

Synthesis and Characterization of New Unsaturated Polyesters Containing Cyclopentapyrazoline Moiety in the Main Chain

Ismail A. Alkskas,¹ Bashir A. El-gnidi,¹ Faizul Azam²

¹Polymer Lab, Department of Chemistry, Faculty of Science, Seventh of October University, Misurata, Libya

²Department of Chemistry, Faculty of Pharmacy, Seventh of October University, Misurata, Libya

Received 10 January 2009; accepted 21 September 2009

DOI 10.1002/app.31475

Published online 13 November 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: 3-*p*-Hydroxyphenyl-6-*p*-hydroxybenzylidene cyclopentapyrazoline (III) and 3-vanillyl-7-vanillylidene cyclopentapyrazoline (IV) were used as new starting materials for preparing new unsaturated polyesters. The polyesters were prepared by reacting (III) or (IV) with adipoyl, sebacoyl, isophthaloyl, and terephthaloyl dichlorides utilizing the interfacial polycondensation technique. The polyester samples have been characterized by elemental and spectral analyses. The polyesters have inherent viscosities of 0.55–0.97 dL/g. All the polyesters are semicrystalline and most of them are partially soluble in most common organic solvents but freely soluble in concen-

trated sulfuric acid. Their glass transition temperatures (T_g) range from 103.34 to 208.81°C, and the temperatures of 10% weight loss as high as 190 to 260°C in air, indicating that these aromatic polyesters have high T_g and excellent thermal stability. Doping with iodine dramatically raised the conductivity and produced dark brown colored semiconductive polymers with a maximum conductivity in the order of $3.1 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3727–3736, 2010

Key words: synthesis; characterization; unsaturated; polyester; pyrazoline

INTRODUCTION

Unsaturated polyesters are one of the most important matrix resins for composite applications. They possess a wide range of properties and are used in marine, automobile, construction, sport, and in self-extinguishing materials,^{1–4} and they have also led to the need and development of high-performance unsaturated polyesters. Several researches have reported the preparation of unsaturated polyesters by the polycondensation of dicarboxylic acids or acid anhydrides with diols, where at least one of the monomers contains an unsaturated carbon–carbon double bond (C=C).^{5–8} Unsaturated polyesters are generally difficult to perform because of their limited solubility in organic solvents and their high-melting temperature or high glass-transition temperature by virtue of their rigid structures. Therefore, development of polyesters for usage at high temperature with improved solubility is an important goal. The presence of heterocyclic rings in polymers lead to specific physical properties and also enhance thermal stability together with excellent solubility that is highly significant in aromatic heterocyclic polymers

with rigid chains.^{9,10} The introduction of pyrazoline ring in the main chain has the direct effect on the solubility and the thermal stability. Moreover, pyrazoline has an interesting ring unit containing both the electron-withdrawing group and the electron-releasing group that lead to interesting optoelectronic properties, such as photoconductivity^{11,12} and photo-refractive applications.^{13,14} Several reports concerning the polymers containing pyrazoline unit in the side chains have been found in literature.^{15,16} However, there are few reports concerning the synthesis of polymers containing pyrazoline unit in the main chain.¹⁷

Up to our knowledge, no work has been yet reported in regard to the synthesis of unsaturated polyesters containing cyclopentapyrazoline moiety in the main chain. The major aim of this work is to investigate the effect of cyclopentapyrazoline moiety in the polymer backbone on the polymer properties. With the aim of shedding light on certain characteristics, solubility, thermal stability, crystallinity, and electrical conductivities were also examined and discussed.

EXPERIMENTAL PROCEDURE

Instrumentation

Melting points were determined on a Perkin–Elmer 240°C electro thermal melting point apparatus and

Correspondence to: I. A. Alkskas (alkskas122@yahoo.com).

are uncorrected. Infrared spectra were recorded on a Shimadzu 2110 PC spectrophotometer with KBr pellets. The $^1\text{H-NMR}$ spectra were recorded on a GNM-LA 400 MHz NMR spectrophotometer at room temperature in DMSO using TMS as the internal reference. Mass spectra were recorded on a Jeol JMS-600 mass spectrometer. Viscosity measurements were made with a 0.5% (w/v) solution of polymers in DMSO at 258°C using an Ubbelohde suspended level viscometer. TGA and DTG measurements were performed on V 5.1 A DuPont 2000 thermal analyzer at a heating rate 10°C/min in air. DSC was carried out in a nitrogen atmosphere using a Shimadzu DSC-50 thermal analyzer. The X-Ray diffractograms of the polymers were obtained with a Phillips X-ray unit (Phillips generator Pw-1710) and Ni-Filtered CuK α radiations. The electrical conductivities were measured as follows: the sample was inserted in a home-made holder between two copper disks (insulated with Teflon); then, the sample resistivity was measured directly using a Keithly electrometer (610C) at 25°C with polymer disks (103.4 mm diameter, 0.65–0.80 mm thickness), which were prepared by compressing the finely powdered polymers at 4000 kg/mL under a vacuum. We measured the conductivity (s) from the Arrhenius equation. Iodine doping was carried out by exposing the disks to iodine vapor until the polymers were saturated, and the contents were calculated from their weight increase. The molecular weights of polyesters were evaluated by quantitative determination of OH and COOH end-groups. The acidity was determined by titration of a known weight of polyester in a mixture of solvents with KOH solution (0.1N). For determination of the OH groups number, an exact amount of polymer has been refluxed for 120 min in 10 mL of an acetylation mixture (pyridine/acetic anhydride), which was titrated with 0.1N KOH solution. The number average molecular weight (M_n) was calculated with the formula:

$$M_n = \frac{2 \times 1000 \times \text{sample wt}}{\text{meq COOH} + \text{meq OH}}$$

Reagents and solvents

4-Hydroxybenzaldehyde (BDH), 4-hydroxy-3-methoxybenzaldehyde (Merck), hydrazine hydrate (98%), and cyclopentanone (Aldrich) were used without purification. Terephthaloyl chloride (Aldrich) was recrystallized from *n*-hexane (mp 83–84°C) and isophthaloyl chloride (BDH) was recrystallized from *n*-hexane (mp 44°C). Adipoyl and sebacoyl dichlorides (Merck) were freshly distilled. Adipoyl dichloride at 125°C/11 Torr, and sebacoyl dichloride at 182°C/16 Torr were used. Benzoyl chloride (BDH) and sodium hydroxide were

of analytical grade. Dichloromethane and all other solvents were of high purity and further purified by standard methods.^{18–20}

