

Synthesis and Characterization of Novel Organosoluble Polyesters Based on a DIOL with Azaquinoxaline Ring

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ABSTRACT: A series of new polyesters were synthesized by polycondensation of aliphatic and aromatic dicarboxylic dichlorides with a novel quinoxaline diol, 2,3-bis(4-hydroxy phenyl)-5-azaquinoxaline (DIOL). The DIOL was synthesized by reacting 4,4'-dihydroxy benzil with 2,3-diaminopyridine (yield: 85%), and characterized by FTIR and ¹H-NMR spectra. All polyesters showed good solubility in most aprotic polar solvents such as NMP (*N*-methylpyrrolidone), DMF (dimethylformamide), DMSO (dimethylsulfoxide), DMAc (dimethylacetamide), HMPA (hexamethylenephosphoramide), and Py (pyridine). The

inherent viscosity of polyesters was obtained in the range of 1.1–1.22 dL/mg. The glass transition temperatures of the polyesters were in the range of 200–280°C, as determined by DSC. The initial decomposition temperatures of the polyesters were above 300°C and the char yield at 750°C ranged from 30 to 60% under nitrogen atmosphere. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3458–3463, 2009

Key words: polyesters; solubility; polycondensation; TGA; DSC

INTRODUCTION

Aromatic polyesters have found a wide range of applications due to their remarkable properties such as good heat and chemical resistance, low shrinkage, low water content, and barrier properties and interesting physico-mechanical properties. However, limitations arise from their high melting temperature and limited solubility in most organic solvents.^{1–3} To obtain polyesters with considerably improved processing properties; several chemical modifications including: (i) the introduction of bulky, or nonsymmetrical substituents; (ii) the use of flexible spacer; (iii) the use of nonlinear or bent monomers; and (iv) copolymerization of different monomers have been previously reported.^{4–13} A number of thermally stable aromatic polyesters have been prepared,^{14–23} but in general the types of structures that impart thermal resistance also result in poor processing characteristics. Among the class of polymers claimed to be thermally stable only a few have achieved technological importance, some of which are polyamides, polyimides, polyquinoxalines, polyquinolines, and polybenzimidazoles. Poly(phenylquinoxaline)s which was first prepared by Hergenrother et al.,^{2,24} continue to attract much attention because of their good oxidative, thermal, and hydrolytic stability, low dielectric constant, high T_g , and good mechanical

properties.^{25–29} Although poly(phenylquinoxaline)s are soluble *m*-cresol and selected chlorinated solvents such as chloroform and tetrachloroethane, but the toxicity of the solvents may limit the use of these polymers in many applications. There are reports of synthesis of thermostable polyesters containing phenylquinoxaline ring in the main chain along with different functional groups such as imide rings,³ oxadiazole rings,³⁰ and ether linkages^{31–33} with improved solubility in the polar aprotic solvents.

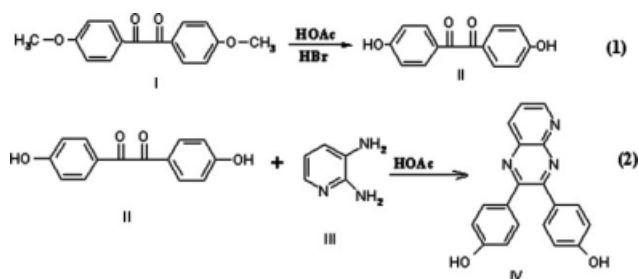
In this article, we describe the synthesis and characterization of a new diol containing the azaquinoxaline ring and polyesters obtained from polycondensation of the diol with aliphatic- and aromatic dicarboxylic dichlorides. The new 2,3-bis(4-hydroxyphenyl)-5-azaquinoxaline was synthesized using 4,4'-dihydroxybenzil and 2,3-diaminopyridine in the presence of acetic acid. The purpose of this investigation is to prepare polyesters containing azaquinoxaline moiety as pendant groups with improved solubility. Polyesters synthesis was performed in DMF solution in the presence of triethylamine. The solubility, inherent viscosity, elemental analysis, and thermal properties of polyesters were measured.

EXPERIMENTAL

Materials and instruments

Benzil, 2,3-diaminopyridine, dimethoxybenzil and all other chemicals were purchased from Fluka (Switzerland).

