

Synthesis and Characterization of Polyesters Based on Diethylketone Moiety

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Abstract A new class of unsaturated polyesters based on diethylketone have been prepared by interfacial polymerization of 2,4-bis(4-hydroxybenzylidene)-3-pentanone (I) and 2,4-bis(4-hydroxy-3-methoxybenzylidene)-3-pentanone (II) with 4,4'-azodibenzoyl chloride and 3,3'-azodibenzoyl chloride at ambient temperature. The model compounds were synthesized by reaction of (I) and (II) with benzoyl chloride. The new monomers, model compounds and polyesters have been characterized by different spectral analyses. The polyesters have inherent viscosity of 0.55–0.80 dL/g and moderate number average molecular weight (M_n) in the range of 6150–7400 g/mol. Most of the compounds exhibited their solubility in aprotic solvents while partial solubility in various halogenated organic solvents was observed. The temperatures of 10% weight loss were high (225–330 °C) in nitrogen, indicating that these polyesters have excellent thermal stability. Doping with iodine dramatically raised the conductivity and produced brown colored semiconductive polymers with a maximum conductivity of $2.7 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. Moreover, the morphological properties of selected example of polyesters were detected by SEM.

Keywords: Diethylketone; Azo; Polyesters; Conductivity.

INTRODUCTION

In the modern history of polymers, unsaturated polyesters have gained mounting importance due to their wide range of applications in different fields like coating, automobile, construction, sport and in self-extinguishing materials^[1,2]. Aromatic azo compounds ($-\text{N}=\text{N}-$) are endowed with a wide range of thermal, chemical, photochemical and biological properties^[3–6]. Polymers based on azo functional groups are photoresponsive, highly stable and permit control of the polymer configuration *via cis-trans* isomerization^[7,8]. In addition, these polymers have proven to have potential to be exploited for various optical applications such as halographic and digital storage of information^[9,10] in the formation of conductive Langmuir-Blodgett films^[11,12] and also NLO materials, which have applications in optical signal processing such as frequency doubling amplifiers, modulators for laser technology, data storage and telecommunications^[13,14]. Moreover, polymers containing azo groups are known to have excellent mesomorphic properties and their molecules may adopt peculiar shape suitable for liquid crystals behavior^[15,16].

Unsaturated polyesters containing azo functional groups within the polymer chain are obtained by polycondensation of dicarboxylic acids or diacid chloride with different diols whereby at least one of the monomers contains an unsaturated carbon-carbon double bond^[17,18]. The presence of ester groups and nitrogen atoms in addition to aromatic ring in the skeleton of polymers makes them thermally and chemically stable; however, the number and position of double bonds are important factors responsible for the solubility, thermal stability and mechanical properties of polyesters^[19,20]. The recent trends of research and development in the field

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of azo polymers are to enhance the dye-fiber affinity and color fastness properties in textiles dyeing.

Nowadays, much emphasis is being given to the synthesis of unsaturated polyesters containing chromophoric groups. For example, the aromatic azo group, which can form a part of the main chain, is being intensively investigated^[21–25]. Therefore, development of these polyesters for use in different applications with improved characteristics is an important goal. In this paper, unsaturated polyesters derived from dibenzylidene diethylketone with azo diacid chlorides were prepared. The major aim of this work was to investigate the effect of inclusion of methyl group, as well as para- and meta-azo groups in the main chain on the polymer properties. In addition, other characteristics of these new polymers, such as thermal stability, solubility, morphology and conductivity, were also studied.

EXPERIMENTAL

Instrumentation

Melting points were determined on an Electrothermal IA9100 melting point apparatus and are uncorrected. Elemental analyses were performed on an Elementar Vario EL III instrument. IR spectra were recorded, as KBr pellets, on a Shimadzu IR-200-91527 spectrophotometer. ¹H-NMR spectra, in DMSO solution, were recorded on a Bruker DRX-300 spectrophotometer at room temperature using TMS as the internal reference. Proton signals at $\delta = \sim 2.5$ and ~ 3.4 are attributed to DMSO and H₂O impurities. Viscosity measurements were made with a 0.5% (W/V) solution of polymers in DMF at 25 °C using an Ubbelohde suspended level viscometer. TGA measurements were performed on a V 5.1 A DuPont 2000 thermal analyzer at a heating rate of 10 K/min in nitrogen. DSC was carried out in nitrogen atmosphere using a Shimadzu DSC-50 thermal analyzer. Joel-JSM-5610 LV scanning electron microscope together with carbon coating system was used to assess the morphology of the produced dry polymer after mechanical crashing. A little amount from the powder of polymer was spreaded on double adhesive sticker fixed on aluminum specimen holder, coated by carbon layer for about 10 nm thickness, and then examined by SEM. 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 mm diameter, 0.65–0.80 mm thickness), which were prepared by compressing the finely powdered polymers at 200 kg/cm² under a vacuum. The conductivity(s) was measured from Arrhenius equation. Iodine doping was carried out by exposing the disks to iodine vapor until the polymers were saturated. The molecular weights of polyesters were evaluated by following the standard protocol^[26].

