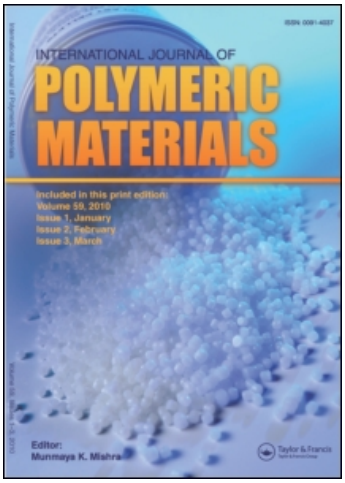

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Coloured Polyesters Containing Imidazolone Ring System

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Coloured polyesters (PD_{1-5}) have been synthesized by interfacial polycondensation reaction of terephthaloyl chloride and various bisazo diols derived form 1-(4-hydroxyphenyl)-2-phenyl-4-(4-hydroxybenzylidene)-5-imidazolone by coupling with various diazotized fast bases. All the coloured polyesters were characterized by elemental analysis, IR spectroscopy, UV-visible spectroscopy, viscometry, solubility, bleeding test and thermogravimetric analysis. The bisazo diols (dyes) were applied on nylon and polyester fabrics and their dyeing performance has been assessed. These dyes showed fair to good fastness to light and very good to excellent fastness to washing, rubbing, perspiration, and sublimation.

Keywords: Coloured polyesters; bisazo diols; nylon; polyester

INTRODUCTION

In continuation of our research work on coloured polyesters derived from bisazo diols containing diarylidene cyclopentanone and diarylidene cyclohexanone moiety [1], the present work comprises the synthesis and characterization of some novel coloured polyesters derived form bisazo diols containing imidazolone ring system.

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EXPERIMENTAL

Materials

Terephthaloyl chloride (Aldrich) was recrystallized from *n*-hexane (m.p. 83–84°C). Sodium hydroxide was of analytical grade. All other chemicals were of high purity and were further purified by standard methods [2].

Preparation of 1-(4-hydroxyphenyl)-2-phenyl-4-(4-hydroxybenzylidene)-5-imidazolone

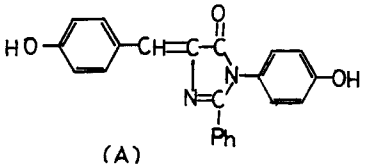
1-(4-hydroxyphenyl)-2-phenyl-4-(4-hydroxybenzylidene)-5-imidazolone were synthesized as described in literature [3].

Preparation of 1-(3-azoaryl-4-hydroxyphenyl)-2-phenyl-4-(3-azoaryl-4-hydroxybenzylidene)-5-imidazolone

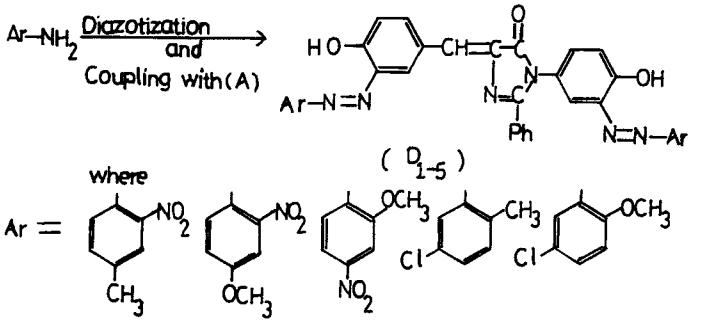
The compounds (D_{1-5}) were prepared by coupling 1-(4-hydroxyphenyl)-2-phenyl-4-(4-hydroxy benzylidene)-5-imidazolone in alkaline medium with diazotized forms of aromatic amines (a–e) (listed in scheme 1) in the usual manner [4]. The purity of the compounds (D_{1-5}) were checked by tlc using *n*-butanol-acetic acid-water (8:2:1) as solvent and silica gel G as adsorbent.