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Scheme 1 The procedure for preparation of DIOL monomer.

$^1\text{H-NMR}$ spectra were recorded on a Bruker advance DRX 500 MHz instrument using DMSO-d_6 as solvent and tetramethyl silane as an internal standard. FTIR spectra were recorded on a Bruker Vector 22 spectrophotometer using KBr pellets. The CHN- 600 Leco (UK) analyzer was used for elemental analysis. Thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC) were performed at $10^\circ\text{C}/\text{min}$ under N_2 atmosphere by using a Perkins–Elmer pyres and a Mettler Toledo 822 $^\circ$, respectively. Inherent viscosity ($\eta_{\text{inh}} = \text{Ln}\eta_{\text{rel}}/C$) of polymers were determined for solution of 0.5 g/dL in NMP at 25°C using an Ubbelohde viscometer.

Synthesis of the monomer

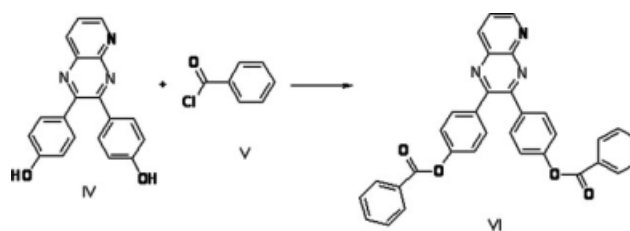
Synthesis of the monomer (DIOL) took place in two steps: first, the synthesis of 4,4'-dihydroxybenzil (DHB), and second, the reaction of DHB with 2,3-diaminopyridine. Both steps are described in Scheme 1.

4,4'-Dihydroxybenzil³⁴

In a 1 L, three-necked, round-bottom flask equipped with a reflux condenser, a magnetic stirrer bar, and a nitrogen inlet were placed 6 g (22 mmol) of 4,4'-dimethoxybenzil, 60 mL of acetic acid (HOAc), and 300 mL HBr (68%). The suspension was heated at reflux with stirring for 4 h to become a homogeneous yellow solution which was cooled to room temperature, during which a yellow solid was formed. The solid was filtered, washed with cold water several times, recrystallized in HOAc, and dried in vacuum oven. The yellow needles obtained in a yield of 82% (3.3 g), which starts to melt at 244°C .

2,3-Bis(4-hydroxy phenyl)-5-azaquinoxaline

A 500 mL, round-bottom flask equipped with a magnetic stirrer bar, a reflux condenser, a Dean–Stark trap, and a nitrogen inlet was charged with 0.48 g (2 mmol) of 4,4'-dihydroxybenzil, 0.22 g (2 mmol) of 2,3-diaminopyridine, 50 mL of toluene, and 36 mL of deoxygenated acetic acid. The reaction mixture



Scheme 2 The procedure for preparation of the model compound.

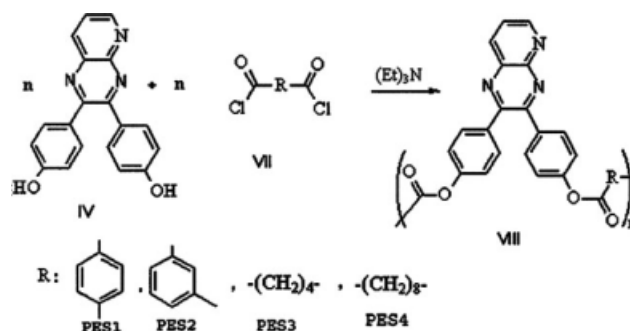
was stirred at reflux for 12 h, during which the generated water was collected in the Dean–Stark trap. The reaction vessel was let to cool to room temperature, and then poured into 500 mL slurry of ice and water containing 7.2 mL of HCl (37%). The precipitate was filtered and recrystallized in ethanol. The dark yellow powder was obtained with a yield of 85% and melting at 324°C .

