

# Antimicrobial Activity of Some New 4-Arylazo-3-methylthiophene Disperse Dyes on Polyester Fabrics

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**ABSTRACT:** A series of novel 4-arylazo-3-methylthiophenes was synthesized by the heterocyclization of 2-arylhydrazono-2-acetyl thioacetanilide derivatives with a variety of  $\alpha$ -halogenated reagents, such as chloroacetone, phenacyl bromide, ethyl chloroacetate, and chloroacetonitrile. The structures of the synthesized thiophene derivatives were confirmed by ultraviolet-visible, IR, and <sup>1</sup>H-NMR spectroscopic techniques and elemental analysis.

The synthesized dyes were applied to polyester fabrics as disperse dyes, and their fastness properties were evaluated. The dyed polyester fabrics displayed antibacterial efficacy against Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 83–89, 2011

**Key words:** azo polymers; dyes/pigments; polyesters

## INTRODUCTION

Polyester is a polymer that is produced from coal, air, water, and petroleum products. It was first commercially produced in 1953 by E. I. Du Pont de Nemours & Co., Inc., in the United States.<sup>1</sup> Polyester is an umbrella term that describes a manufactured fiber whose substance is any long-chain synthetic polymer where at least 85 wt % of the polymer is an ester of terephthalic acid. Most polyester is made of poly(ethylene terephthalate) (PET). The properties of polyester fabrics vary, depending on their composition, web structure, and processing, but some general features are found with nearly all polyester fabrics.

The emergence of polyester (PET) as the most successful of the man-made fibers is due to a number of factors in its favor, including the following:

1. PET fiber is made from raw materials that are cheap and available because of the large manufacturing infrastructure it shares with other common products, such as antifreeze and soda bottles. The polymerization byproducts are non-polluting, and the polymer can be recycled.
2. The melt-spinning process used for PET fibers is clean and economical.
3. The thermoplastic fiber is tough, with a relatively high temperature resistance. It can be processed into yarns that maintain their properties at elevated environmental temperatures,

such as in tire reinforcement or for permanent-press fabrics.

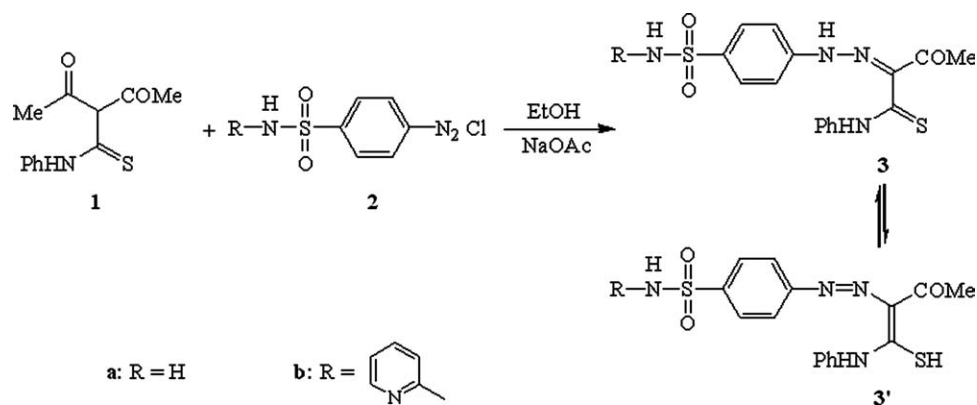
4. The basic polymer can be modified with additives or copolymers to confer specific properties for special end-use needs.<sup>2</sup>

Polyester is used in the manufacturing of many products, including clothing, home furnishings, industrial fabrics, computer and recording tapes, and electrical insulation. Polyester has several advantages over traditional fabrics such as cotton. It does not absorb moisture but does absorb oil; this quality makes polyester the perfect fabric for the application of water-, soil-, and fire-resistant finishes. Its low absorbency also makes it naturally resistant to stains. Polyester clothing can be preshrunk in the finishing process, and thereafter, the fabric resists shrinking and will not stretch out of shape. The fabric is easily dyeable and is not damaged by mildew. Textured polyester fibers are an effective, nonallergenic insulator, so the material is used for filling pillows, quilting, outerwear, and sleeping bags.

