

Synthesis and studies of coloured polyesters derived from bis-azo diols

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A series of coloured polyesters have been synthesized by interfacial polycondensation reaction of terephthaloyl chloride and various bis-azo diols. The bis-azo diols have been prepared from two different heterocyclic diols, 7,7'-dihydroxy-4,4,4',4'-tetramethyl-2,2'-spirobis [chroman] and 2,9-di(2-dimethyl-*p*-hydroxy benzyl)-5a,10b-dihydro benzofuro [2,3-b] benzofuran by coupling with various diazotized fast bases. These bis-azo diols (dyes) were characterized by their m.p., % yield, elemental analysis and uv-visible spectroscopy and applied on nylon and polyester fibres and their dyeing performance were assessed. These dyes showed fair to fairly good fastness to light and very good to excellent fastness to washing, rubbing, perspiration and sublimation. All the coloured polyesters were characterized by their elemental analysis, ir and uv-visible spectroscopy. Their viscosity, solubility, bleeding test and thermogravimetric analysis were also studied.

In continuation to our previous work^{1,2}, the present paper describes the synthesis of a series of bis-azodiols and coloured polyesters. All the coloured polyesters were characterized by their elemental analysis, IR and UV-Visible spectroscopy, viscometry, solubility, thermogravimetric analysis (TGA) and bleeding test.

Experimental Procedure

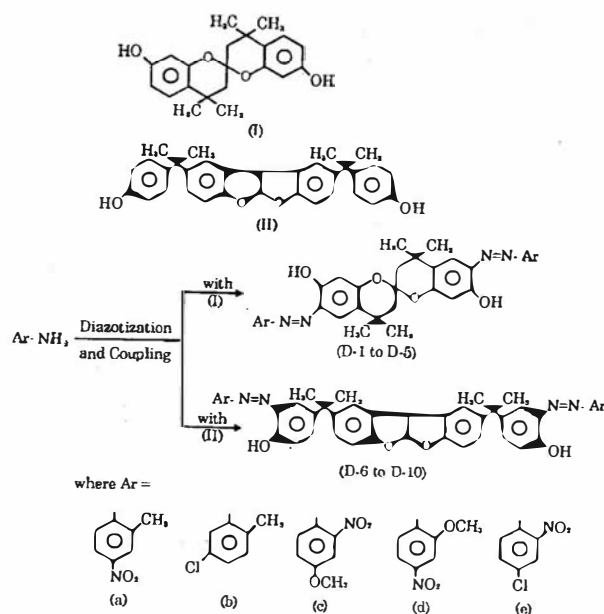
Terephthaloyl chloride (Aldrich) was recrystallized from *n*-hexane [m.p. 83-84 °C]; 7,7'-dihydroxy-4,4,4',4'-tetramethyl-2,2'-spirobi[chroman] and 2,9-di(2-dimethyl-*p*-hydroxy benzyl)5a,10b-dihydrobenzofuro[2,3-b]benzofuran were synthesized as described in literature^{3,4} respectively.

Synthesis of monomer (D1-D5 & D6-D10)—7,7'-Dihydroxy-4,4,4',4'-tetramethyl-2,2'-spirobi[chroman] (0.005 mol) was dissolved in water (25 mL) containing sodium hydroxide (3 mL, 10 % w/v). This solution was further diluted by addition of water (25 mL) and cooled in an ice-bath at temperature below 5 °C. Further, freshly prepared diazo solution (0.01 mol) of Fast base (a-e) was added to it dropwise over a period of 2 h keeping temperature below 5 °C. The pH of the reaction mass was adjusted to 7.5-8.0 by addition of 10 % sodium carbonate solution. The reaction mixture was stirred for 4 h at 0-5 °C. The products (D1-D5) were neutralized by acetic acid, filtered, washed with water, dried and crystallized from acetic acid. Similarly using 2,9-di(2-dimethyl-*p*-hydroxy benzyl)5a,10b-dihydrobenzofuro[2,3-b]benzo-

furan as coupling component with different azoaryl compounds (a-e), D6-D10 were prepared⁵ (Scheme 1).

All the monomers (D1-D10) were characterized by their melting point, element analysis, ir and uv-visible spectroscopy. The data regarding m.p., percentage yield, elemental analysis and maximum absorbance (λ_{max}) are listed in Table 1.