Synthesis of the model compound

Model compound (VI) was prepared from 2,3-bis(4-hydroxyphenyl)-5-azaquinoxaline and benzoyl chloride by using conventional method, Scheme 2. A two-necked round-bottom flask equipped with a magnetic stirrer bar, a reflux condenser, and a nitrogen inlet/outlet tube was charged with DIOL (0.314 g, 1 mmol) in 20 mL DMF and 0.8 mL triethylamine. A solution of benzoyl chloride (0.244 g, 2 mmol) in 10 mL DMF was added drop wise at 0°C . The reaction was stirred for 5 h at room temperature. The solution was then poured into water, and the precipitate was filtered and washed several times with the solution of NaHCO_3 . The solid product was then dried in a vacuum oven at 60°C .

Synthesis of polyesters

Polyesters were prepared from polycondensation of 2,3-bis(4-hydroxyphenyl)-5-azaquinoxaline with aromatic and aliphatic dicarboxylic dichlorides such as terephthaloyl dichloride, isophthaloyl dichloride,



Scheme 3 The procedure for preparation of the polyesters.

TABLE I
FTIR and $^1\text{H-NMR}$ Spectra Data, Elemental Analysis Results, and the Yield of Different Products Synthesized in this Study

Substrate	IR (KBr, cm^{-1})	$^1\text{H-NMR}$ (DMSO- d_6 , δ , ppm)	Elemental analysis						Yield (%)
			Calc.			Found			
			C	H	N	C	H	N	
DHB	3404 (OH), 1651 (C=O), 1600, 1569 (arom. ring)	6.91–7.74 (8H, phenyl), 7.80–7.85 (H, aromatic), 9.84 (2H, hydroxyl).	–	–	–	–	–	–	82
DIOL	3257 (OH), 1666 (C=O), 1598 (C=N), 1556, 1521 (aromatic ring)	6.20–6.28 (4H, phenyl), 6.60–6.89 (4H, phenyl), 7.30–7.34 (1H, pyridine), 7.94–8.02 (1H, pyridine), 8.55–8.57 (1H, pyridine), 9.32–9.35 (2H, hydroxy).	–	–	–	–	–	–	85
Mo	3061 (CH arom.), 1738 (C=O), 1600 (C=N)	6.75–6.78 (4H, phenyl), 7.34–7.38 (4H, phenyl), 7.58–7.75 (10H, phenyl), 7.91–7.92 (1H, pyridine), 8.12–8.15 (1H, pyridine), 9.19–9.20 (1H, pyridine).	75.7	4.0	8.0	75.5	3.9	8.3	95
PES1	3064 (CH arom.), 1737 (C=O), 1605 (C=N)	6.76–6.79 (4H, phenyl), 7.36–7.40 (4H, phenyl), 7.62–7.66 (4H, phenyl) (TPA), 7.83–7.93 (1H, pyridine), 8.34–8.61 (1H, pyridine), 9.14–9.20 (1H, pyridine).	72.8	3.3	9.4	72.5	3.5	9.8	92
PES2	3096 (CH arom.), 1754 (C=O), 1649 (C=N)	6.73–6.76 (4H, phenyl), 7.13–7.15 (4H, phenyl), 7.34–7.40 (4H, phenyl) (IPA), 7.77–7.81 (1H, pyridine), 8.46–8.49 (1H, pyridine), 9.06–9.07 (1H, pyridine).	72.8	3.3	9.4	73.1	3.1	9.1	92
PES3	3067 (CH arom.), 1738 (C=O), 1605 (C=N)	0.97–1.19 (8H, aliphatic), 6.75–6.79 (4H, phenyl), 7.34–7.39 (4H, phenyl), 7.62–7.66 (1H, pyridine), 7.83–7.88 (1H, pyridine), 9.13–9.19 (1H, pyridine).	70.5	4.4	9.8	70.2	4.6	10.0	95
PES4	3068 (CH arom.), 1739 (C=O), 1606 (C=O)	0.96–1.2 (16H, aliphatic), 6.74–6.79 (4H, phenyl), 7.34–7.39 (4H, phenyl), 7.62–7.66 (1H, pyridine), 7.83–7.88 (1H, pyridine), 9.13–9.19 (1H, pyridine).	72.3	5.6	8.7	72.5	5.2	8.9	95

sebacoyl dichloride, and adipoyl dichloride. A typical synthesis procedure for the preparation of polyesters was conducted in three-necked, round-bottom flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer bar. The flask was charged with the DIOL (0.628 g, 2 mmol) in 20 mL DMF and

0.8 mL triethylamine. A solution of terephthaloyl dichloride (0.406 g, 2 mmol) in 10 mL DMF was added drop wise at 0°C . The reaction was stirred for 5 h at room temperature. The solution was then poured into water, and the precipitate was filtered and washed several times with the solution of NaHCO_3 . The solid product was then dried in a vacuum oven at 60°C . The synthesis procedure and the polymer designations are shown in Scheme 3.