Disperse dyes are a very popular and important class of dyes for dyeing polyester fabrics because of their brilliancy, wide range of hues, excellent fastness properties, and environmental and economic reasons.<sup>3</sup> Especially useful in this respect are azo dyes, which are derived from the coupling of diazonium salts with sulfur and/or nitrogen heterocyclic compounds as coupling components. These sulfur and/or nitrogen heterocyclic azo dyes provide bright strong shades that range from yellow, orange, red, and blue to green.<sup>4–7</sup>

Moreover, the thiophene nucleus has been proven to constitute the active part of several biologically

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Scheme 1

active compounds.<sup>8–10</sup> In view of these findings and in continuation of our previous studies<sup>11–15</sup> on the synthesis of a variety of thiazole and thiophene derivatives from the readily obtainable cheapest starting materials for the dyeing of polyester fabrics, we now report on the successful synthesis of several new 4-aryldiazo-3-methylthiophenes and their application as disperse dyes for the dyeing of polyester fabrics. Also, the antibacterial activities of the dyed polyester fabrics were studied.

## EXPERIMENTAL

### Materials and instrumentation

The starting thiocarbamoyl derivative (1) was prepared according to the previous literature.<sup>16</sup> Polyester fabrics were kindly supplied by Misr Co. (Kafr El-Dawar, Egypt) for synthetic fabrics. The dispersing agent Setamol WS was supplied by BASF (Ludwigshafen, Germany).

All melting points were measured on an electrothermal Gallenkamp melting apparatus (Weiss-Gallenkamp, London, UK). Elemental analyses were carried out at the Microanalytical Unit, Faculty of Science, University of Mansoura, Egypt; the results were in satisfactory agreement with the calculated values. Ultraviolet–visible (UV–vis) spectra were recorded on a PerkinElmer Lambda 551 S spectrometer with dichloromethane as the solvent. IR spectra (KBr) were obtained on a Mattson 5000 FTIR spectrometer (not all frequencies are reported). The <sup>1</sup>H-NMR spectra were acquired with a Bruker WP 300 spectrometer at 300 MHz with trimethyl silane (TMS) as an internal standard.

### Methods

Synthesis of 2-aryldiazo-2-acetyl thioacetanilide derivatives (3; Scheme 1)

A solution of sodium nitrite (0.70 g in 10 mL of water) was gradually added to a well-cooled (0–5°C) solution of aromatic amine (10.0 mmol) in concen-

trated HCl (3.0 mL). The diazonium salt solution (2) was added with continuous stirring to a cold (0–5°C) solution of 1 (10.0 mmol) in ethanol (50.0 mL) and sodium acetate (4.0 g). The reaction mixture was allowed to stir at 0–5°C for 2 h, and then, the solid was collected by filtration. The obtained precipitate was dried and recrystallized from ethanol.

### 2-Acetyl-2-[4-sulfamoyl phenyl hydrazono] thioacetanilide (3a)

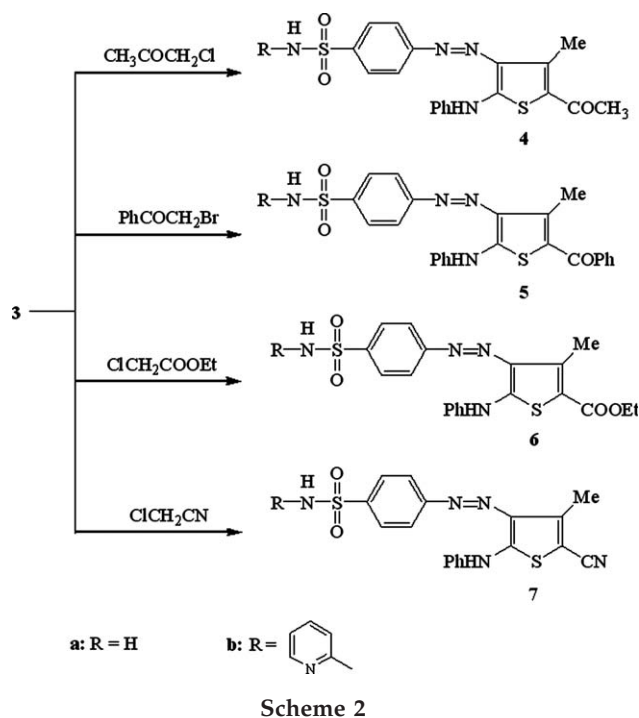
mp = 176°C. Yield = 69%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3346, 3278, 1664, 1596, 1556. <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 2.6 (s, 3H,  $\text{COCH}_3$ ), 7.2–7.8 (m, 9H, Ar–H), 9.8 (s, 1H, NH), 11.5 (s, 1H, NH), 13.1 (s, 1H, NH). ANAL. Calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_3\text{S}_2$  (376.45): C, 51.05%; H, 4.28%; N, 14.88%. Found: C, 51.14%; H, 4.33%; N, 14.79%.