Reagents and Solvents

4-Hydroxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and 3-pentanone (Aldrich) were used without purification. 4-Nitrobenzoic acid, 3-nitrobenzaldehyde (Park), benzoyl chloride and sodium hydroxide (BDH) were of analytical grade. Dichloromethane and all other solvents were of high purity.

Synthesis of the Azo Diacid Chlorides

4,4'-Azodibenzoyl chloride and 3,3'-azodibenzoyl chloride were prepared according to the method described in the literature^[27].

Monomer Synthesis

2,4-Bis(4-hydroxybenzylidene)-3-pentanone (I)

A mixture of 4-hydroxybenzaldehyde (0.10 mol/L) and 3-pentanone (0.05 mol/L) was dissolved in 50 mL ethanol at 75 °C. Dry HCl gas, as a catalyst, was introduced to the reaction mixture with stirring. After 4 h of continuous stirring, water was added to the reaction mixture when a solid product separated out. It was filtered, washed with several portions of water, dried and recrystallized from acetone. Yield 70%, m.p. 200 °C. Elemental analysis for C₁₉H₁₈O₃ (%): Calcd: C, 77.53; H, 6.16; Found: C, 77.35; H, 5.99. IR (KBr, ν cm⁻¹): 1600 cm⁻¹ (C=C), 1665 cm⁻¹ (C=O), 2915–2965 cm⁻¹ (C–H stretch), 3320 cm⁻¹ (OH stretch). ¹H-NMR (DMSO, δ): 9.207 (2H of 2–OH groups), 6.563–6.909 (8H of Ar–H), 7.291–7.332 (2H of 2–CH=C), 1.901 (6H of –CH₃) (Fig. 1).

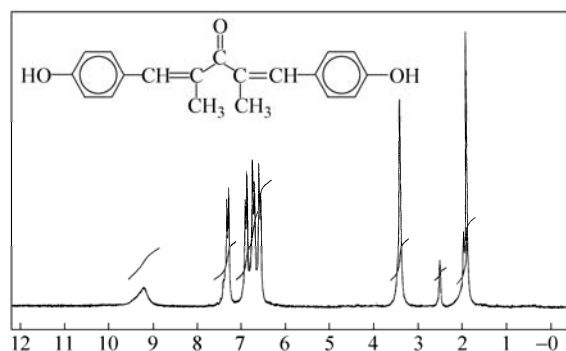


Fig. 1 ^1H -NMR spectrum of monomer I

2,4-Bis(4-hydroxy-3-methoxybenzylidene)-3-pentanone (II)

A mixture of 4-hydroxy-3-methoxybenzaldehyde (0.10 mol/L) and 3-pentanone (0.05 mol/L) was dissolved in 50 mL ethanol at 75 °C. Dry HCl gas, as a catalyst, was introduced to the reaction mixture with stirring. After 4 h of continuous stirring, water was added to the reaction mixture when a solid product separated out. It was filtered, washed with several portions of water, dried and recrystallized from a mixture of hexane and acetone (1:1). Yield 75%, m.p. 160 °C. Elemental analysis for $\text{C}_{21}\text{H}_{22}\text{O}_5$ (%), Calcd: C, 71.17; H, 6.26; Found: C, 70.95; H, 6.14. IR (KBr, ν cm^{-1}): 1585 cm^{-1} (C=C), 1610 cm^{-1} (C=O), 2920–2959 cm^{-1} (C–H stretch), 3415 cm^{-1} (OH stretch). ^1H -NMR (DMSO, δ): 10.01 (2H of 2–OH groups), 7.165–8.003 (8H of Ar–H), 4.259 (2H of 2–CH=C), 3.654 (6H of –OCH₃), 1.964 (6H of –CH₃).