Monomer synthesis

2,5-Bis(4-hydroxybenzylidene)cyclopentanone (I),
2,5-divanillylidene cyclopentanone (II)

2,5-Bis(4-hydroxybenzylidene)cyclopentanone (I) and 2,5-divanillylidene cyclopentanone (II) were prepared as described in the literature.²¹

3-p-Hydroxyphenyl-6-p-hydroxybenzylidene cyclopentapyrazoline (III)

A mixture of 0.01 mol (2.92 g) of dibenzylidene cyclopentanone(I) and 0.05 mol (2.50 g) of hydrazine hydrate 98% in methanol (100 mL) was stirred under reflux for 1.5 h. The reaction mixture was then allowed to cool and was kept at 0°C for 24 h. The precipitated product was filtered off, washed with petroleum ether 60–80, and was recrystallized from a mixture 30 : 1 of methanol-hydrazine hydrate to yield 80%. The pure product was conserved in a dark bottle in the refrigerator, mp. 340°C. Calculated composition of C₁₉H₁₈N₂O₂: C, 74.50; H, 5.88; N, 9.15% Found: C, 74.21; H, 5.39; N, 9.76%. IR(KBr, ν cm⁻¹): at 1595 cm⁻¹ (s, C=C), at 1630 cm⁻¹ (s, C=N), at 2940 cm⁻¹ (Ar-H stretch) at 3145 cm⁻¹ (—NH stretch) and at 3490 cm⁻¹ (br, OH stretch). The mass spectrum showed a molecular ion peak at $m/z = 306.17$ (27%) which is in agreement with its molecular formula (C₁₉H₁₈N₂O₂) Figure 1. $^1\text{H-NMR}$ (DMSO-*d*₆): at 8.60 (s, H of NH), at 8.0 (m, 2H of 2OH groups), at 7.70–6.75 (m, 8 H of Ar-H of dibenzylidene), at 6.5 (s, 1H of CH=C), at 3.0 (s, 1H of CH benzal), at 2.55 (s, 1H at C3a of cyclopentapyrazoline), at 1.6 (s, 2H of —CH₂— at C5 of cyclopentapyrazoline), and at 1.1 (s, 2H of —CH₂— at C4 of cyclopentapyrazoline) ppm Figure 2.

3-vanillyl-6-vanillylidene cyclopentapyrazoline(IV)

A mixture of 0.01 mol (3.52g) of 2,5-divanillylidene cyclopentanone (II) and 0.05 mol (2.50 g) of hydrazine hydrate 85% in methanol(100 mL) was stirred under reflux for 1.5 h. The reaction mixture was then allowed to cool and was kept at 0°C for 24 h. The precipitated product was filtered off, washed with petroleum ether 60–80°, and was recrystallized from chloroform to yield 79%. The pure product was conserved in a dark bottle in the refrigerator, mp. 200°C. Calculated composition of C₂₁H₂₂N₂O₄: C, 76.01; H, 5.88; N, 7.90% Found: C, 76.18; H, 5.32; N, 7.15%. IR(KBr, ν cm⁻¹): at 1597 cm⁻¹ (s, C=C), at 1635 cm⁻¹ (s, C=N), at 2945 cm⁻¹ (Ar-H stretch), at 3140 cm⁻¹ (—NH stretch), and at 3450 cm⁻¹ (br,

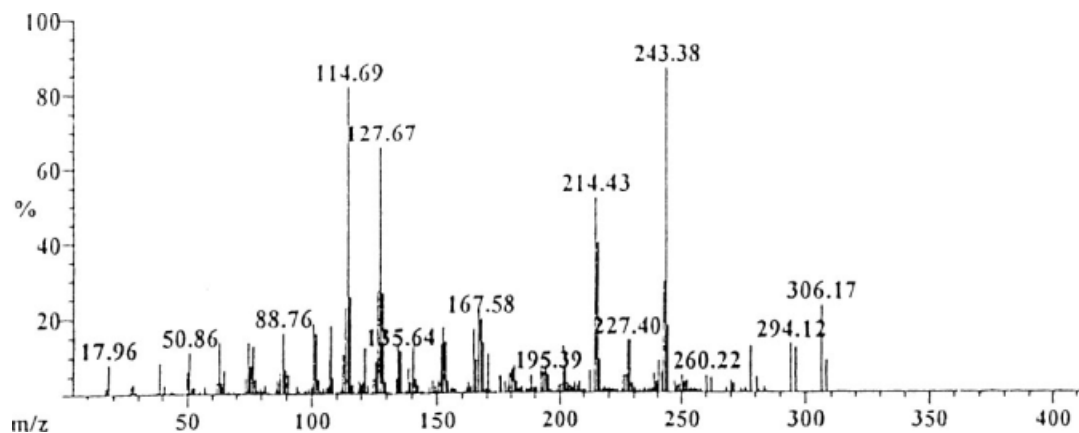


Figure 1 Mass spectrum of monomer III.

OH stretch). The mass spectrum showed a molecular ion peak at $m/z = 366.21$ (45%) which is in agreement with its molecular formula ($C_{21}H_{22}N_2O_4$). 1H -NMR (DMSO- d_6): at 8.40 (s, H of NH), at 7.50 (m, 2H of 2OH groups), at 7.40–6.50 (m, 8 H of Ar–H of dibenzylidene), at 6.0 (s, H of CH=C), at 4.50 (s, 6H of 2-OCH₃), at 3.20 (s, H of CH benzal), at 2.65 (s, 1H at C3a of cyclopentapyrazoline), at 1.80 (s, 2H of –CH₂– at C5 of cyclopentapyrazoline), and at 1.20 (s, 2H of –CH₂– at C4 of cyclopentapyrazoline) ppm.