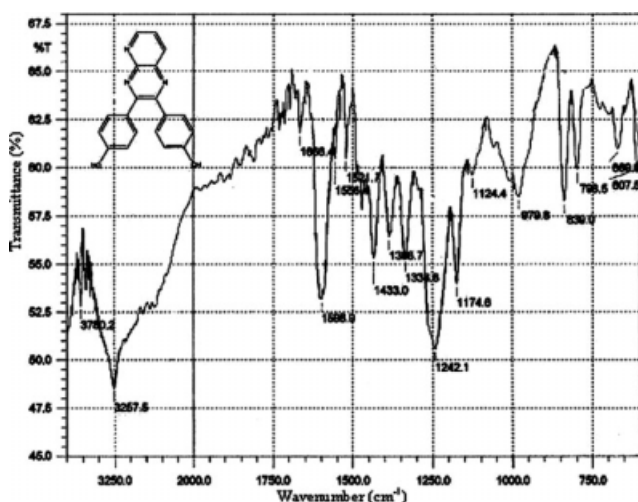


Figure 1 FTIR spectrum of DIOL.

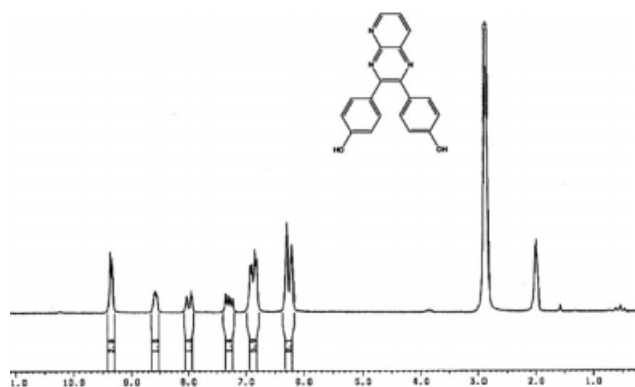


Figure 2 $^1\text{H-NMR}$ spectrum of DIOL.

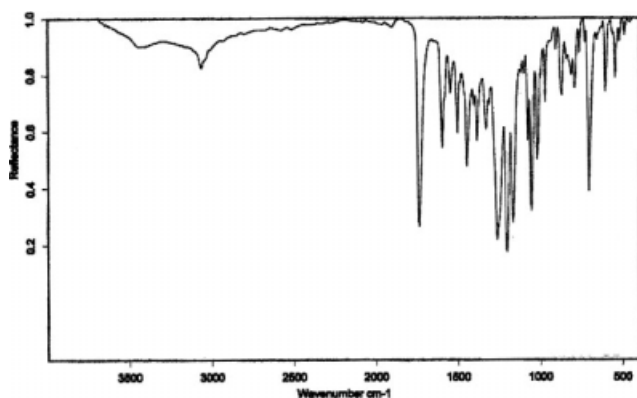


Figure 3 FTIR spectrum of model compound.

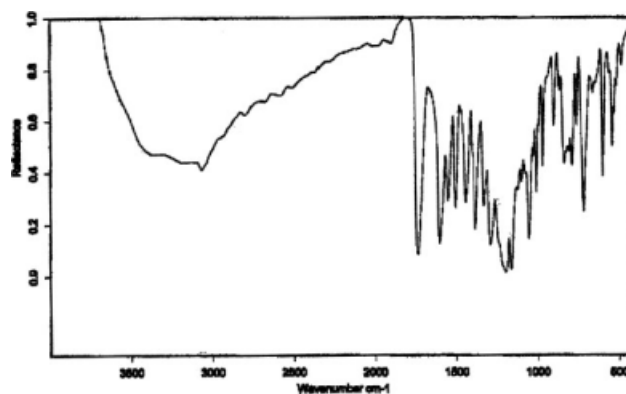


Figure 5 FTIR spectrum of the polyester PES3.