Synthesis of Model Compounds

General procedure

Monomer I or II (0.001 mol/L) was dissolved in aqueous sodium hydroxide solution (0.002 mol/L) with stirring at 25 °C. Benzoyl chloride (0.002 mol/L) was then added to the reaction mixture. At the end of reaction time, the solid product was filtered off, washed with water and ether, dried and recrystallized from ethanol.

2,4-Bis(4-hydroxybenzylidene)-3-pentanone dibenzoate (III)

Reaction time: 2 h, Yield 85%, dark yellow needle, m.p. 110 °C. Elemental analysis for $\text{C}_{33}\text{H}_{26}\text{O}_5$ (%): Calcd: C, 78.87; H, 5.21; Found: C, 78.56; H, 4.99. IR (KBr, ν cm^{-1}): 1158 cm^{-1} (C–O–C), 1599 cm^{-1} (C=C), 1695 cm^{-1} (C=O), 1731 cm^{-1} (–O–CO–), 2921–2959 cm^{-1} (C–H stretch) (Fig. 2). ^1H -NMR (DMSO, δ): 7.126–8.134 (8H of Ar–H and 10H of Ar–H), 4.369 (2H of 2–CH=C), 1.9 (6H of –CH₃) (Fig. 3).

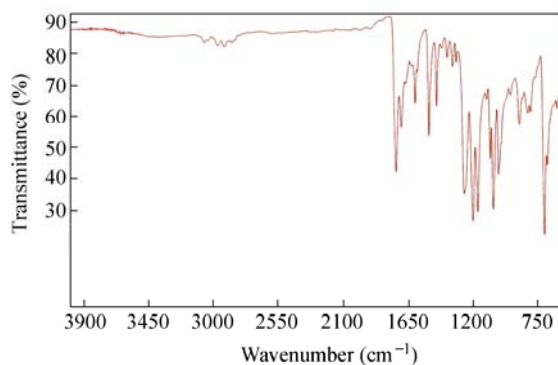


Fig. 2 IR spectrum of model compound III

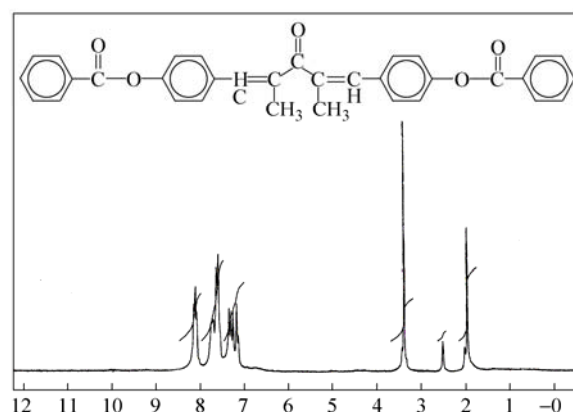


Fig. 3 ^1H -NMR spectrum of of model compound III

2,4-Bis(4-hydroxy-3-methoxybenzylidene)-3-pentanone dibenzoate (IV)

Reaction time: 2 h, Yield 85%, dark yellow needle, Yield 85%, m.p. 170 °C. Elemental analysis for $\text{C}_{35}\text{H}_{28}\text{O}_7$ (%): Calcd: C, 74.72; H, 5.37, Found: C, 74.41; H, 5.06. IR (KBr, $\nu\text{ cm}^{-1}$): 1156 cm^{-1} (C—O—C), 1601 cm^{-1} (C=C), 1645 cm^{-1} (C=O), 1736 cm^{-1} (—O—CO—), 2934–2964 cm^{-1} (C—H stretch). ^1H -NMR (DMSO, δ): 6.556–8.123 (8H of Ar—H and 10H of Ar—H), 4.369 (2H of 2—CH=C), 3.776 (6H of —OCH₃), 1.8 (6H of —CH₃).

Polymer Syntheses

In a three-necked flask equipped with a mechanical stirrer (2000 r/min), dry nitrogen inlet and outlet, and dropper, a mixture of (0.001 mol/L) dibenzylidene-3-pentanone (I or II) in 75 mL methylene chloride and sodium hydroxide solution (0.002 mol/L, 100 mL) was taken. After mixing, 0.001 mol/L of acid chlorides dissolved in 25 mL methylene chloride was added over a period of 2 min at 25 °C and vigorous stirring. After complete addition of acid chloride, stirring was continued for 1–2 h when a dark yellowish solid polymer separated out. The solid polymer was filtered off, washed with water, hot ethanol, and dried under reduced pressure (1×10^{-4} MPa) at 80 °C. The synthesized polyesters, their yield and some of their properties are listed in Table 1.