### 2-Acetyl-2-[[4-(pyridin-2-ylsulfamoyl) phenyl] hydrazono] thioacetanilide (3b)

mp = 163°C. Yield = 71%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3320, 3312, 1667, 1580, 1535. <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 2.6 (s, 3H,  $\text{COCH}_3$ ), 7.2–8.0 (m, 13H, Ar–H), 10.2 (s, 1H, NH), 12.4 (s, 1H, NH), 13.6 (s, 1H, NH). ANAL. Calcd for  $\text{C}_{21}\text{H}_{19}\text{N}_5\text{O}_3\text{S}_2$  (453.54): C, 55.61%; H, 4.22%; N, 15.44%. Found: C, 55.53%; H, 4.17%; N, 15.60%.

### Synthesis of 5-anilino-4-aryldiazo-3-methylthiophene dyes (4–7; Scheme 2)

**General procedures.** To a solution of 3 (5 mmol) in 25 mL of dimethylformamide (DMF), solid potassium carbonate (10 mmol) and the appropriate  $\alpha$ -halogenated reagent (5 mmol; chloroacetone, phenacyl bromide, ethyl chloroacetate, or chloroacetonitrile) were added. The reaction mixture was stirred for 12 h. The reaction mixture was poured into cold  $\text{H}_2\text{O}$  and neutralized with dilute HCl; the solid product that formed was filtered and recrystallized from ethanol or an ethanol–DMF (2 : 1) mixture to afford the corresponding thiophene dyes (4–7).



2-Acetyl-5-anilino-3-methyl-4-(4-sulfamoyl phenyl azo) thiophene (**4a**)

mp = 184°C. Yield = 76%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3413, 3320, 1664, 1588, 1533.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 2.2 (s, 3H,  $\text{CH}_3$ ), 2.6 (s, 3H,  $\text{COCH}_3$ ), 7.2–7.8 (m, 9H, Ar–H), 10.8 (s, 1H, NH), 12.8 (s, 1H, NH). ANAL. Calcd for  $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_3\text{S}_2$  (414.50): C, 55.05%; H, 4.38%; N, 13.52%. Found: C, 55.23%; H, 4.44%; N, 13.37%.

2-Acetyl-5-anilino-3-methyl-4-[[4-(pyridin-2-ylsulfamoyl) phenyl] azo] thiophene (**4b**)

mp = 212°C. Yield = 73%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3372, 3312, 1661, 1595, 1543.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 2.2 (s, 3H,  $\text{CH}_3$ ), 2.6 (s, 3H,  $\text{COCH}_3$ ), 7.2–8.0 (m, 13H, Ar–H), 11.4 (s, 1H, NH), 13.5 (s, 1H, NH). ANAL. Calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_5\text{O}_3\text{S}_2$  (491.59): C, 58.64%; H, 4.31%; N, 14.25%. Found: C, 58.58%; H, 4.39%; N, 14.37%.

5-Anilino-2-benzoyl-3-methyl-4-[4-sulfamoyl phenyl azo] thiophene (**5a**)

mp = 193°C. Yield = 71%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3410, 3286, 1658, 1568, 1543.  $^1\text{H-NMR}$  (dimethyl sulfoxide,  $\delta$ , ppm): 2.3 (s, 3H,  $\text{CH}_3$ ), 7.1–7.7 (m, 14H, Ar–H). ANAL. Calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_3\text{S}_2$  (476.57): C, 60.49%; H, 4.23%; N, 11.76%. Found: C, 60.61%; H, 4.32%; N, 11.65%.