RESULTS AND DISCUSSION

The elemental analysis results and the characteristic peaks of the spectroscopic methods found for the DHB, the DIOL, the model compound and the synthesized polyesters are listed in Table I.

4,4'-Dihydroxybenzile (DHB) was synthesized from dimethoxybenzile according to the procedure given in the literature.²⁷ FTIR, ¹H-NMR, and melting point were used to confirm the structure of DHB which is in good agreement with those given in the literature. FTIR spectra of DHB showed characteristic IR peaks at (cm⁻¹): 3404 (OH), 1651 (C=O), 1600, 1569 (C=C aromatic), and 844, 810 (Benzene ring). ¹H-NMR signals of DHB were at (ppm): 9.84 (2H, hydroxyl), 6.91–7.74 (H, aromatic), and 7.80–7.85 (H, aromatic).

2,3-Bis (4-hydroxy phenyl)-5-azaquinoxaline was synthesized from the reaction of DHB with 2,3-diaminopyridine. FTIR, ¹H-NMR, and melting point were used to confirm the structure of the DIOL. Scheme 1 displays the structures of the starting materials and the products. FTIR spectra of DIOL showed characteristic peaks at (cm⁻¹): 3550–3257 (OH), 1666 (C=O), 1598 (C=N), and 1521–1556 (C=C aromatic). ¹H-NMR signals of DIOL were at (ppm): 6.20–6.28 (4H, phenyl), 6.60–6.89 (4H, phe-

nyl), 7.30–7.34 (1H, pyridine), 7.94–8.02 (1H, pyridine), 8.55–8.57 (1H, pyridine), and 9.32–9.35 (2H, hydroxyl). IR and ¹H-NMR spectra of DIOL are shown in Figures 1 and 2, respectively.

2,3-Bis (4-hydroxyphenyl)-5-azaquinoxaline was used for preparation of the model compound in reaction with benzoyl chloride. The structure of the model compound was confirmed by common spectroscopic methods such as FTIR, ¹H-NMR, and elemental analysis. The FTIR spectra of the model compound in Figure 3 show characteristic peaks at (cm⁻¹): 3061 (CH aromatic), 1738 (C=O), and 1600 (C=N). ¹H-NMR signals of the model compound in Figure 4 are at (ppm): 6.75–6.78 (4H, phenyl), 7.34–7.38 (4H, phenyl), and 7.58–7.75 (10H, phenyl), and the characteristic signals of pyridine ring in the range of 7.91–9.20 ppm. Optimized conditions obtained from the study of model compound were applied for the preparation of polyesters. The polyesters were prepared in good yields by reaction between DIOL and dicarboxylic dichlorides such as terephthaloyl dichloride, isophthaloyl dichloride, sebacoyl dichloride, and adipoyl dichloride. Triethylamine acts as catalyst and also for neutralization of the formed HCl. The polyesters have been designated as PES1, PES2, PES3, and PES4 for different dicarboxylic dichlorides as shown in Scheme 3. The

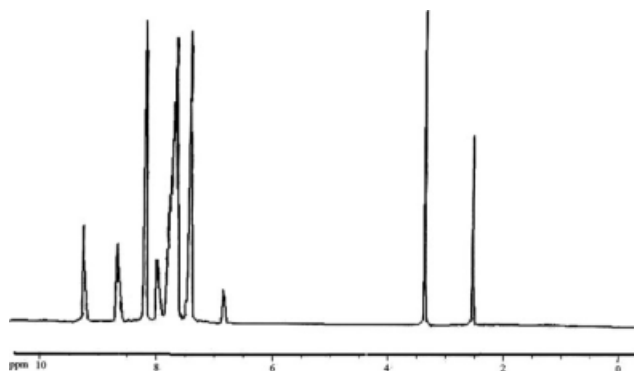


Figure 4 ¹H-NMR spectrum of model compound.