Polymer synthesis

In a three-necked flask equipped with a mechanical stirrer 2000 rpm, dry nitrogen inlet, outlet, and dropper, a mixture of 1 mmol dibenzylidene cyclopentapyrazoline III or IV, 25 mL methylene chloride, and sodium hydroxide solution 2 mmol was introduced. After mixing, 1 mmol of acid chlorides Va-d dissolved in 30 mL methylene chloride was added over

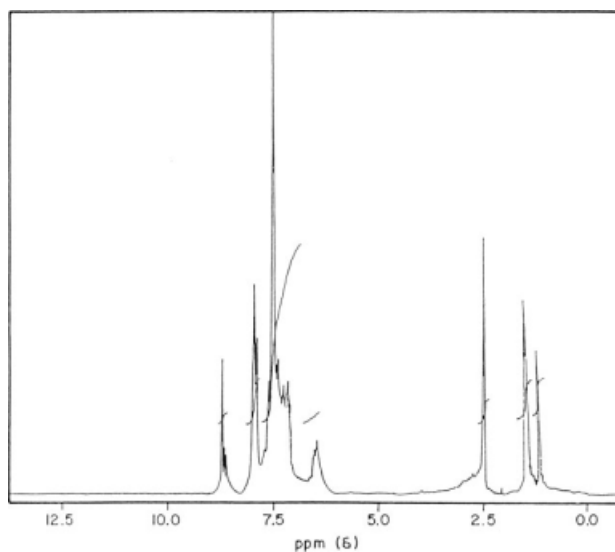


Figure 2 1H -NMR spectrum of monomer III.

a period of 2 min at 25°C and vigorously stirred. After complete addition of acid chloride, stirring was continued for 1–2 h, and a dark yellow solid polymer separated out. The solid polymer was filtered off, washed with water, hot alcohol, and eventually dried under reduced pressure 1 mmHg at 80°C for 1 day. The yield and some properties of the synthesized polyesters are listed in Table I, whereas their analytical data are summarized as following:

Polymer VIa

IR(KBr, ν cm^{-1}): at 1595 cm^{-1} (s, C=C), at 1630 cm^{-1} (s, C=N), at 1745–1757 cm^{-1} (s C=O), at 2960 cm^{-1} (Ar–H stretch), and at 3145 cm^{-1} (N–H stretch) Figure 3. 1H -NMR (DMSO- d_6): at 8.20 (s, H of NH), at 8.00–7.00 (m, 8 H of Ar–H of dibenzylidene and 4 H of Ar–H of terphthalate), at 6.00 (s, H of CH=C), at 2.95 (s, H of CH benzal), at 2.40 (s, 1H at C3a of cyclopentapyrazoline), at 1.30 (s, 2H of –CH₂– at C5 of cyclopentapyrazoline), and at 1.20 (s, 2H of –CH₂– at C4 of cyclopentapyrazoline) ppm (Fig. 4).

Polymer VIb

IR(KBr, ν cm^{-1}): at 1590 cm^{-1} (s, C=C), at 1625 cm^{-1} (s, C=N), at 1740 cm^{-1} (s C=O), at 2980 cm^{-1} (Ar–H stretch), and at 3150 cm^{-1} (N–H stretch). 1H -NMR (DMSO- d_6): at 8.10 (s, H of NH), at 8.10–7.30 m, 8 H of Ar–H of dibenzylidene and 4 H of Ar–H of isophthalate), at 5.80 (s, H of CH=C), at 2.75 (s, H of CH benzal), at 2.50 (s, 1H at C3a of cyclopentapyrazoline), at 1.35 (s, 2H of –CH₂– at C5 of cyclopentapyrazoline), and at 1.25 (s, 2H of –CH₂– at C4 of cyclopentapyrazoline) ppm.

Polymer VIc

IR(KBr, ν cm^{-1}): at 1590 cm^{-1} (s, C=C), at 1640 cm^{-1} (s, C=N), at 1735 cm^{-1} (s C=O), at 2990

TABLE I
Elemental Analysis, Yields, Molecular Weight, and Inherent Viscosities of Polyesters VIa–d and VIIa–d

Polymer code	Yield (%)	M_n^a	η_{inh}^b (dL g ⁻¹)	Molecular formula (mol. wt)	Elemental analyses			
					C%	H%	N%	
VIa	85	7520	0.85	C ₂₇ H ₂₀ O ₄ N ₂ (436)	Calc.	78.44	4.58	6.42
					Found	78.02	4.16	6.95
VIb	80	6890	0.94	C ₂₇ H ₂₀ O ₄ N ₂ (436)	Calc.	78.44	4.58	6.42
					Found	78.89	4.03	6.32
VIc	75	6700	0.63	C ₂₅ H ₂₄ O ₄ N ₂ (416)	Calc.	72.11	5.76	6.73
					Found	72.53	5.86	7.08
VI d	75	6500	0.59	C ₂₉ H ₃₂ O ₄ N ₂ (472)	Calc.	73.72	6.77	5.90
					Found	73.14	6.18	5.73
VIIa	86	8345	0.97	C ₂₉ H ₂₄ O ₆ N ₂ (496)	Calc.	70.16	4.83	5.64
					Found	70.83	5.09	5.18
VIIb	85	7965	0.90	C ₂₉ H ₂₄ O ₆ N ₂ (496)	Calc.	70.16	4.83	5.64
					Found	70.51	4.88	5.19
VIIc	80	6440	0.74	C ₂₇ H ₂₈ O ₆ N ₂ (476)	Calc.	68.06	5.88	5.88
					Found	68.48	6.14	5.62
VII d	78	6550	0.55	C ₃₁ H ₃₆ O ₆ N ₂ (532)	Calc.	79.26	6.76	5.26
					Found	79.81	6.22	5.84

^a Measured by end group analysis.

^b Measured for solutions in dimethylformamide, with $c = 0.5$ g/100 mL at 25°C.

cm⁻¹ (Ar–H stretch), and at 3155 cm⁻¹ (N–H stretch). ¹H-NMR (DMSO-d₆): at 8.15 (s, H of NH), at 7.90–7.35 (m, 8 H of Ar–H of dibenzylidene), at 6.10 (s, H of CH=C), at 3.15 (s, H of CH benzal), at 2.60 (s, 1H at C3a of cyclopentapyrazoline), at 2.4–1.8 (m, 8 H of CH₂ adipate), at 1.35 (s, 2H of –CH₂– at C5 of cyclopentapyra-

zoline), and at 1.20 (s, 2H of –CH₂– at C4 of cyclopentapyrazoline) ppm.