Preparation of Coloured Polyesters (PD_{1-5})

A three necked flask equipped with a mechanical stirrer (2000 rpm/min), dry nitrogen inlet and outlet, and a dropper, was charged with a mixture of 1-(3-azoaryl-4-hydroxyphenyl)-2-phenyl-4-(3-azoaryl-4-hydroxybenzylidene)-5-imidazolone (0.01 mol), methylene chloride (25 ml) and a suitable quantity of sodium hydroxide. A stoichiometric quantity (0.02 mol) or 100% excess (0.04 mol) of the latter dissolved in water (100 ml) was also introduced. After mixing, terephthaloyl chloride (0.01 mol) dissolved in methylene chloride (25 ml) was added over 2 min. period at 25°C and vigorously stirred. After complete addition of acidchloride, stirring was continued for an hour whereby a highly coloured solid separated out, which was filtered off; washed



(A)



Scheme 1

with water, hot alcohol and hot acetone and dried at 100°C under reduced pressure (1 mm Hg). The general synthesis of the coloured polyesters is shown in reaction scheme 2.

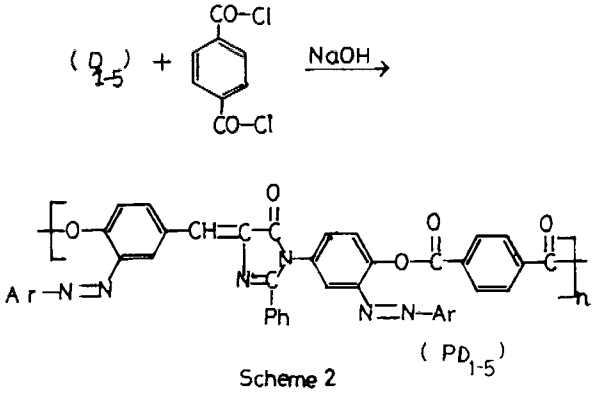
Dyeing of Nylon and Polyester

The fibres were dyed with the bisazo diols (D_{1-5}) using the method described in literature [5].

MEASUREMENTS

Fastness Tests

Fastness to light, sublimation and perspiration were assessed in accordance with BS:1006–1976. The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC-1961, and the wash fastness test in accordance with IS: 765–1979.



Scheme 2

Bleeding Test

Coloured polyester (0.5 g) was transferred in a glass test tube. To it solvent (15 ml) was poured; shaked well and the test tube along with the coloured polyester and solvent was kept overnight for their settlement at room temperature. The colouration of the solvent was assessed and the fastness of the coloured polyester was rated from 1 to 5 (1 = very high colouration, 2 = high colouration, 3 = moderate colouration, 4 = slight colouration, 5 = no colouration).

Spectral Analysis

The IR spectra of compounds (D_{1-5}) and (PD_{1-5}) were scanned in KBr on a Nicolet 400D FT-IR Spectrophotometer.

Viscometry

The intrinsic viscosity of the coloured polyesters were measured using ubbelohde suspended level viscometer in DMF at $30 \pm 0.5°C$.

Molecular Weight

Number average molecular weights ($\overline{Mn}$) of the soluble fraction were determined by Gel permeation chromatography (GPC) using Water's gel permeation chromatography station consisting of 600 E multi-solvent delivery system, ultrastyragel GPC columns packed with

styrene-DVB porous copolymer beads of 10^3 A° and 10^6 A° pore size connected in series, 410-Differential Refractive Index detector and powermate 386/25 NEC data station with 820 maximum GPC software was used. Toluene was used as a mobile phase at 1.0 ml/mm flow rate. GPC system was calibrated with eight polystyrene standards of different molecular weight.

Thermogravimetric Analysis

Thermogravimetric analysis of the coloured polyesters were carried out on a Du pont 951 Thermogravimetric Analyzer coupled with plug in modul model 990 Thermal Analyzer at a heating rate of 10°C/min. in N_2 atmosphere.