5-Anilino-2-benzoyl-3-methyl-4-[[4-(pyridin-2-ylsulfamoyl) phenyl] azo] thiophene (**5b**)

mp = 203°C. Yield = 77%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3354, 3291, 1660, 1576, 1546.  $^1\text{H-NMR}$  (dimethyl sulfoxide,  $\delta$ , ppm):

2.3 (s, 3H,  $\text{CH}_3$ ), 7.0–7.9 (m, 18H, Ar–H). ANAL. Calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_5\text{O}_3\text{S}_2$  (553.65): C, 62.91%; H, 4.19%; N, 12.65%. Found: C, 62.78%; H, 4.26%; N, 12.74%.

5-Anilino-2-ethoxycarbonyl-3-methyl-4-(4-sulfamoyl phenyl azo) thiophene (**6a**)

mp = 187°C. Yield = 79%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3334, 3058, 1692, 1602, 1531.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.3 (t, 3H,  $\text{CH}_3$ ), 2.2 (s, 3H,  $\text{CH}_3$ ), 4.3 (q, 2H,  $\text{CH}_2$ ), 7.2–7.6 (m, 9H, Ar–H), 10.2 (s, 1H, NH), 12.6 (s, 1H, NH). ANAL. Calcd for  $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_4\text{S}_2$  (444.53): C, 54.04%; H, 4.53%; N, 12.60%. Found: C, 54.21%; H, 4.42%; N, 12.71%.

5-Anilino-2-ethoxycarbonyl-3-methyl-4-[[4-(pyridin-2-ylsulfamoyl) phenyl] azo] thiophene (**6b**)

mp = 214°C. Yield = 61%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3334, 3058, 2231, 1679, 1642, 1531.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.3 (t, 3H,  $\text{CH}_3$ ), 2.3 (s, 3H,  $\text{CH}_3$ ), 4.4 (q, 2H,  $\text{CH}_2$ ), 7.1–7.9 (m, 13H, Ar–H), 10.6 (s, 1H, NH), 13.2 (s, 1H, NH). ANAL. Calcd for  $\text{C}_{25}\text{H}_{23}\text{N}_5\text{O}_4\text{S}_2$  (521.61): C, 57.57%; H, 4.44%; N, 13.43%. Found: C, 57.40%; H, 4.38%; N, 13.38%.

5-Anilino-2-cyano-3-methyl-4-[4-sulfamoyl phenyl azo] thiophene (**7a**)

mp = 194°C. Yield = 71%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3231, 3082, 2196, 1605, 1533.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 2.2 (s, 3H,  $\text{CH}_3$ ), 7.3–7.7 (m, 9H, Ar–H), 11.8 (s, 1H, NH), 12.4 (s, 1H, NH). ANAL. Calcd for  $\text{C}_{18}\text{H}_{15}\text{N}_5\text{O}_2\text{S}_2$  (397.47): C, 54.39%; H, 3.80%; N, 17.62%. Found: C, 54.31%; H, 3.84%; N, 17.68%.

5-Anilino-2-cyano-3-methyl-4-[[4-(pyridin-2-ylsulfamoyl) phenyl] azo] thiophene (**7b**)

mp = 219°C. Yield = 64%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3262, 3099, 2198, 1602, 1544.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 2.2 (s, 3H,  $\text{CH}_3$ ), 7.2–7.8 (m, 13H, Ar–H), 12.1 (s, 1H, NH), 13.6 (s, 1H, NH). ANAL. Calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_6\text{O}_2\text{S}_2$  (474.56): C, 58.21%; H, 3.82%; N, 17.71%. Found: C, 58.37%; H, 3.87%; N, 17.60%.

### Dyeing procedure

Dyeing at 130–135°C and high pressure (24–30 psi) is a convenient method for dyeing polyester fabrics in the laboratory. A laboratory-model glycerin-bath high-temperature beaker dyeing machine was used. A dispersion of the dye was produced by dissolution of the appropriate amount of dye (2% shade) in 1 mL of acetone and then added dropwise with stirring to the dye bath (liquor ration 20 : 1) containing 1% Setamol WS as anionic dispersing agent (BASF). The pH of the dye bath was adjusted to 5.5 with