Table 1. Results of elemental analyses, and some physical properties of polyesters V–VIII

Polymer code	Yield (%)	M_n^a	η_{inh}^b (dL/g)	Molecular formula/ molecular weight	Elemental analyses			
						C%	H%	N%
V	80	7400	0.76	$C_{33}H_{24}N_2O_5/508$	Calc.	74.90	4.58	5.30
					Found	74.03	4.21	5.75
VI	77	6150	0.60	$C_{33}H_{24}N_2O_5/508$	Calc.	74.90	4.58	4.30
					Found	75.36	4.31	4.28
VII	82	6950	0.80	$C_{35}H_{28}N_2O_7/560$	Calc.	71.42	4.79	4.76
					Found	72.01	4.07	5.12
VIII	79	6500	0.55	$C_{35}H_{28}N_2O_7/560$	Calc.	71.42	4.79	4.76
					Found	71.83	4.11	4.49

^a Measured by end group analysis;

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

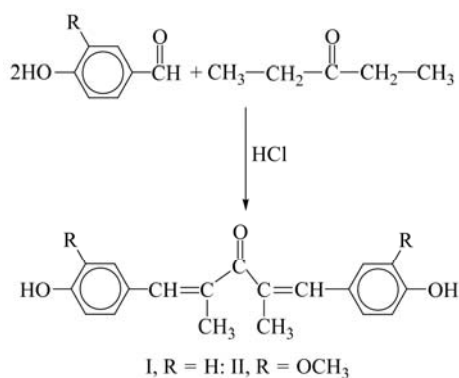
RESULTS AND DISCUSSION

Monomers

Owing to their potential applications, a novel class of unsaturated polyesters containing azo groups in the main chain based on two new monomers, 2,4-bis(4-hydroxybenzylidene)-3-pentanone (I) or 2,4-bis(4-hydroxy-3-methoxybenzylidene)-3-pentanone (II), was prepared in good yields. The monomers (I and II) were prepared in an appreciable quantity by condensation of 2 moles of 4-hydroxybenzaldehyde or 4-hydroxy-3-

methoxybenzaldehyde with one mole of 3-pentanone in the presence of ethanol and catalytic amount of concentrated HCl, as shown in Scheme 1.

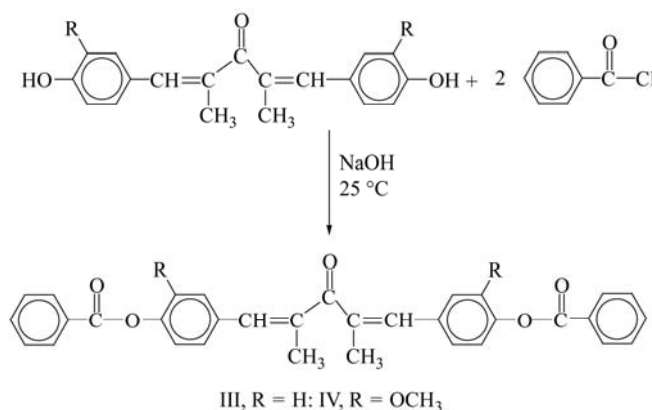
The structure of these new monomers was elucidated by elemental and spectral analyses (see Experimental part).



Scheme 1 Synthesis of monomers I and II

Model Compounds

Before attempting the polymerization, the model compounds were synthesized by the interaction of two moles of benzoyl chloride with one mole of the monomer, I or II (Scheme 2). The elemental and spectral analyses data of the synthesized compounds were in accord with their anticipated structures.



Scheme 2 Synthesis of model compounds III and IV

Polymerization

The polymerization of 2,4-bis(4-hydroxybenzylidene)-3-pentanone (I) and 2,4-bis(4-hydroxy-3-methoxybenzylidene)-3-pentanone (II) with 3,3'-azodibenzoylchloride or 4,4'-azodibenzoylchloride, resulted in the formation of novel unsaturated polyesters. Typical polymerization conditions involved the reaction of the stoichiometric amount of (I) or (II) with azo diacid chlorides and the application of interfacial polycondensation with NaOH/CH₂Cl₂ at ambient temperature afforded new polyesters as shown in Scheme 3. The reaction time varied from 1–2 h. The polymers (dark orange solid) were immediately isolated at the end of the reaction (see Experimental).