RESULTS AND DISCUSSION

Azodiols

All the bisazo diols (D_{1-5}) were characterized by their maximum absorption value λ_{max}, melting point, percentage yield, elemental analysis and R_f values. The characterization data of these bisazo diols (dyes) are given in Table I. Melting points of all the dyes are uncorrected.

TABLE I Characterization data of bisazo diols (Dyes) D_{1-5}

Dye No.	λ_{max} *nm* *log* (ϵ)	*Yield* %	*m.p.*[a] (°C)	*Molecular formula*	R_f^b *value*	*Elemental analysis, Found (Cal)*		
						C(%)	*H*(%)	*N*(%)
D_1	451 (4.39)	78	167	$C_{36}H_{26}O_9N_7$	0.855	63.5 (63.3)	3.6 (3.8)	18.6 (18.5)
D_2	448 (4.22)	82	178	$C_{36}H_{26}O_9N_9$	0.862	59.9 (60.1)	3.7 (3.6)	17.9 (17.7)
D_3	442 (4.15)	76	185	$C_{36}H_{26}O_9N_9$	0.832	60.3 (60.1)	3.6 (3.9)	17.6 (17.7)
D_4	456 (4.20)	77	174	$C_{36}H_{26}O_3N_7Cl_2$	0.869	65.8 (65.4)	3.6 (3.9)	14.5 (14.8)
D_5	442 (4.08)	83	178	$C_{36}H_{26}O_5N_7Cl_2$	0.875	62.1 (62.3)	3.9 (3.8)	14.0 (14.1)

[a] All the melting points are uncorrected.
[b] Determined on tlc using *n*-butanol acetic acid-water (8:2:1) solvent system.

The results of exhaustion and fixation study of bisazo diols reveal that % exhaustion and % fixation values ranges from 51–64% and 71–79% respectively for nylon and 42–55% and 63–72% respectively for polyester fibres.

The examination of the results of the dyeing properties of all the bisazo diols reveal that all of them gave light yellow, lemon yellow, orange or brownish orange shades. The light fastness of bisazo diols on nylon is fair (2–3) to fairly good (3–4) and fair (2–3) for polyester fibres. The obtained results of washing and rubbing fastness on both the fibre shows that they are exceptionally good (4–5) to excellent (5–6). The perspiration and sublimation fastness is excellent (5–6) for both the fibres, these can be attributed to thermal and chemical stability of the dye molecule.

Coloured Polyesters

All the coloured polyesters (PD_{1-5}) were characterized by elemental analysis, viscosity, UV-visible spectra (Tab. II), thermogravimetric analysis (Tab. V), bleeding properties (Tab. VI) and IR spectra. Coloured polyesters are found to be fibrous material, soluble in DMF, sparingly soluble in tetrahydrofuran, toluene and insoluble in most of the other organic solvents. They could be spun into fibres with the help of spinnerette. The polyesters are fractionated into two fractions by

TABLE II Characterization data of coloured polyesters (PD_{1-5})

Polymer no.	*Viscosity* (η) *dl/gm*	λ_{max} *nm*	*Yield* %	*Elemental analysis, Found (Cal.)*		
				C%	*H%*	*N%*
PD_1	0.157	405	85	65.3 (65.0)	3.3 (3.4)	13.6 (13.8)
PD_2	0.160	395	88	62.1 (62.5)	3.2 (3.3)	13.1 (13.2)
PD_3	0.155	385	92	62.4 (62.5)	3.2 (3.3)	13.0 (13.2)
PD_4	0.178	395	90	66.9 (66.7)	3.4 (3.5)	10.5 (10.6)
PD_5	0.179	390	91	64.0 (64.1)	3.3 (3.4)	10.1 (10.2)

refluxing in toluene for 2 hrs. The percentage of soluble and insoluble fractions are given in Table III. The comparative data of viscosity measurements of these polyesters (PD_{1-5}) as such and the fractions (a) and (b) are furnished in Table IV. The soluble fractions were characterized by GPC technique. The $\overline{Mn}$ of the toluene soluble fraction ranges from 1300–1600 which indicates that the soluble fraction is mainly the dimer!