Synthesis of coloured polyesters (Polymeric Dyes PD1-PD10)—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 dyes (D1-D5/D6-D10) (0.01 mol), methylene



Scheme-I

*For correspondence

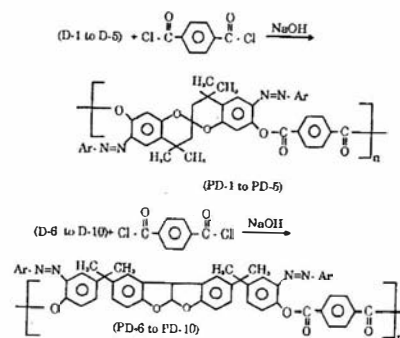
Table 1 — Characteristic parameters of coloured monomers

Compd. No.	λ_{\max} , in nm	Yield %	m.p. ^a °C	Molecular formula	Elemental analysis		
					% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)
D1	458	80	134	C ₃₅ H ₃₄ O ₈ N ₆	62.89 (63.06)	5.08 (5.10)	12.58 (12.61)
D2	420	79	140	C ₃₅ H ₃₄ O ₄ N ₄ Cl ₂	65.20 (65.11)	5.32 (5.27)	8.75 (8.68)
D3	475	78	136	C ₃₅ H ₃₄ O ₁₀ N ₁₀	60.08 (60.17)	4.96 (4.87)	12.12 (12.03)
D4	448	80	130	C ₃₅ H ₃₄ O ₁₀ N ₆	60.97 (60.17)	4.98 (4.87)	12.14 (12.03)
D5	400	78	133	C ₃₃ H ₂₈ O ₈ N ₆ Cl ₂	55.95 (56.01)	4.00 (3.96)	11.89 (11.85)
D6	450	82	97	C ₄₆ H ₄₀ O ₆ N ₆	68.82 (68.65)	5.12 (4.97)	10.54 (10.44)
D7	430	78	110	C ₄₆ H ₄₀ O ₄ N ₄ Cl ₂	70.56 (70.49)	5.09 (5.11)	7.09 (7.15)
D8	460	83	92	C ₄₆ H ₄₀ O ₁₀ N ₇	66.18 (66.02)	4.80 (4.78)	10.13 (10.04)
D9	440	81	97	C ₄₆ H ₄₀ O ₁₀ N ₆	66.18 (66.02)	4.69 (4.70)	10.12 (10.04)
D10	400	82	107	C ₄₄ H ₃₄ O ₈ N ₆ Cl ₂	62.38 (62.48)	4.10 (4.02)	10.02 (9.94)

^aAll the melting points are uncorrected.

chloride (25 mL) and a suitable quantity of sodium hydroxide. A stoichiometric quantity (0.02 mol) or 100% excess (0.04 mol) of the NaOH dissolved in water (100 mL) was also introduced. After mixing, terephthaloyl chloride (0.01 mol) dissolved in methylene chloride (25 mL) was added in a period of 2 min at 25 °C and vigorously stirred. After complete addition of acid chloride, stirring was continued for an hour whereby a highly coloured solid separated out, which was filtered off, washed with water, hot alcohol and hot acetone and dried under reduced pressure (1 mm Hg) at 100 °C (Scheme 2).

Measurements—The ir spectra of the samples were scanned on a Nicolet 400 D FT-IR spectrophotometer. UV-Visible spectra were recorded on a Shimadzu-160 A. Intrinsic viscosity of the coloured polyesters was measured in dimethylformamide (DMF) at 30 ± 0.5 °C using a Ubbelohde suspended level viscometer. Thermal stability was measured on a Du Pont 951 thermogravimetric analyzer coupled with a plug-in module model Du Pont 990 thermal analyzer at a heating rate of 10 °C/min in static air. Fastness to light, sublimation and perspiration were assessed in accordance with BS-1006-1978. The rubbing fastness test was carried out with a



Scheme-II

crockmeter (Atlas) in accordance with AATCC-1961, and the wash fastness test in accordance with IS 765-1979. Bleeding test of coloured polyesters was performed in the usual manner².