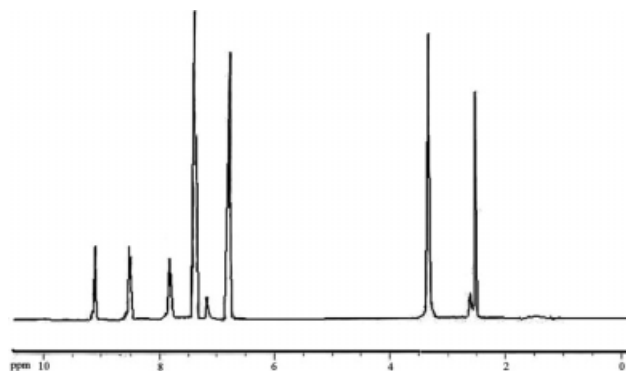


Figure 6 ¹H-NMR spectrum of the polyester PES4.

TABLE II
Solubility^a and Inherent Viscosity of Polyesters

Polymer code	NMP	DMF	DMSO	TCE	Py	THF	H ₂ SO ₄	HMPA	DMAc	Acetone	η_{inh}^b (dl/g)
MO	+	+	+	±	+	±	+	+	+	–	0.37
PES1	+	+	+	±	+	±	+	+	+	–	1.16
PES2	+	+	+	±	+	±	+	+	+	–	1.22
PES3	+	+	+	±	+	±	+	+	+	–	1.1
PES4	+	+	+	±	+	±	+	+	+	–	1.1

+, soluble; ±, partially soluble; –, insoluble; NMP, *N*-methylpyrrolidone; DMF, dimethylformamide; DMSO, dimethylsulfoxide; TCE, tetrachloroethane; Py, pyridine; THF, tetrahydrofuran; HMPA, hexamethylenphosphoramide; DMAc, dimethylacetamide.

^a Fifty milligrams polymer in 10 mL solvent at room temperature.

^b Measured at 25°C in NMP.

structure of the synthesized polyesters was confirmed by elemental analysis and spectroscopic methods. The FTIR spectra of the representative polyester PES3 in Figure 5 show absorption bands at cm^{-1} : 3067 (CH aromatic), 1738 (C=O), 1605 (C=N), and the ¹H-NMR spectra of the representative polyester PES4 in Figure 6 show signals at: 0.96–1.2 (16H, aliphatic), 6.74–6.79 (4H, phenyl), 7.34–7.39 (4H, phenyl), 7.62–7.66 (1H, pyridine), 7.83–7.88 (1H, pyridine), and 9.13–9.19 (1H, pyridine). The inherent viscosity of the polyesters was measured at a concentration of 0.5 g/dL in NMP at 25°C and the results are listed in Table II. The inherent viscosity of the polyesters in the range of 1.10–1.22 dL/g indicated the relatively high molecular weight. The solubility of polyesters was tested in different organic solvents at room temperature and the results are shown in Table II. All the polyesters showed very good solubility in common aprotic polar solvents such as NMP, DMF, DMSO, Py, HMPA, and DMAc. The good solubility of the polyesters can be due to presence of bulky azaquinoxaline ring as side group. The presence of azaquinoxaline rings create a distance between macromolecular chains and facilitate

the diffusion of small solvent molecules by disturbing packing of macromolecular chains. The solubilizing bulky pendants frustrate entanglement of the polymer chains leading to greater solubility. The higher solubility makes the present polyesters potential candidate for practical applications in castings and spin coating processes. However, no sacrifice in thermal stability was made for the sake of solubility.

Typical DSC thermograms of the representative polyesters (PES1 and PES3) are shown in Figure 7. The DSC measurements showed no evidence of crystallization or melting, which proves amorphous morphology. Glass transition temperatures (T_g), taken as the midpoint of the change in slope of the base line of DSC measurement, are in the range of 200–220°C for the polyesters containing aliphatic chain coming from dicarboxylic dichlorides and in the range of 240–280°C for those prepared from aromatic dicarboxylic dichlorides. The polyester PES2 containing isophthaloyl ring in the repeating unit showed a lower T_g than that of polyester PES1 containing terephthaloyl ring. Also, the polyester PES4 with longer aliphatic chain in the repeating unit showed lower T_g than that of polyester PES3 containing shorter aliphatic chain. The thermal stability of the polyesters was studied by TGA under nitrogen atmosphere. TGA curves of the representative polyesters PES1 and PES4 are shown in Figure 8, they all