All the IR spectra (not shown) showed common characteristic absorption bands in the region 3450–3200 cm^{-1} due to the bonded O—H and N—H stretching vibrations. Disappearance of broad characteristic absorption band of the O — H group at 3400–3600 cm^{-1} and appearance of carbonyl (C=O) group of ester linkage at 1740–1750 cm^{-1} indicates the formation of polyester. An absorption band at 1680–1695 (s) cm^{-1} is assigned for the carbonyl (C=O) group of imidazolone ring. In the region 1280–1300 cm^{-1} strong band is observed due to C—H stretching.

Examination of the thermograms (not shown) of the coloured polyesters show that upto 200°C the polyesters are quite stable and show negligible weight loss. The thermograms above 265°C are very

TABLE III Percentage of soluble and insoluble fraction of coloured polyesters (PD_{1-5})

Polymer no.	*%Soluble fraction (a) in toluene*	*% Insoluble fraction (b) in toluene*	*Number ave. mole. wt. ($\overline{Mn}$) of soluble fraction (a) by GPC in toluene*
PD_1	16.5	83.5	1600
PD_2	14.8	85.3	1700
PD_3	13.6	86.4	1650
PD_4	15.1	84.9	1550
PD_5	16.4	83.6	1650

TABLE IV Intrinsic viscosity parameters of PD_{1-5} in DMF

Polymer no.	*Polyester as such (dl/gm)*	*Soluble fraction in toluene (dl/gm)*	*Insoluble fraction in toluene (dl/gm)*
PD_1	0.157	0.089	0.121
PD_2	0.160	0.081	0.129
PD_3	0.155	0.087	0.124
PD_4	0.178	0.075	0.156
PD_5	0.179	0.080	0.150

TABLE V Thermal properties of coloured polyesters containing diazotized arylamino moiety

Polymer no.	T_0 (°C)	T_{max} (°C)	*IPDT* (°C)	*E* *Kj/mole*	*Temperature (°C) for various% decomposition*				
					10	20	30	40	50
PD_1	250	425	550.0	27.3	325	390	410	415	425
PD_2	225	435	544.7	28.4	350	422	430	435	490
PD_3	225	375	572.7	26.8	300	355	380	415	485
PD_4	215	400	425.0	28.6	335	370	375	390	410
PD_5	220	460	405.0	21.8	360	390	410	425	440

TABLE VI Evaluation of bleeding properties of coloured polyesters(PD_{1-5})

Polymer no.	*Water*	*Acetone*	*Ethanol*	*Cellosolve*	*n-butanol + xylene (1:9)*
PD_1	5	4–5	5	3	4–5
PD_2	5	4	5	2–3	5
PD_3	5	4–5	4–5	3	5
PD_4	5	4–5	5	2–3	4–5
PD_5	5	4–5	4–5	3	5

similar. In the range of 390–490°C the polyester show 40 to 50% weight loss. In order to determine the thermal stability trend, TG parameters such as T_0 (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss), T_{max} (temperature of maximum rate of degradation), IPDT (integral procedure decomposition temperature) and the activation energy E, of the degradation process were calculated by Doyle's [6] and Broido's [7] method respectively.

T_0 and T_{10} are the two main criteria used to indicate the heat stability of polymers. The higher the values of T_0 and T_{10}, the higher the thermal stability of the system [8]. However T_0, T_{10} and T_{max} are single feature of the TGA curves. To obtain the quantitative picture of the relative stability, IPDT values can be regarded of significant importance, since they represent the overall nature of TGA curve.

Looking to the results of the bleeding test (Tab. VI), it has been observed that the fastness of coloured polyesters are excellent to water and excellent to very good to ethanol, *n*-butanol + xylene (1:9) and good to very good to acetone, but fair to good to cellosolve solvent.

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