Results and Discussion

All the azodiols and coloured polyesters were characterized by their maximum absorption value (λ_{\max}), melting point, percentage yield and C, H, N analysis. The data of these compounds are given in Tables 1 and 2. Only a slight difference in the λ_{\max} value was observed for the polymeric dyes compared to the corresponding monomeric dyes.

Table 2—Physical properties of coloured polyesters

Polymeric Dye	Viscosity η (dl/g)	λ_{max}^a in nm	Yield (%)	Elemental analysis		
				% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)
PD1	0.117	455	89	64.72 (64.82)	4.46 (4.12)	10.62 (10.55)
PD2	0.148	378	85	66.58 (66.58)	4.71 (4.64)	7.30 (7.22)
PD3	0.140	466	87	62.40 (62.31)	4.30 (4.34)	10.32 (10.24)
PD4	0.177	420	91	62.22 (62.31)	4.29 (4.34)	10.10 (10.14)
PD5	0.156	400	92	58.82 (58.78)	3.65 (3.58)	10.14 (10.03)
PD6	0.158	365	86	69.50 (69.37)	4.53 (4.49)	9.08 (8.99)
PD7	0.153	350	87	71.05 (70.97)	4.56 (4.60)	6.23 (6.13)
PD8	0.166	362	91	67.12 (67.08)	4.43 (4.34)	8.76 (8.69)
PD9	0.176	400	88	67.18 (67.08)	4.29 (4.34)	8.65 (8.69)
PD10	0.141	350	92	63.95 (64.00)	3.51 (3.69)	8.58 (8.61)

^a λ_{max} measured in DMF

IR spectra of monomeric and the corresponding polymeric dyes are shown in Fig. 1. IR spectra of all the polyesters showed the disappearance of the characteristic absorption band of the O-H group at 3400-3600 cm^{-1} and the appearance of the carbonyl (C=O) group of ester linkage at 1740-1750 cm^{-1} . Absorption band at 1380-1385 cm^{-1} is assigned for the $>C(CH_3)_2$ group, band at 1100 cm^{-1} is for the cyclic ether linkage. The other characteristic absorptions of various compounds also showed the following signals:

C-CH₃ stretching at 1390-1450 cm^{-1} (PD1, PD2, PD6, PD7)

C-Cl stretching at 625-640 cm^{-1} (PD2, PD5, PD7, PD10)

All the coloured polyesters were found to be soluble in DMF, sparingly soluble in tetrahydrofuran and toluene and insoluble in most of the other organic solvents. The intrinsic viscosities of all coloured polyesters are listed in Table 2.

Thermogravimetric study of coloured polyesters—

Thermogravimetric studies were carried out for all the coloured polyesters at a heating rate of 10 °C/min in static air. The selected thermograms are shown in Fig.2. Table 3 summarizes the thermal behaviour data of the coloured polyesters. To determine the thermal stability trend, thermogravimetric parameters such as

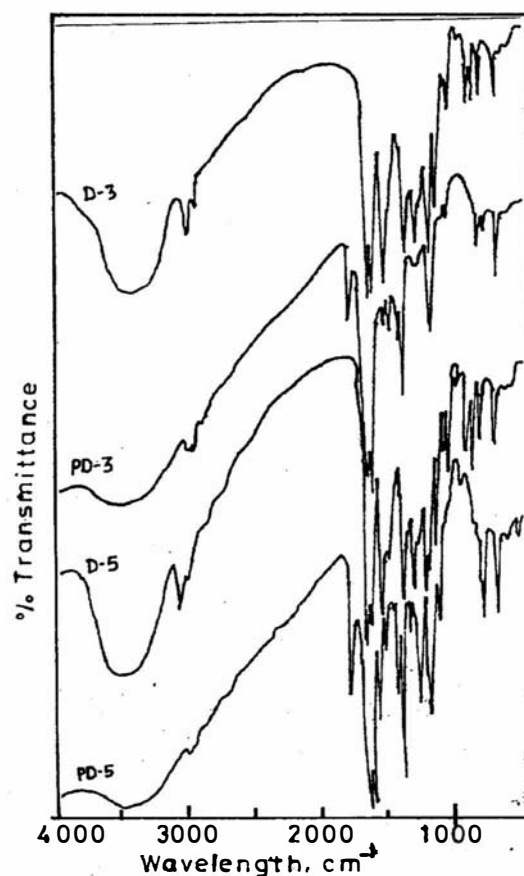


Fig. 1 — IR spectra of monomeric and polymeric dyes.