Polymer VI d

IR(KBr, v cm⁻¹): at 1600 cm⁻¹ (s, C=C), at 1620 cm⁻¹ (s, C=N), at 1740 cm⁻¹ (s C=O), at 2980 cm⁻¹

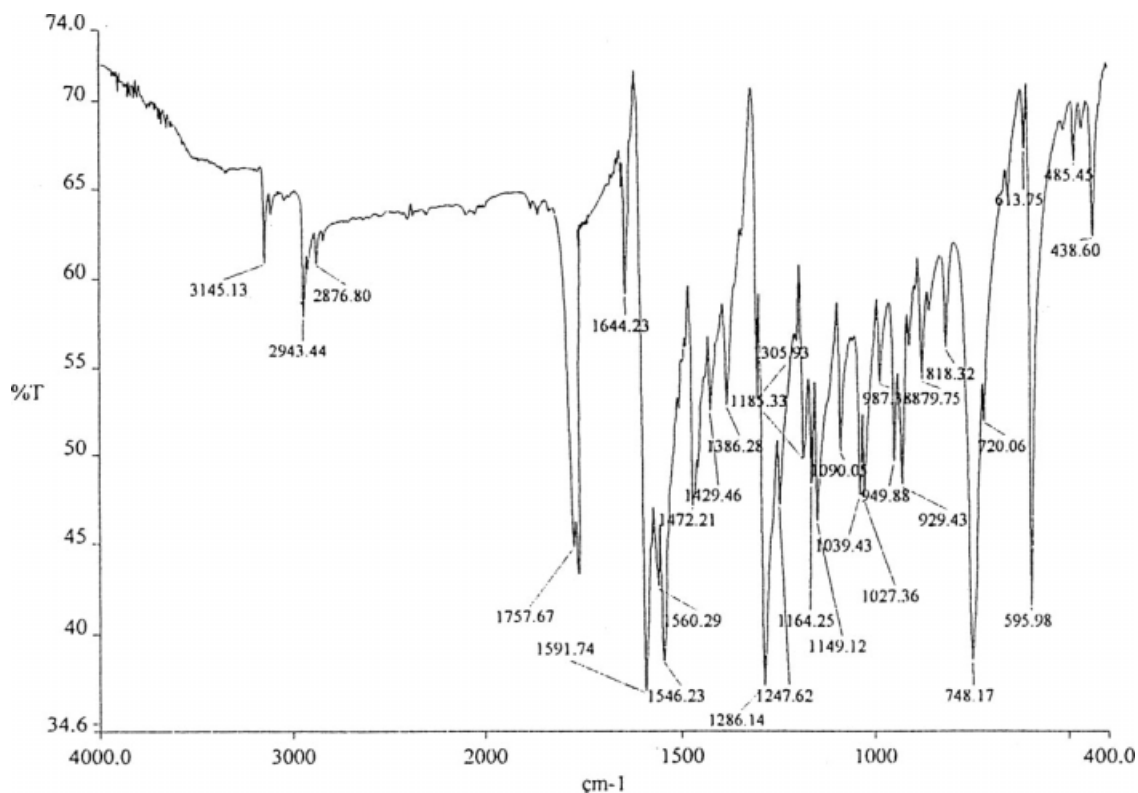


Figure 3 IR spectra of polymer VI_a.

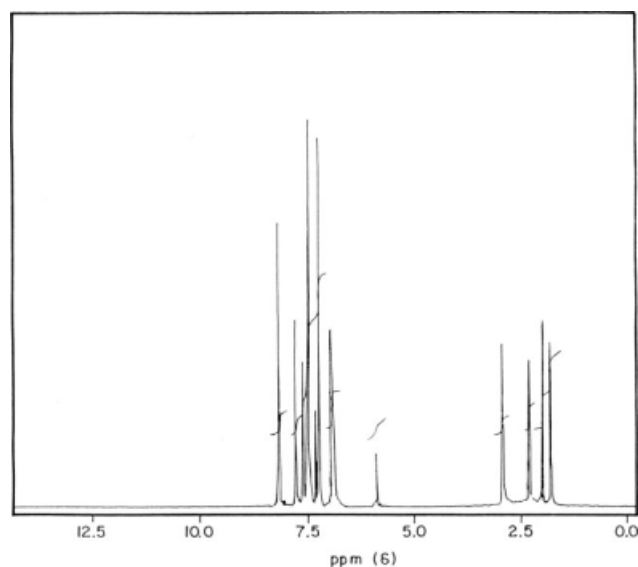


Figure 4 $^1\text{H-NMR}$ spectrum of polymer VI_a.

(Ar—H stretch), and at 3150 cm^{-1} (N—H stretch). $^1\text{H-NMR}$ (DMSO- d_6): at 8.00 (s, H of NH), at 7.85–7.35 (m, 8 H of Ar—H of dibenzylidene), at 6.20 (s, H of CH=C), at 3.10 (s, H of CH benzal), at 2.50 (s, 1H at C3a of cyclopentapyrazoline), 2.3–1.6 (m, 16 H of CH₂ sebasate), at 1.40 (s, 2H of —CH₂— at C5 of cyclopentapyrazoline), and at 1.25 (s, 2H of —CH₂— at C4 of cyclopentapyrazoline) ppm.

Polymer VIIa

IR(KBr, $\nu\text{ cm}^{-1}$): at 1590 cm^{-1} (s, C=C), at 1640 cm^{-1} (s, C=N), at 1730 cm^{-1} (s C=O), at 2995 cm^{-1} (Ar—H stretch), and at 3145 cm^{-1} (N—H stretch). $^1\text{H-NMR}$ (DMSO- d_6): at 8.20 (s, H of NH), at 7.95–7.10 (m, 8 H of Ar—H of dibenzylidene and 4 H of Ar—H of terphthalate), at 5.70 (s, H of CH=C), at 2.90 (s, H of CH benzal), at 2.50 (s, 1H at C3a of cyclopentapyrazoline), at 1.30 (s, 2H of —CH₂— at C5 of cyclopentapyrazoline), and at 1.25 (s, 2H of —CH₂— at C4 of cyclopentapyrazoline) ppm.

Polymer VIIb

IR(KBr, $\nu\text{ cm}^{-1}$): at 1595 cm^{-1} (s, C=C), at 1615 cm^{-1} (s, C=N), at 1725 cm^{-1} (s C=O), at 2960 cm^{-1} (Ar—H stretch), and at 3155 cm^{-1} (N—H stretch). $^1\text{H-NMR}$ (DMSO- d_6): at 8.10 (s, H of NH), at 7.95–7.20, at 5.50 (s, H of CH=C), at 2.95 (m, 8 H of Ar—H of dibenzylidene and 4 H of Ar—H of isophthalate), at 2.85 (s, H of CH benzal), at 2.50 (s, 1H at C3a of cyclopentapyrazoline), at 1.35 (s, 2H of —CH₂— at C5 of cyclopentapyrazoline), and at 1.15 (s, 2H of —CH₂— at C4 of cyclopentapyrazoline) ppm.

Polymer VIIc

IR(KBr, $\nu\text{ cm}^{-1}$): at 1595 cm^{-1} (s, C=C), at 1620 cm^{-1} (s, C=N), at 1730 cm^{-1} (s C=O), at 2980 cm^{-1} (Ar—H stretch), and at 3145 cm^{-1} (N—H stretch). $^1\text{H-NMR}$ (DMSO- d_6): at 8.15 (s, H of NH), at 7.80–7.30 (m, 8 H of Ar—H of dibenzylidene), at 5.80 (s, H of CH=C), at 3.00 (s, H of CH benzal), at 2.55 (s, 1H at C3a of cyclopentapyrazoline), 2.3–1.6 (m, 8 H of CH₂ adipate), at 1.40 (s, 2H of —CH₂— at C5 of cyclopentapyrazoline), and at 1.25 (s, 2H of —CH₂— at C4 of cyclopentapyrazoline) ppm.

