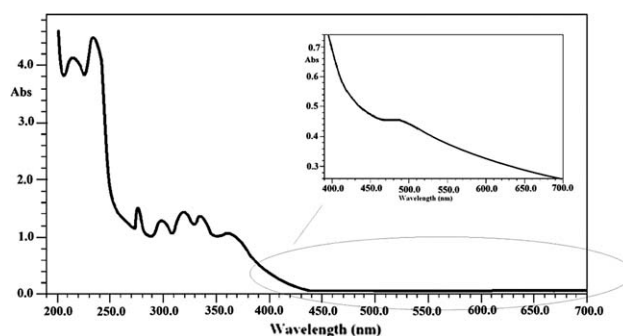


Figure 3 UV–vis absorption spectra of P3MT solution in chloroform.

The surface resistivity study

The electrical resistance of P3MT powder in pressed tablet was determined equal to 1 k Ω . As the data shown, the decreasing of electrical resistance of P3MT-coated polyester from 10^9 to 10^{15} Ω to at least around 10^3 – 10^6 Ω is because of coating a homogeneous thin layer of high conductive polymer particles on the surface. Table I shows the effects of the reaction duration (time; 2, 5, and 8 h) and temperature (0, 25, and 40°C) and oxidant concentration (0.2, 0.6, and 1M) on the surface electrical resistance.^{16,23} The measurements attributed to 24 h after polymerization. It seems that surface electrical resistance decreases with increase in reaction time, temperature, and oxidant concentration is derived from thicker coating layer.²³ This is proved by the darker red-dish-brown color of P3MT-coated polyester prepared in higher reaction time, temperature, and oxidant concentration. The surface electrical resistance has

TABLE I
The Surface Resistance of Samples in Various Amount of Oxidant Concentration (0.2, 0.6, and 1M)

Run order	Molar ratio (oxidant/monomer)	Time (h)	Temperature (°C)	Surface resistance ($\text{M}\Omega/\square$)
A	1/1	2	0	6.2
		2	20	4
		2	40	Break up
		5	20	2.4
		8	0	0.8
		8	20	0.32
C	3/1	8	40	Break up
		2	0	195×10^{-3}
		2	20	180×10^{-3}
		2	40	Break up
		5	20	155×10^{-3}
		8	20	98×10^{-3}
D	5/1	8	40	Break up
		2	0	0.85
		2	20	0.6
		2	40	Break up
		5	20	185×10^{-3}
		8	20	157×10^{-3}