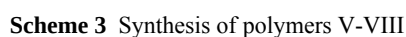


Fig. 4 IR spectrum of polymer V

The number average molecular weights (M_n) of unsaturated 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 (0.1 mol/L). 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 0.1 mol/L KOH solution. The number average molecular weight (M_n) was calculated by using the formula:

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

The number average molecular weight (M_n) of the unsaturated polyesters ranged between 6150 g/mol and 7400 g/mol. The inherent viscosity (η_{inh}) of polymers was measured in DMF at 25 °C, and the results are presented in Table 1. These results revealed that the polymers were of moderate molecular weight.

Solubility

The solubility of synthesized polyesters in different solvents is shown in Table 2. It was observed that all the polymers dissolved readily in concentrated sulfuric acid at room temperature giving deep red color that may be attributed to the degradation of polymer chains during dissolving. All polymers were soluble in various aprotic polar solvents such as dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP). The good solubility of these polymers may be attributed to the loose packing of the macromolecules because of methyl group attached with bezylidene ring and low crystallinity^[28]. Among halogenated solvents like methylene chloride, chloroform and carbon tetrachloride, it was found that all the polymers were partially soluble in methylene chloride and insoluble in others. Moreover, all polyesters were insoluble in most common organic solvents. Comparing the solubility of polyesters containing 3,3'-azo-linkage (VI and VIII) with those containing 4,4'-azo-linkage (V and VII), it was found that the former possessed better solubility than the latter. This may be ascribed to the close packing of the polymer chain in the latter polymers. It should be noted that the polymers VII and VIII were more soluble than V and VI because of the steric hindrance effect of the methoxy group, which may cause unsymmetrical orientation thereby making solvation easier^[29, 30].

Table 2. Solubility characteristics of polyesters V–VIII

Polymer Number	DMF	DMSO	NMP	CCl ₄	CH ₂ Cl ₂	CHCl ₃	C ₂ H ₆ CO	H ₂ SO ₄
V	+	++	+	–	+	–	–	++
VI	++	++	++	–	+	–	–	++
VII	++	++	++	–	+	–	–	++
VIII	++	++	++	–	+	–	–	++

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

Thermal Properties

The thermal properties of the polyesters were evaluated by DSC and TGA. The analysis results are presented in Table 3. All of the polymers except polyester VII showed a distinct glass transition temperature (T_g) at 225.18–250.32 °C on the second DSC heating scans. In Fig. 5, TGA curves showed a small weight loss in the range 2%–4% starting at 10 °C until 80 °C, which may be attributed to the loss of adsorbed moisture and entrapped solvents. The polyesters started to lose weight, because of thermal degradation between 200–490 °C. The 10% weight loss of the polymers as a criterion for the thermal stability of the polymers was in the range of 225–330 °C, which indicates excellent thermal stability of the prepared polymers. The obtained results are given in Table 3.

Table 3. Thermal properties of polyesters V–VIII

Polymer number	Temperature (°C) for various % decomposition ^a					Thermal behavior of polyesters		
	10	20	30	40	50	T_g^b (°C)	T_m^c (°C)	T_d^d (°C)
V	230	350	410	440	480	230.54	363.59	416.32
VI	320	345	385	440	460	225.18	359.61	398.41
VII	330	350	420	465	490	250.32	373.52	431.92
VIII	225	255	310	375	450	233.29	369.53	389.06

^a The values were determined by TGA at a heating rate of 10 K/min in nitrogen;

^{b–d} Measured by DSC at a heating rate of 10 K/min in nitrogen

A comparison between polyesters based on 3,3'-azolinkage (VI and VIII) and 4,4'-azo-linkage (V and VII) showed that the latter are somewhat more thermally stable than the former. The polymers based on the *meta*-azo linkage are less thermally stable than those based on the *para*-azo linkage and this may be attributed to the difference in the stereoregularity. The 4,4'-structure leads to more compact packing of the polymer chains as

compared to 3,4-structure^[31]. However, the first step in the thermal decomposition of these polymers may be attributed to the elimination of azo groups as molecular nitrogen^[32]. In agreement with this, it has been reported that the first step in the thermal decomposition of certain aromatic polymers prepared by oxidative coupling of primary amines occurs by loss of nitrogen^[33]. Furthermore, the expected nature of decomposition of these polymers is a pyrolytic oxidation of $-\text{C}=\text{C}-$, scission of many bonds, in addition to the formation of char as an end product^[26, 34].