Polymer VIId

IR(KBr, $\nu\text{ cm}^{-1}$): at 1959 cm^{-1} (s, C=C), at 1630 cm^{-1} (s, C=N), at 1730 cm^{-1} (s C=O), at 29 cm^{-1} (Ar—H stretch), and at 3150 cm^{-1} (N—H stretch). $^1\text{H-NMR}$ (DMSO- d_6): at 8.00 (s, H of NH), at 7.85–7.35 (m, 8 H of Ar—H of dibenzylidene), at 6.00 (s, H of CH=C), at 3.10 (s, H of CH benzal), at 2.60 (s, 1H at C3a of cyclopentapyrazoline), 2.4–1.6 (m, 16 H of CH₂ sebasate), at 1.30 (s, 2H of —CH₂— at C5 of cyclopentapyrazoline), and at 1.15 (s, 2H of —CH₂— at C4 of cyclopentapyrazoline) ppm.

RESULTS AND DISCUSSION

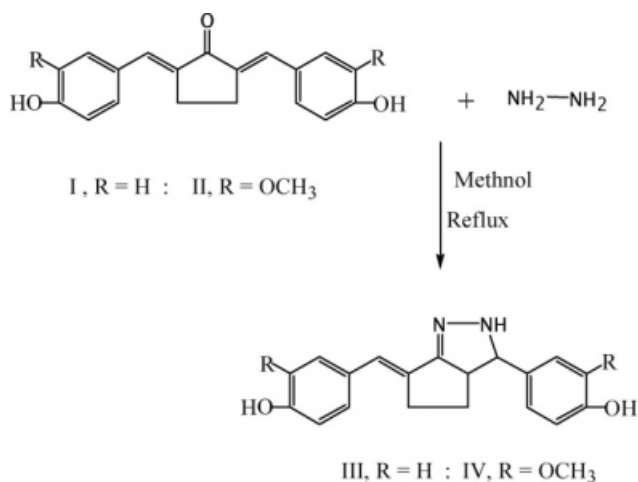
Monomers

In 1964, by using Michael condensation, Sammour et al.²² has reported some substituted cycloalkanones with phenyl hydrazine. In another study,²³ doubly unsaturated ketones such as dibenzylideneacetone showed the two double bonds in dibenzylidene acetone underwent Michael condensation independent on each other. In this study, new monomers based on cyclopentapyrazoline moiety were prepared by condensation of 2,5-bis(*p*-hydroxybenzylidene)cyclopentanone I or 2,5-divanillylidene cyclopentanone II with hydrazine hydrate, as shown in Scheme 1.

The structures of these new monomers were elucidated by elemental and spectral analyses (see Experimental Section).

Polymerization

The polymerization of 3-*p*-hydroxyphenyl-6-*p*-hydroxybenzylidene cyclopentapyrazoline III or 3-vanillyl-6-vanillylidene cyclopentapyrazoline IV with adipoyl, sebacoyl, isophthaloyl, or terephthaloyl dichlorides resulted in the formation of novel unsaturated polyesters. Typical polymerization conditions involved in the reaction of the stoichiometric amount of III or IV with diacid chlorides Va–d and the application of interfacial polycondensation with NaOH/CH₂Cl₂ at ambient temperature to afford new unsaturated polyesters was shown in Scheme 2.



Scheme 1 Synthesis on monomers III and IV.

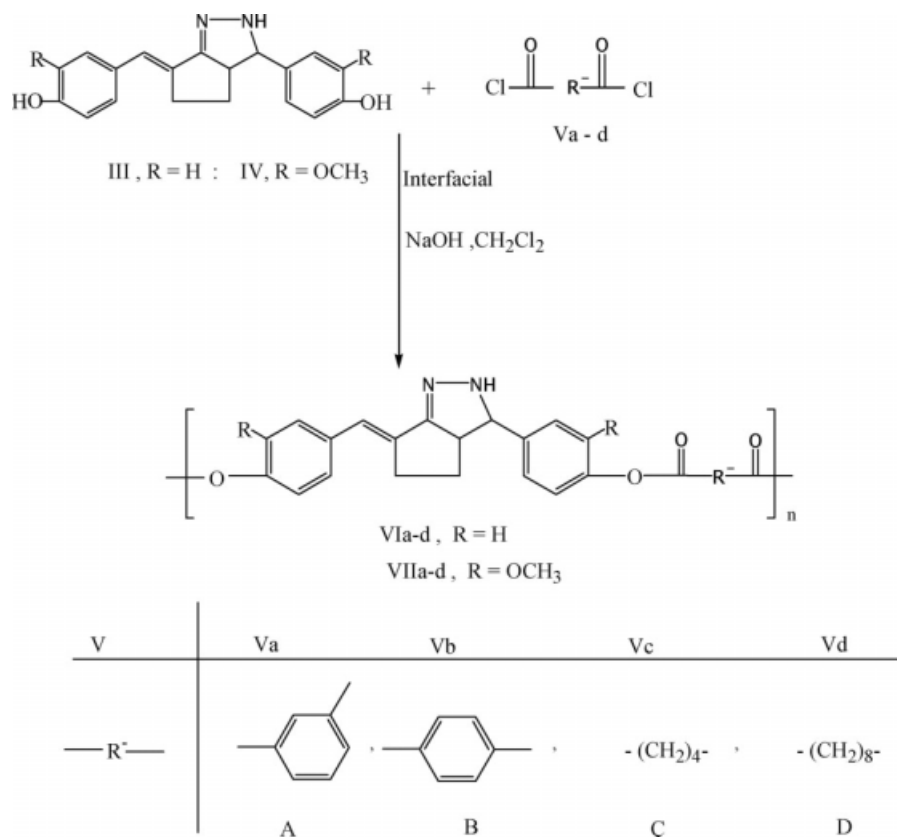
Reaction times varied from 1 to 2 h and the resulting dark yellow solid polymer were isolated immediately at the end of the reaction period. The elemental analyses of newly synthesized monomers as well as polymers (Table I) were found in accordance with their theoretical values showing a deviation of 0.30 to 0.80%. However, it is common for polymers to trap solvent molecules within the polymer matrix, especially polymers of high molecular weight and those polymers containing polar groups that are ca-

pable of hydrogen bonding with solvent molecules. IR data obtained in KBr disks for all polyesters indicated the disappearance of the characteristic absorption band of the OH group and the appearance of the of ester groups at 1730–1757 cm^{-1} , at 1615–1640 cm^{-1} for the C=N of cyclopentapyrazoline, at 1590–1600 cm^{-1} for C=C groups, at 2876 cm^{-1} for C–H aliphatic, –NH group of cyclopentapyrazoline at 3145–3155 cm^{-1} ; and other characteristic absorption bands as well as $^1\text{H-NMR}$ spectral data for rest of the molecules are given in Experimental Section. The number average molecular weight (M_n) of the unsaturated polyesters was determined using end-group titration techniques, and it ranges between 6440 and 8345 g per mol, and the analytical data are presented in Table I.