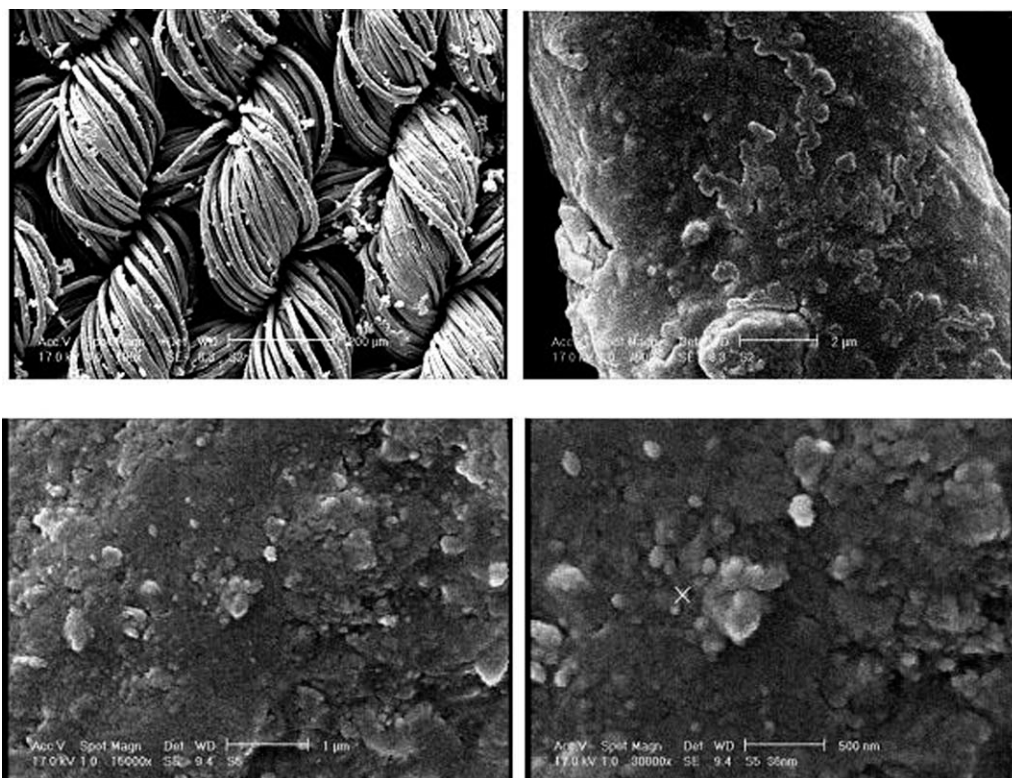


Figure 4 Scanning electron microscopy photographs of P3MT-coated fabric (average size of particles = 110 nm).

been decreased with increasing reaction temperature, but the structure of fabric was lost its strength at up to 40°C.

The surface morphology

The size and homogeneity of polymer particles on the surface of fabric were recorded by SEM photographs. A partially thin, homogeny, and coherent P3MT was coated on the surface of fabric after *in situ* chemical oxidative polymerization, as shown in Figure 4. On the base of the photographs, the formation of particles in nanometer scale by the chemical polymerization process without any chemical additives was possibility, and this leads to enhanced sensitivity and stability of conductive polymer on polyester fabric.

Pressure-dependence reflectance analysis

The color of P3MT in the solid state changes under high pressure (up to 700 MPa), as shown in Figure 5. When the brown powder of P3MT was pressed by an IR pellet, the smooth powder turned to the metallic green and partially sticky after application of pressure. Similar color change is displayed in P3MT-coated polyester fabric, which is shown in Figure 6. Figure 6(a,b) shows low and high-thickness-coated fabrics, respectively. By applying a high pressure,

the color of coated fabric changes from brown to green. Because the difference between two samples in Figure 6(a,b) is the thickness of polymer on the surface of polyester, the comparison of color change in samples shown on Figure 6(a,b) revealed that the thickness of polymer on the fabric plays the effective role on the piezochromic behavior.²⁴ Figure 7 shows the pressure dependence of the P3MT coated-polyester fabric visible reflectance spectra. The blue shift of the maximum wavelength from 750 nm (brown-red color) to 655 nm (green) was investigated in reflectance spectra under different applied pressure. Considering the reports, for poly(3-alkylthiophene) with shorter R groups, the color changes under the high pressure were not so obvious, but here the specific color change in P3MT coated-polyester reflectance

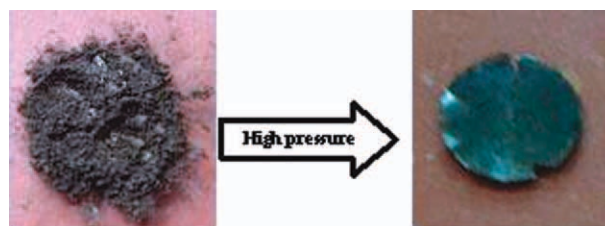


Figure 5 Piezochromism in P3MT powder at high pressure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

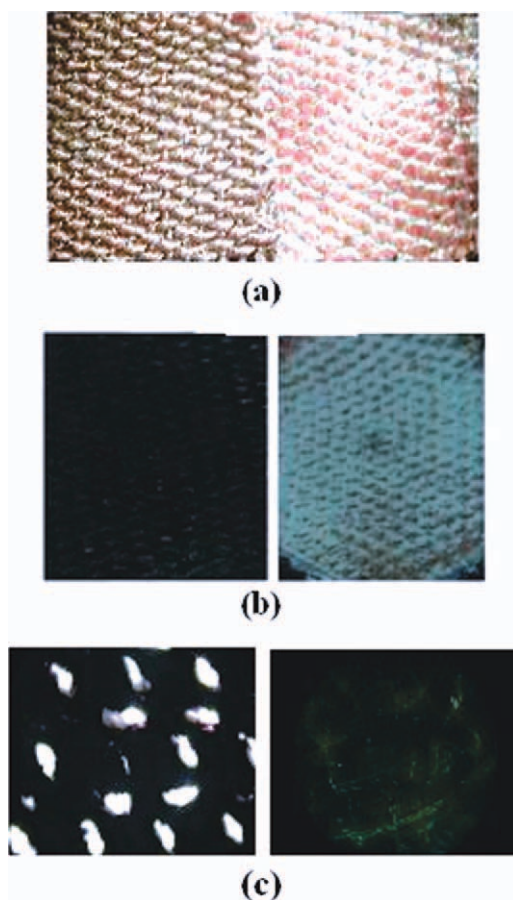


Figure 6 Color change of P3MT-coated polyester fabric with different condition of polymerization process, (left) P3MT-coated polyester fabric at atmosphere pressure, and (right) P3MT-coated polyester fabric, stereo microscope images (a) 1 : 1, 5 h, and 20°C; (b) 3 : 1, 8 h, and 20°C; and optical microscope(3 : 1, 8 h, and 20°C) images (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