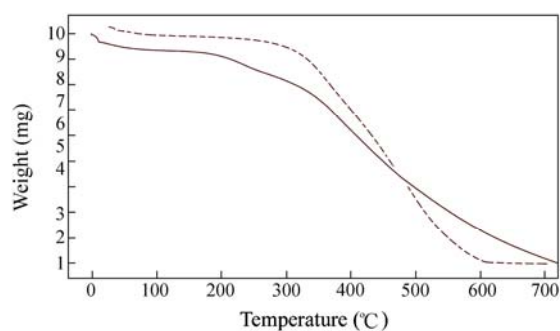


Fig. 5 The TGA traces of polymers V (—) and VII (---) in nitrogen at a heating rate of 10 K/min

Morphological Properties

The morphology of the synthesized polyester VI was examined by SEM using a Joel-JSM-5610 LV instrument. The SEM sample was prepared by a little amount spreaded on double adhesive sticker fixed on aluminum foil and coated by carbon layer. SEM images were taken on a Mamiya 6×7 roll film at an accelerating voltage of 10 kV using low dose techniques^[35]. The SEM study of polyester VI (Fig. 6) shows that the surface of polyester is coarsen with several irregular porous structure and a large number of slots.

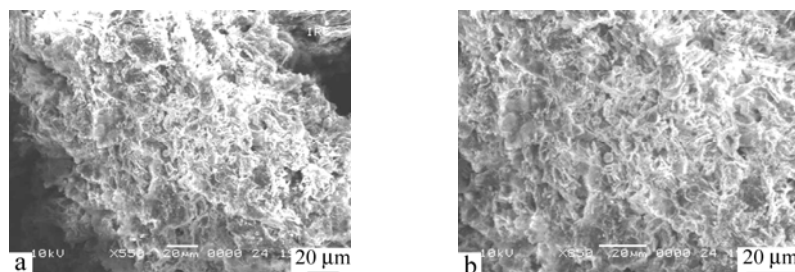


Fig. 6 SEM micrographs of different magnifications showing the morphology of the polyester VI particles

Electrical Conductivity

The electrical conductivity of the azopolymers is ranged from 10^{-11} to $10^{-12} \Omega^{-1}\text{cm}^{-1}$ at 25 °C (Table 4). Polymers V and VI, which contain 3,3'-azo-linkage, was less conductive than those containing 4,4'-azo-linkage (VII and VIII). Here, it may be assumed that the electrical conductivity in this sort of polymers is probably due to charge transport which occurs preferentially along the *p*-conjugated system (4,4'-azo-linkage)^[36]. Moreover, the presence of the methyl group attached to the double bond of benzylidene ring (hyperconjugation) in the main chain provides electrical connectivity. The doping with iodine as an electron acceptor was performed until the polymer was saturated with iodine. The doped polyesters (V and VIII), which had an affinity (absorbed amount) of ~15 wt% toward iodine, were light to brown in color. Those with more than 79 wt% were dark brown after being left overnight. Polymers V, VI, VII and VIII absorbed 80 wt%, 82 wt%, 81 wt% and 79 wt% of iodine per polymer, respectively. As can be seen from Table 4, the electrical conductivities were successfully raised by iodine doping and reached as high as 10^{-6} – $10^{-8} \Omega^{-1}\text{cm}^{-1}$ upon iodine doping of ~79 wt%. Thus, the unsaturated polyesters containing azo groups are good insulators, but they have been converted into semiconductors by

doping with iodine. Moreover, present findings are better than previous work where the conductivity values obtained were in the range of $3.1 \times 10^{-7} \Omega^{-1}\text{cm}^{-1}$ [26].

Table 4. Electrical conductivity of polyesters V–VIII

Polymer number	Affinity toward I ₂ ^a (wt%)	Electrical Conductivity ^b ($\Omega^{-1}\text{cm}^{-1}$)	
		Undoped	I ₂ Doped
V	80	2.4×10^{-11}	2.3×10^{-7}
VI	82	3.1×10^{-12}	2.1×10^{-8}
VII	81	4.7×10^{-11}	2.7×10^{-6}
VIII	79	2.6×10^{-12}	1.4×10^{-8}

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

^b Measured by DC electrical conductivity at 25 °C

CONCLUSIONS

Linear unsaturated polyesters based on dibenzylidene-3-pentanone 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. TGA showed that the polyesters based on 4,4'-azolinkage are more thermally stable than those based on 3,3'-azolinkage. Upon doping with iodine, the synthesized polyesters became semiconductors exhibiting conductivity of 10^{-6} – $10^{-8} \Omega^{-1}\text{cm}^{-1}$.

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