TABLE I  
Optical Measurements of the Synthesized Dyes on the Polyester Fabrics

Dye	Absorption [ $\lambda_{\max}$ (nm)]	K/S	$L^*$	$a^*$	$b^*$	$C^*$	H
4a	446	9.27	81.07	3.34	20.41	40.58	80.71
5a	442	13.36	40.99	3.32	41.81	54.73	49.81
6a	463	11.43	74.23	8.16	37.20	48.71	76.21
7a	458	9.36	89.36	-1.78	3.14	43.51	85.84
4b	448	10.25	72.91	4.17	47.57	58.63	76.13
5b	444	12.63	73.22	-1.45	23.11	43.85	76.74
6b	468	13.65	65.51	0.37	30.77	53.24	72.58
7b	461	13.04	80.93	-1.55	14.02	44.62	82.15

aqueous acetic acid, and the wetted-out polyester fibers were added. We performed dyeing by raising the dye bath temperature to 130°C at a rate of 3°C/min and holding it at this temperature for 60 min under pressure. After they were cooled to 50°C, the dyed fibers were rinsed with cold water and reduction-cleared (1 g/L sodium hydroxide, 1 g/L sodium hydrosulfite, 10 min, 80°C). The samples were rinsed with hot and cold water and, finally, air-dried.

#### Colorfastness tests

Fastnesses to washing, perspiration, rubbing, sublimation, and light were tested according to reported methods.<sup>17</sup>

##### Fastness to washing

A specimen of the dyed polyester sample was stitched between two pieces of undyed cotton and polyester fabrics (10 × 4 cm<sup>2</sup>), all of equal weight, and then washed at 50°C for 30 min. The staining of adjacent fabrics was assessed with the gray scale: (1) poor, (2) fair, (3) moderate, (4) good, and (5) excellent.

##### Fastness to perspiration

A composite sample was sandwiched on each side by undyed cotton, all of equal length, and then immersed in an acid or alkaline solution for 30 min. The staining on the undyed adjacent fabric was assessed according to the gray scale: (1) poor, (2) fair, (3) moderate, (4) good, and (5) excellent. The acid solution (pH = 3.5) contained sodium chloride (10 g/L), lactic acid (1 g/L), disodium orthophosphate (1 g/L), and histidine monohydrochloride (0.25 g/L). The alkaline solution (pH = 8) contained sodium chloride (10 g/L), ammonium chloride (4 g/L), disodium orthophosphate (1 g/L), and histidine monohydrochloride (0.25 g/L).

##### Fastness to rubbing

The dyed polyester fibers were placed on the base of a crockmeter so that they rested flat on the abrasive

cloth with its long dimension in the direction of rubbing. A square of white testing cloth was mounted over the end of the finger, which projected downward onto the dry specimen, which slid back and forth 20 times with 10 complete turns of the crank at the rate of one turn per second. For the wet rubbing test, the testing squares were thoroughly wetted in distilled water and squeezed between filter papers through hand wringer under standard conditions. The rest of the procedure was the same as the dry crocking test.

##### Fastness to sublimation

The sublimation fastness was measured with an iron tester (Yasuda no. 138, Yasuda Seiki Seisakusho, Ltd., Hyogo, Japan). The dye samples were stitched between two pieces of undyed polyester, all of equal length, and were then treated at 180 and 210°C, each for 1 min.

##### Fastness to light

Light fastness was determined with a Xenon test 150 (original Hanau, GmbH, Germany, chamber temperature = 25–30°C, black panel temperature = 60°C, relative humidity = 50–60%) dark glass (UV filter system) for 40 h. The changes in color were assessed according to the blue scale: (1) poor, (3) moderate, (5) good, and (8) very good.

#### Color assessment

The colorimetric parameters (Table I) of the dyed polyester fibers were determined on a reflectance spectrophotometer (Gretag-Macbeth CE 7000a, Neu-Isenburg, Germany) equipped with a D65/10° source and barium sulfate as the standard blank, UV excluded, specular component included, and three repeated measurements average settings.

#### Antimicrobial test method

The antimicrobial activity of the dyed polyester fabrics was evaluated by a quantitative shake-flask antimicrobial test method. A Gram-negative bacterium



TABLE II  
Fastness Properties of the Synthesized Dyes on the Polyester Fabrics

Dye	Washing	Perspiration		Rubbing		Sublimation		Light (40 h)
		Acid	Alkali	Dry	Wet	Staining at 180°C	Staining at 210°C	
4a	4-5	4-5	4-5	4-5	4-5	3	3	7
5a	4-5	4	4-5	3	3	4	4	6-7
6a	4-5	4-5	4-5	3-4	4-5	4	4	6
7a	4-5	4	4	4	4	3	3	7
4b	4-5	4-5	4-5	3	3	3-4	4	6
5b	4-5	4-5	4-5	3	3	4	4	5-6
6b	4-5	4-5	4-5	3	3	4	4	5-6
7b	4-5	4-5	4-5	4	4	4	4	6-7

(*Escherichia coli* ATCC 25922) and a Gram-positive bacterium (*Staphylococcus aureus* ATCC X6538P) were used as the test organisms. They were provided from the Regional Center for Mycology and Biotechnology, AL-Azher University, Nasr City, Cairo, Egypt.