spectra at high pressure was displayed. Table II shows the values of L^* (lightness), a^* (red-green axis), and b^* (blue-yellow axis) parameters of $L^*a^*b^*$ color system of P3MT particles-coated polyester under different pressure. If the L^* value is 100, the sample has highest lightness. Positively, the a^* values show the color of sample tends to red, whilst negative the a^* value shows the color of sample tends to green. In

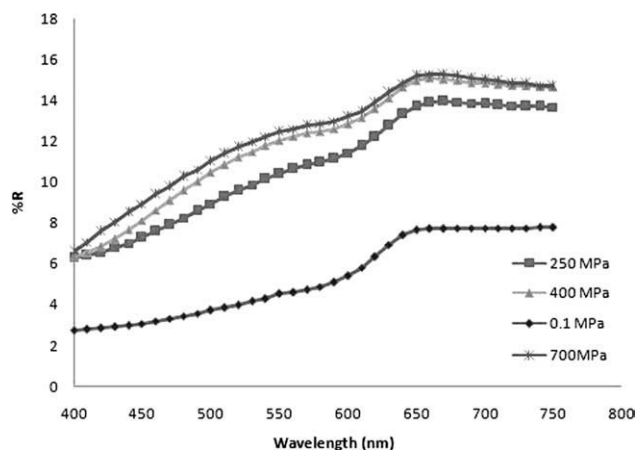


Figure 7 Reflectance spectral graph of P3MT-coated polyester fabric (3 : 1, 8 h, 20°C).

the case of the b^* value, positive and negative values represent bluish and yellowish, respectively. By increasing applied pressure from atmosphere to 700 MPa, the L^* values of samples increases from 24.47 to 41.63 showing that the lightness of samples increases. On the other hand, increasing applied pressure from atmosphere to 700 MPa results in decrease in a^* values. This confirms the color change of the nanocoated samples from reddish brown to green as mentioned earlier. The changes in wavelength, a^* and b^* parameters considerably confirm the color change in polyester.

XRD study

Figure 8 compares X-ray diffraction (XRD) patterns of the original P3MT powder and pressed-P3MT under high pressure. As shown in Figure 8, the XRD pattern of pressed- P3MT exhibits some strong and sharp peaks at about $2\theta = 12^\circ$, 24.7° , and 29.2° , indicating that the polymer molecules become crystalline and a better-ordered structure under high pressure in comparison with the amorphous structure of P3MT powder. This fact could be due to the changes in structural order of disordered structure of P3MTcoating on the surface of polyester fabrics under variable pressures, which leads to some

TABLE II
The Changes of $L^*a^*b^*$ Color System Parameters of P3MT Nanoparticles-Coated Polyester Under Different Pressure

C^*	b^*	a^*	L^*	% Reflectance	Wavelength (nm)	Applied pressure (MPa)
9.32	8.24	4.36	24.97	7.78	750	Atmosphere
10.07	9.85	2.12	38.42	13.92	680	250
11.07	11.04	0.79	40.93	15.05	660	400
11.70	11.68	0.70	41.63	15.27	655	700

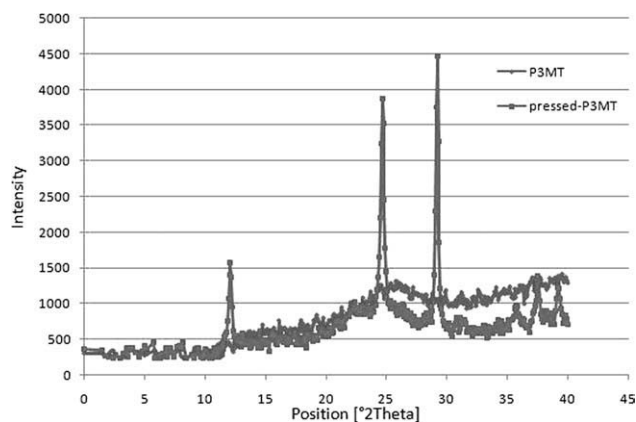


Figure 8 X-ray diffraction (XRD) patterns, comparing of the original P3MT powder and pressed-P3MT under high pressure.

interesting chromic behavior (the color changing under external stimulus).