The inherent viscosities (η_{inh}) of polyesters VIa–d and VIIa–d were determined in DMF at 25°C with an Ubbelohde suspended level viscometer. The inherent viscosity value is defined as:

$$\eta_{\text{inh}} = (2.3 \log t/t_0)/C$$

Where t_0 and t represent the viscometer flow periods for DMF and the polymer solution, respectively, while solution concentration C is 0.5 g/100 mL. It can be clarified from Table I that polyesters having high inherent viscosity values ranged from 0.55 to 0.97 dL/g.



Scheme 2 Synthesis of polyesters VIa–d and VIIa–d.

TABLE II
Solubility Characteristics of Polymers VIa–d and VIIa–d

Polymer number	DMF	DMSO	NMP	THF	DCM	Chloroform + Acetone (1 : 1)	TCE	Concentrated H ₂ SO ₄
VIa	+	++	+	+	+	+	–	++
VIb	++	++	++	+	+	+	–	++
VIc	++	++	++	++	+	+	+	++
VIId	++	++	++	++	++	++	+	++
VIIa	++	++	+	+	+	+	–	++
VIIb	++	++	+	+	+	+	+	++
VIIc	++	++	++	++	++	++	+	++
VIIId	++	++	++	++	++	++	++	++

++, Soluble at room temperature (RT); +, Partially soluble at (RT); –, Insoluble at (RT).

POLYMER CHARACTERIZATION

Solubility

The solubility of unsaturated polyesters synthesized in this study was determined for the powdery samples in various organic solvents including dimethylsulfoxide (DMSO), *N-N* dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), tetrahydrofuran (THF), dichloromethane (DCM), tetrachloromethane (TCE), chloroform-acetone (1 : 1), and concentrated sulfuric acid at 3.0% (w/v), and the results are presented in Table II. It was found that all the polymers dissolved readily in concentrated H₂SO₄ at room temperature giving deep red color due to unstability of the polymers. All polymers were soluble in various aprotic polar solvents such as DMSO, DMF, NMP, and THF. The good solubility of these polymers may be elucidated by loose of packing of the macromolecules because of rigid pyrazoline rings and low crystallinity.²⁴ Moreover, introducing the pyrazoline ring as polar group into polyheterocyclic polymers gives rise to slight increase in solubility of the polymers. In common organic solvents and halogenated hydrocarbons, the polymers VIa,b,c and VIIa,b were partly soluble (except polymer VIId, and VIIc,d are soluble) that may be attributed to the presence of aliphatic chain with four and eight methylene groups, with the rigid cyclopentapyrazoline position of the main chain causing increase in solubility. It should be realized that the polymer VIIc is more soluble than VIc, and this behavior could be attributed to the steric hindrance effect of the methoxy group, which causes unsymmetrical orientation thereby making solvation easier.²⁵ Therefore, the bulkiness of the cyclopentapyrazoline rings may play a more important role than rigidity in the improvement of the polyester solubility.

X-ray analysis

The X-ray diffraction confirmed that the polymers were semicrystalline because of a small portion of crystalline peaks in the region $2\theta = 10^\circ$ – 60° or

(d in Å) as shown in Figure 5. In spite of small crystalline regions in every case, amorphous patterns are due to a lower packing of the unsymmetrical polymer back bones. In particular, the bulky cyclopentapyrazoline rings along the backbone most probably is the main reason for the amorphous nature of the present polyesters; it is also evident that the presence of the pyrazoline ring in the polymer main chain tends to destroy the efficiency of polymer to form crystalline structures. The presence of four and eight methylene groups in polymers VIc,d and

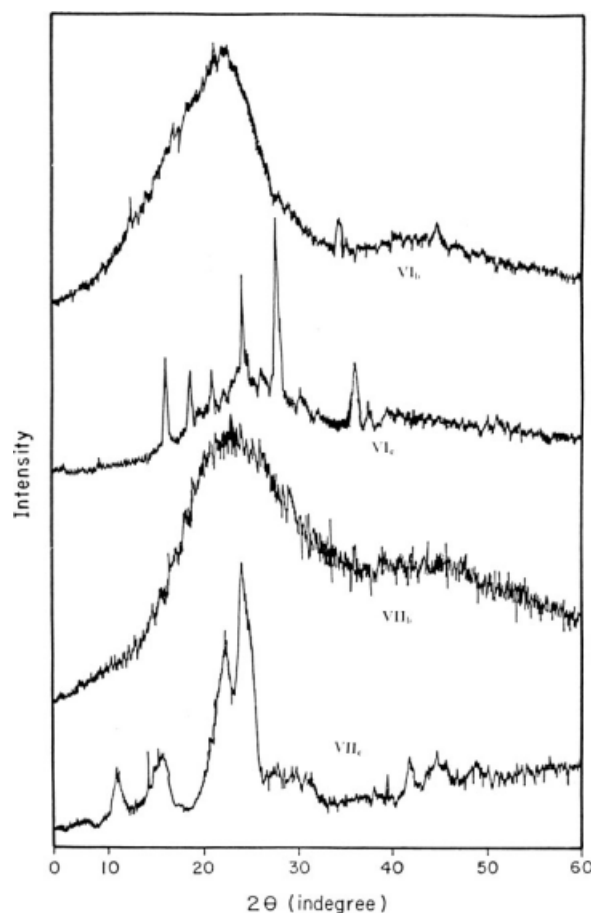


Figure 5 X-ray diffraction patterns of polymers VI_{b,c} and VII_{b,c}.