Tryptic soy agar and tryptic soy broth were used to grow the bacterial cultures of *E. coli* and *S. aureus*, respectively. Bacteria were cultivated at 35°C for 24 h. Potassium hydrogen phosphate buffer solution (pH 7.2) used as a test medium. Sterile potassium hydrogen phosphate buffer solution (100 mL) was added to a sterile Erlenmeyer flask (300 mL), which was inoculated with 1.0 mL of a bacterial inoculum and a piece (1 × 1 cm<sup>2</sup>) of dye-free fabric. Time zero counts were made by the removal of 1.0 mL aliquots from the Erlenmeyer flask and triplicate withdrawals of 0.1 mL were placed in separate media, and after 24 h of incubation at 37°C, the initial number of bacterial colonies, or the zero-time counts of viable bacteria, were determined. One gram of sterile dyed fabric cut into pieces (1 × 1 cm<sup>2</sup>) was put in the flask and shaken for 1 h. One-hour counts were made in accordance with the previously described procedure.

The flask was shaken at 37°C for the prescribed different times (1–12 h), and three repeats were needed for each sample.

The percentage of bacterial reduction (*R*; %) was calculated with the following equation:

$$R = [(B - A)/B] \times 100$$

where *B* is number of bacterial colonies from undyed fabrics and *A* is the number of bacterial colonies from dyed fabrics.<sup>18</sup>

## RESULTS AND DISCUSSION

The treatment of  $\alpha$ -phenylthiocarbonyl acetylacetone<sup>16</sup> (**1**) with the aromatic diazonium chloride (**2**) in ethanol-containing sodium acetate affected one acetyl group cleavage (Japp–Klingmann type reaction<sup>19,20</sup>) with the formation of the corresponding thiocarbonyl intermediate (**3**). The versatile **3**

underwent heterocyclization with several  $\alpha$ -halogenated reagents, including chloroacetone, phenacyl bromide, ethyl chloroacetate, and chloroacetonitrile in DMF containing sodium carbonate to furnish the corresponding 4-arylaZO-3-methyl-2-substituted thiophene dyes (**4–7**, respectively).

The formation of thiophene derivatives **4–7** from the reaction of **3** with the appropriate alkylating agent, such as chloroacetone, phenacyl bromide, ethyl chloroacetate, and chloroacetonitrile, started through the nucleophilic attack of the thiolate group to form the nonisolable S-alkylated intermediate, which via nucleophilic addition and intramolecular cyclocondensation by water elimination, gave the corresponding 3-methyl-substituted thiophenes **4–7**.

The structures of the highly functionalized 3-methylthiophene dyes (**4–7**) were elucidated on the basis of their elemental analyses and spectral data. The IR spectrum of dye **4a** showed an absorption peak at 3413 and 3320 cm<sup>-1</sup>, corresponding to NH groups, and a broad absorption peak at 1664 cm<sup>-1</sup>, corresponding to the carbonyl group. The <sup>1</sup>H-NMR spectrum of **4a** showed singlet signals at 2.2 and 2.6 ppm due to methyl protons and a multiplet signal in the region 7.2–7.8, corresponding to the aromatic protons, in addition to singlet signals at 10.8 and 12.8 ppm due to the presence of NH groups.

The IR spectrum of compound **6a** displayed absorption bands related to the stretching vibrations of NH groups (3334 cm<sup>-1</sup>) and a band due to the carbonyl group (CO; 1692 cm<sup>-1</sup>). The <sup>1</sup>H-NMR spectrum of the same compound exhibited triplets and quadruplets due to protons of the ethyl ester group (1.3 and 4.3 ppm, respectively), a singlet signal from protons of the CH<sub>3</sub> groups (2.2 ppm), the lines of aromatic protons (7.2–7.6 ppm), and signals from the protons of the NH groups (10.2–12.6 ppm).