CONCLUSIONS

The coating of polyester fabric with P3MT was performed by chemical polymerization using FeCl_3 as an oxidizing agent in an anhydrate medium. By this method, a thin uniform layer of P3MT was coated on the surface. The surface electrical resistance of polyester was decreased with increasing of reaction time and temperature less than 40°C and oxidant to monomer molar ratio up to 3 : 1. The conductivity and sensitivity under a stimulus of coated fabrics could enhance due to the formation of P3MT nanoparticles in polymerization process. These conductive textiles with considerable optical and electrical properties, for instance, piezochromic and other interesting chromic behavior, could be a potential candidate for high performance applications.

References

1. Anbarasan, R.; Paruthimal, K. G.; Vasudevan, T.; Gopalan, A. *Int J Polym* 1999, 5, 247.
2. Kim, S. H.; Seong, J. H.; Oh, K. W. *J Appl Polym Sci* 2002, 83, 2245.
3. Kim, B.; Koncar, V.; Devaux, E.; Dufour, C.; Viallier, P. *Synth Methods* 2004, 146, 167.
4. Wu, J.; Zhou, D.; Too, C. O.; Wallace, G. G. *Synth Methods* 2005, 155, 698.
5. Hong, K. H.; Oh, K. W.; Kang, T. J. *J Appl Polym Sci* 2005, 97, 1326.
6. Li, Y.; Cheng, X. Y.; Leung, M. Y.; Tsang, J.; Tao, X. M.; Yuen, M. C. W. *Synth Methods* 2005, 155, 89.
7. Gonçalves, V. C.; Balogh, D. T. *Eur Polym J* 2006, 42, 3303.
8. Malinauskas, A. *Polymer* 2001, 42, 3957.
9. Knittel, D.; Schollmeyer, E. *Synth Methods* 2009, 159, 1433.
10. Hirase, R.; Shikata, T.; Shirai, M. *Synth Methods* 2004, 146, 73.
11. Almeida, S.; Rivera, E.; Reyna-Gonzalez, J. M.; Huerta, G.; Tapia, F.; Aguilar-Martinez, M. *Synth Methods* 2009, 159, 1215.
12. Muramatsu, Y.; Yamamoto, T.; Hasegawa, M.; Yagi, T.; Koizumi, H. *Polymer* 2001, 42, 6673.
13. Levesque, I.; Leclerc, M. *Macromolecules* 1997, 30, 4347.
14. Faid, K.; Frechette, M.; Ranger, M.; Mazerolle, L.; Levesque, I.; Leclerc, M. *Chem Mater* 1995, 7, 1390.
15. Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J. *Synth Met* 1987, 22, 79.
16. Meador, M. B.; Hardy-green, D.; Auping, V.; Gaier, R.; Ferrara, L. A.; Papadopoulos, D. S.; Smith, J. W.; Keller, D. J. *J Appl Polym Sci* 1997, 63, 821.
17. Kunzelman, J.; Gupta, M.; Crenshaw, B. R.; Schiraldi, D. A. *Macromol Mater Eng* 2009, 294, 246.
18. Hotta, S.; Soga, M.; Sonoda, N. *Synth Methods* 1988, 26, 273.
19. Lanzi, M.; Bizzarri, P. C.; Paganin, L.; Cesari, G. *Synth Methods* 2007, 157, 723.
20. Mellah, M.; Labbe, E.; Nedelec, J. Y.; Perichon, J. *New J Chem* 2002, 26, 208.
21. Udum, Y. A.; Pekmez, K.; Yildiz, A. *Eur Polym J* 2004, 40, 1060.
22. Ma, X.; Li, G.; Xu, H.; Wang, M.; Chen, H. *Thin Solid Films* 2006, 515, 2701.
23. Lee, E. K.; Choi, S. Y. *Kor J Chem Eng* 2006, 23, 1055.
24. Sato, T.; Yagi, T.; Tajima, H.; Fukuda, T.; Yamamoto, T. *React Funct Polym* 2008, 68, 372.