TABLE III
Thermal Properties of Polymers VIa–d and VIIa–d

Polymer number	Temperature (°C) for various % decomposition ^a					Thermal behavior of polyesters			
	10	20	30	40	50	T_g (°C) ^b	T_c (°C) ^c	T_m (°C) ^d	T_d (°C) ^e
VIa	260	350	410	465	525	208.81	–	–	420.48
VIb	250	360	395	435	530	202.25	–	381.22	407.22
VIc	200	250	340	395	460	123.72	291.82	365.82	396.38
VIId	195	240	325	375	430	113.46	278.53	–	397.59
VIIa	250	355	405	450	520	197.92	–	398.41	415.17
VIIb	245	365	400	430	515	178.56	–	–	412.83
VIIc	195	240	335	385	450	106.57	298.63	325.42	372.81
VIIId	190	235	320	375	430	103.34	384.25	318.72	365.25

^a The values were determined by TGA at a heating rate of 10°C/min.

^{b–e} Measured by DSC at a heating rate of 10°C/min in nitrogen.

VIIc,d increases polymer chain flexibility and that might be responsible for the approach and mutual attractions of adjacent chains and thus induce small crystalline peaks. Moreover, the presence of N–N or C=N as polar groups in addition to high C=C bond levels induces some order between two adjacent chains in the polymer, leading to some extent of crystallinity.²⁶ It should be also noted that the inclusion of pyrazoline moiety as rigid group in the polymer main chain causes slight decrease in the degree of crystallinity compared with those polyesters based on diarylidene cycloalkanones that were revealed in literature.^{27,28}

Thermal properties

DSC and TGA measurements were performed to study the thermal behavior and thermal stability of the prepared unsaturated polyesters. The results are summarized in Table III. Investigation of DSC curves (Fig. 6) showed that the glass transition temperatures (T_g) of polyesters as a second order transition were in the range of 190–260°C, and the T_g decreases as the number of methylene groups of the polyesters increases. The polyesters derived from diols with bulky pyrazoline group and aromatic diacid chlorides with more ordered structures showed higher T_g values. As expected, and shown in the Table III, the polyester VIb, which was prepared from unsymmetrical diol IIIa and diacid chlorides Va, has the highest T_g . This is reasonable because a bulky cyclopentapyrazoline ring inhibits the free rotation of the polymer chain and leads to an enhanced T_g value.²⁹ Polymer VIId, which was prepared from diol IV containing methoxy group and diacid chlorides Vd, has the lowest T_g . This decrease in the glass transition temperature can be explained by some compatibilization of flexible methylene units and rigid blocks, whereas polyesters containing 4 and 8 methylene groups has crystallization temperature as reflected by T_c in DSC plot. It can be suggested that

the methylene chain breaks during heating and rearrange to form a closely packed polymer chain. The DSC curves also showed endothermic peaks of polyesters appearing at around 372.81–420.48°C which can be interpreted as a melting process accompanied by decomposition.

The thermal behavior of these polyester VIa–d and VIIa–d was evaluated by TGA in air at a heating rate 10°C/min. The thermographs of these polymers are given in Figure 7. Table III gives the temperature for various percentages of weight loss. In Figure 7 the TGA curves show a small weight loss in the range of 2–6% starting at 120°C until 185°C, which may be attributed to loss of adsorbed moisture and entrapped solvents. The thermographs also indicated in Figure 6 that the polymers decompose in two stages and the mass loss is seen to be rapid between ~ 200 and 500°C for the polymer VIa in the first region and between ~ 500 and 560°C in the second region. For the polymer VIc, the mass loss was rapid between ~ 185 and 450°C in the first region and between ~ 450 and 550°C in the second region. All the studied polymers decompose in the first stage between 185 and 500°C, whereas in the second stage

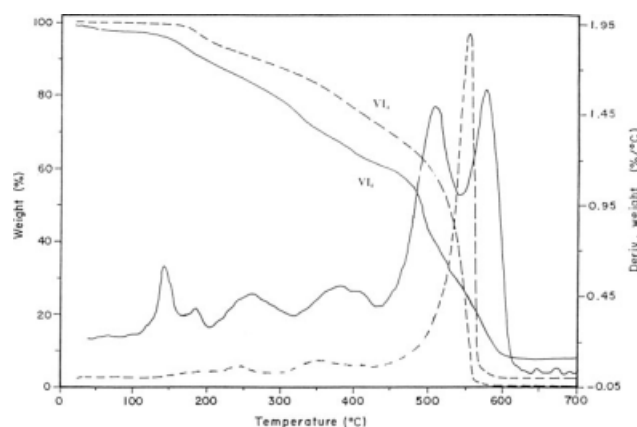


Figure 6 The TGA and DTG traces of polymers VI_{a,c} in air at a heating rate of 10°C/min.

they decompose from 500 to 560°C, which depends on the nature of the polyester. The expected nature of decomposition of these polymers is a pyrolytic oxidation of $-C=C-$,³⁰ scission of many bonds, in addition to the formation of char as an end product. The temperature for 10% weight loss is considered to be polymer decomposition temperature, and it ranges between 190 and 260°C, and the temperature for 50% weight loss was found between 430 and 530°C. Therefore, the data in Table III indicate that the thermal stabilities of these polymers are in the order VIa > VIIa > VIb > VIIIb > VIc > VIId > VIIc > VIId. It should be noted that the aromatic based polyester VIa,b and VIIa,b are more thermally stable than the aliphatic based polymers. In particular, the inclusion of the cyclopentapyrazoline ring as a rigid group into the polymer chain increases the thermal stability of these polymers.

Electrical conductivity

The electrical conductivity of the pyrazoline polymers ranged from 10^{-11} to $10^{-12} \Omega^{-1} \text{cm}^{-1}$ at 30°C (Table IV). Polymers VIc,d and VIIc,d, which contain four and eight methylene groups respectively, were the less conductive among these examined polymers. The doping with iodine as an electron acceptor was performed until the polymer was saturated with iodine. The doped polyesters (VIa-d and VIIa-d), which had an affinity (absorbed amount) of circa 15 wt % toward iodine, were light to dark brown in color. Those with more than 70 wt % were black after being left overnight, whereas the undoped ones were pale orange to deep orange solids. Polymers VIa,b and VIIa,b absorbed 85, 84, 80, and 81 wt % of iodine per polymer, respectively. As can be seen from Table IV, the electric conductivities were successfully raised by iodine doping and reached as high as 10^{-7} – $10^{-8} \Omega^{-1} \text{cm}^{-1}$ upon iodine doping of

TABLE IV
Electrical Conductivity of Polymers VIa-d and VIIa-d

Polymer number	Affinity toward I ₂ (wt %) ^a	Electrical conductivity ^b (S cm ⁻¹)	
		Undoped	I ₂ Doped
VIa	85	2.6×10^{-11}	2.3×10^{-7}
VIb	84	1.1×10^{-12}	2.1×10^{-7}
VIc	73	2.2×10^{-12}	3.1×10^{-8}
VIId	70	2.4×10^{-12}	3.2×10^{-8}
VIIa	80	5.1×10^{-11}	3.1×10^{-7}
VIIb	81	6.1×10^{-11}	2.5×10^{-7}
VIIc	77	2.3×10^{-12}	2.4×10^{-8}
VIIId	78	3.1×10^{-12}	2.5×10^{-8}

^a The iodine content was calculated from the weight increase.