### Dyeing and fastness properties

The functionalized 4-arylaZO-3-methyl-2-substituted thiophene disperse dyes **4–7** were applied to polyester fabrics at 2% shade by a high-temperature pressure technique (130°C), and a range of color shades was

TABLE III  
Effect of the Contact Time on the Antibacterial Efficacy

Contact time (h)	Bacteria	Bacterial reduction (%) for the fabric dyed by							
		4a	5a	6a	7a	4b	5b	6b	7b
1	<i>E. coli</i> (negative)	23	28	22	30	25	30	23	32
	<i>S. aureus</i> (positive)	25	32	25	38	28	36	26	40
2	<i>E. coli</i> (negative)	26	31	27	34	31	32	27	36
	<i>S. aureus</i> (positive)	28	36	28	44	32	38	30	46
4	<i>E. coli</i> (negative)	33	36	34	39	33	36	33	42
	<i>S. aureus</i> (positive)	36	40	35	46	35	43	33	49
6	<i>E. coli</i> (negative)	38	37	36	40	38	38	36	43
	<i>S. aureus</i> (positive)	38	42	38	48	42	45	40	51

obtained, as the visual color shades varied from red to reddish violet. The dyeings on the polyester fabrics were evaluated in terms of their fastness properties (e.g., fastnesses to washing, perspiration, rubbing, sublimation, and light) with a standard method.<sup>17</sup> The results are given in Table II, and they reveal that these dyes had good fastness properties.

#### Color assessment

The color of dyeing on polyester fabrics is expressed in terms of CIELAB values (Table I), and the following CIELAB coordinates were measured: lightness ( $L^*$ ); chroma ( $C^*$ ); hue angle ( $H$ ) from 0 to 360°;  $a^*$ , whose value represents the degree of redness (positive) and greenness (negative); and  $b^*$ , whose value represents the degree of yellowness (positive) and blueness (negative). A reflectance spectrophotometer (Gretag Macbeth CE 7000a) was used for the colorimetric measurements of the dyed samples. The  $K/S$  values (where  $K$  is the absorbance coefficient and  $S$  is the scattering coefficient) given by the reflectance spectrometer were calculated at  $\lambda_{\max}$  (wavelength of maximum absorption) and were directly correlated with the dye concentration on the dye substrate according to the Kubelka–Munk equation:<sup>21</sup>

$$K/S = (1 - R)^2/2R$$

where  $R$  is the reflectance ratio.

In general, the color hues of the thiophene dyes **7a** and **7b** (which were substituted with nitrile groups) on the polyester fabric shifted to the greenish directions; this was indicated by the negative values of  $a^*$  (red–green axis). The positive values of  $b^*$  (yellow–blue axis) indicated that the color hues of the thiophene dyes **4–7** on the polyester fabric shifted to the yellowish directions.

#### Antibacterial activity of the synthesized dyes 4–7

The antibacterial activity of the dyed polyester fabrics with dyes (2% weight of fabric (w.o.f.), pH 5.5, liquor ratio (LR) = 20 : 1, temperature = 130°C for

60 min) was studied against Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria, as shown in Table III:

- All of the dyed fabrics gave antibacterial activity against Gram-positive and Gram-negative bacteria with different degrees, depending on the dye used.
- The antibacterial activity of the fabrics increased with increasing contact time up to 6 h of contact.
- The functionalized thiophene dye **7** (which was substituted with nitrile groups) showed higher antibacterial efficacy compared to the other corresponding 2-substituted thiophene dyes (**4–6**). Such a conclusion was also supported by the results obtained by Balaz et al.<sup>22</sup> and Singh et al.<sup>23</sup>

#### CONCLUSIONS

We studied the dyeing of polyester fabrics using functionalized thiophene dyes **4–7**, which were synthesized by the reaction of thiocarbonyl derivatives (**3**) with a variety of  $\alpha$ -halogenated reagents. The fastness properties of the dyed polyester fabrics with the synthesized thiophene dyes were evaluated. All of the dyes exhibited very good fastnesses to washing and perspiration, depending on the amount of dye fixed. The light fastnesses of the dyed polyester ranged from very good to excellent. Finally, all of the dyed fabrics exhibited antibacterial efficacy against Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria, and 2-cyanothiophene dyes showed higher activities than the other 2-substituted thiophene dyes.

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