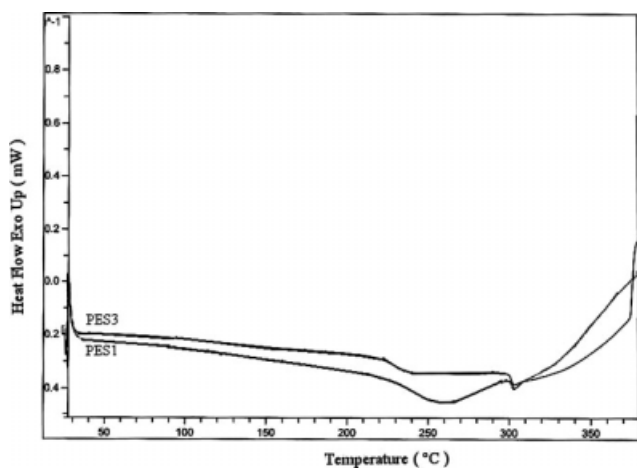


Figure 7 DSC thermograms of the polyesters PES1 and PES3.

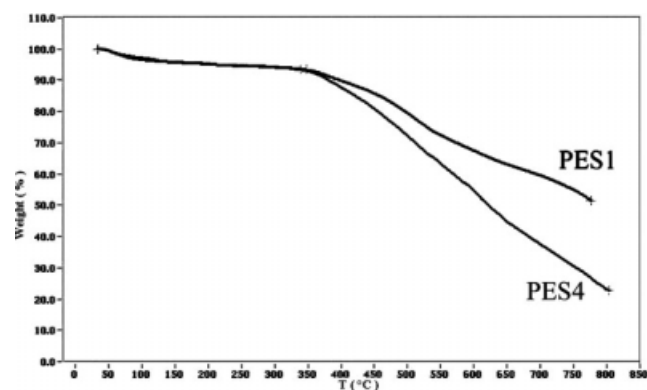


Figure 8 TGA curves of the polyesters PES1 and PES4.

TABLE III
Thermal Analysis Data of the Polyesters

Polyester code	$T_{10\%}$ (°C) ^a	$T_{20\%}$ (°C) ^b	Ch. Y.% ^c at 750°C
PES1	480	550	57
PES2	480	550	52
PES3	430	480	48
PES4	400	460	30

^a Temperature of 10% weight loss.

^b Temperature of 20% weight loss.

^c Char yield percent at 750°C.

showed suitable thermostability. The obtained results from TGA curves are collected in Table III. All polyesters showed less than 10% weight loss in the temperature range of 50–100°C which is due to the absorbed moisture. They began to decompose in the temperature range of 300–360°C, and the weight loss at 500°C is in the range of 15–25%. There is not much difference in the initial decomposition temperature of aromatic and semi aromatic polyesters. This can be attributed to the ability of the more flexible chain to dissipate thermal energy more readily by chain motion, but there is difference in the rate of the weight reduction and also in the amount of the char yields. The semi aromatic polyesters containing aliphatic chain coming from dicarboxylic dichlorides showed lower residue at 750°C than those of containing fully aromatic chain. For example, the char yield for polyester PES4 is 30% and for PES1 is 57% at 750°C. This indicates that polyesters containing $-\text{CH}_2-$ units in the main chain forms more volatile products and leaves fewer residues during thermal degradation.

CONCLUSION

A series of polyesters containing azaquinoxaline moiety as pendant groups to the main chain were prepared in good yields from the solution polycondensation of different dicarboxylic dichlorides with the prepared diol of 2,3-bis (4-hydroxyphenyl)-5-azaquinoxaline. The polyesters were fully characterized and their thermal properties were also studied. The introduction of azaquinoxaline side groups resulted in polyesters with very good solubility in aprotic solvents such as NMP, DMF, DMSO, pyridine, HMPA, and DMAC. The polyesters solution in NMP showed inherent viscosity in the range of 1.10–1.22 dL/g indicating a relatively high molecular weight. The glass transition temperatures of the polyesters measured by using DSC were in the range of 200–280°C depending on the structure of dicarboxylic dichlor-

ide, and the initial decomposition temperatures measured by using TGA were in the range of 300–360°C. 15–25% weight losses were observed at 500°C depending on the structures of the dicarboxylic dichlorides used in the preparation of the polyesters.

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