^b Measured by DC electrical conductivity at 25°C.

circa 70 wt %. Thus, the unsaturated polyesters containing pyrazoline moiety are good insulators, but they have been converted into semiconductors by doping with iodine. Moreover, the study of the electrical conductivity temperature dependence, curing, and irradiation of these polymers is in progress and the results will be published in the near future.

CONCLUSIONS

Linear unsaturated polyesters based on diarylidene-cyclopentapyrazoline derivatives have been prepared. An interfacial polycondensation synthesis technique at ambient temperature was used. The majority of the polyesters were soluble in aprotic polar solvents and H₂SO₄. TGA showed that the aliphatic based polyester were somewhat less thermally stable than their aromatic counterparts. X-ray diffraction analyses showed that the inclusion of pyrazoline group in the polymer chain causes decrease in the degree of crystallinity. Upon doping with iodine, the synthesized polymers became semiconductors (10^{-7} – $10^{-8} \Omega^{-1} \text{cm}^{-1}$).

References

- Vijayakumar, C. T.; Sivasamy, P.; Rajkumar, T. *Eur Polym J* 2007, 43, 3028.
- Han, H.; Bhowmik, P. K. *Prog Polym Sci* 1997, 22, 1431.
- Li, H.; Wang, D.; Fan, L.; Yang, S. *Eur Polym J* 2006, 42, 534.
- Murali, M.; Samui, A. B. *J Polym Sci Part A: Polym Chem* 2006, 44, 51.
- Marvel, C. S.; Young, C. H. *J Am Chem Soc* 1951, 73, 1066.
- Podkoscielny, W.; Rudz, W. *Eur Polym J* 1993, 29, 1115.
- Hirano, H.; Watase, S.; Tanaka, M. *J Appl Polym Sci* 2004, 91, 1865.
- Morgan, P. W. *Condensation Polymers by Interfacial and Solution Methods*; Interscience: New York, 1965.
- Xiao, D.; Xi, L.; Yang, W.; Fu, H.; Shuai, Z.; Fang, Y.; Yao, J. *J Am Chem Soc* 2003, 125, 6740.
- Gaina, C.; Gaina, V.; Cozan, V. *Eur Polym J* 2001, 37, 79.
- Mylnikov, V. S. *Adv Polym Sci* 1994, 115, 1.
- Yamamoto, T. *Macromol Rapid Commun* 2002, 23, 583.

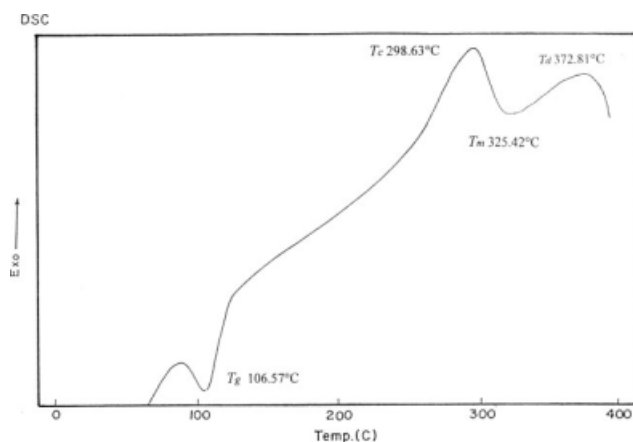


Figure 7 The DSC curve of polymer VIIc.

13. Ma, C.-Q.; Zhang, L.-Q.; Zhou, J.-H.; Wang, X.-S.; Zhang, B.-W.; Cao, Y.; Bugnon, P.; Scher, M.; Nusch, F.; Zhang, D.-Q.; Qiu, Y. *Chin J Chem* 2002, 20, 929.
14. Ma, C.-Q.; Zhang, L.-Q.; Li, X.-H.; Wang, X.-S.; Zhang, B.-W.; Cao, Y.; Wang, D.-M.; Jiang, X.-Y.; Zhang, Z. L.; Zhang, D.-Q.; Qiu, Y. *Acta Chim Sinica* 2002, 60, 847.
15. Kaufman, F. B.; Engler, E. M. *J Am Chem Soc* 1979, 101, 547.
16. Kaufman, F. B.; Schroeder, A. H.; Engler, E. M.; Patel, V. V. *Appl Phys Lett* 1980, 36, 422.
17. Fang, Q.; Yamamoto, T. *J Polym Sci Part A: Polym Chem* 2004, 42, 2686.
18. Vogel, A. *Textbook of Practical Organic Chemistry*, Vol. 1; Longmans & Green: London, 1967.
19. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.
20. Tomlinson, M. L. *J Chem Soc* 1980, 1946, 756.
21. Abd-Alla, M. A.; Aly, K. I.; Hammam, A. S. *High Perform Polym* 1989, 1, 223.
22. Sammour, A.; Marei, A.; Haseein, M. H. *J Chem UAR* 1969, 12, 451.
23. Khalaf, A. A.; El-Shafei, A. K.; El-Sayed, A. M. *J Heterocycl Chem* 1982, 19, 609.
24. Liaw, D.; Liaw, B.; Hsu, J.; Cheng, Y. *J Polym Sci Part: A Polym Chem* 2000, 38, 4451.
25. Aly, K. I.; Khalaf, A. A.; Alkskas, I. A. *Eur Polym J* 2003, 39, 1035.
26. Alkskas, I. A.; Esbata, A. A. *J Macromol Sci A Chem* 2008, 45, 218.
27. Aly, K. I.; Khalaf, A. A. *J Appl Polym Sci* 2000, 77, 1218.
28. Abd-Alla, M. A.; El-Zohary, M. F.; Aly, K. I.; Abdel-Whab, M. M. *J Appl Polym Sci* 1993, 47, 323.
29. Korshak, V. V.; Vinogradova, S. V.; Salazkin, S. N.; Komarova, L. F. *Eur Polym J* 1974, 10, 967.
30. Aly, K. I.; Khalaf, A. A.; Alkskas, I. A. *Eur Polym J* 2003, 39, 1273.