Table 3 — Thermal properties of coloured polyesters

Polymeric dye	T_0 °C	T_{max} °C	IPDT °C	E kJ/mol	Temperature (°C) for various % decomposition				
					10	20	30	40	50
					PD1	225	487	523.5	25.2
PD2	215	400	427.5	29.4	275	312	342	365	381
PD3	250	490	530.0	26.2	302	392	450	487	500
PD4	225	425	515.3	27.2	282	315	350	365	384
PD5	237	465	415.2	28.8	270	292	400	447	475
PD6	250	500	505.9	24.5	306	400	462	470	487
PD7	262	487	540.0	28.6	343	437	475	495	506
PD8	225	425	525.0	30.2	310	367	395	412	437
PD9	212	412	500.0	23.4	287	325	381	405	412
PD10	200	475	537.5	25.8	255	287	405	440	465

IPDT- Integral Procedure Decomposition Temperature; E -Activation energy

Table 4 — Shades and fastness properties of monomeric dyes on nylon and polyester fibres

Compd	Shade on		Fastness to													
			Light		Washing		Rubbing				Perspiration		Sublimation			
			N	P	N	P	Dry		Wet		Acid		Alkaline		N	P
D1	Orange	Brown orange	3	3-4	4	4-5	5	4	4	4	4-5	5	5	5	4	4
D2	Yellow	Yellow	3	3	5	5	4-5	5	4-5	4-5	5	5	5	5	5	4-5
D3	Reddish brown	Reddish brown	3-4	2-3	4-5	4	4-5	5	5	5	4	5	4-5	4-5	5	4
D4	Brown orange	Brownish orange	3-4	3	5	4	4	4	4-5	4	5	4-5	5	5	4	4-5
D5	Orange	Orange	3	3	5	4-5	4-5	4-5	4	5	4-5	5	4	5	5	4-5
D6	Orange	Orange	3	3-4	4	4	4-5	4-5	4	5	4-5	4-5	5	4	4-5	4
D7	Yellow	Yellow	3	2-3	5	4-5	5	4-5	4	5	4	5	4-5	5	5	5
D8	Yellow orange	Yellow orange	2-3	3	4-5	4	4	5	4-5	5	5	5	4	4	4-5	4-5
D9	Orange	Orange	3	3-4	4-5	5	4-5	4	5	4-5	4-5	4	4	4-5	5	5
D10	Yellow	Light yellow	3-4	3	5	5	4-5	4-5	5	5	5	5	5	5	5	5

N-Nylon; and P-Polyester

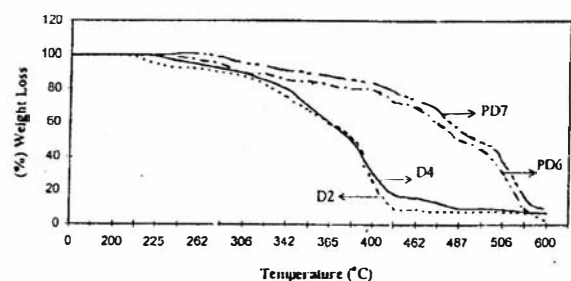


Fig. 2 — TG thermograms of monomeric and polymeric dyes

temperature of onset of decomposition (T_0), temperature for 10 % weight loss (T_{10}), temperature of maximum rate of degradation (T_{max}), intergral procedure decomposition temperature (IPDT) and the activation energy (E) of the degradation process were calculated by methods reported earlier^{6,7}.

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 system⁸. 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

Table 5 — Evaluation of bleeding properties of PD1-PD5 and PD6-PD10

Polymeric dye	Water	Acetone	Ethanol	Cellosolve	<i>n</i> -butanol: xylene (1:9)
PD1	5	4	4-5	3	5
PD2	5	4-5	5	2-3	4-5
PD3	5	4-5	4-5	3	5
PD4	5	4-5	4-5	3	4-5
PD5	5	4	5	2-3	4-5
PD6	5	4	5	2-3	5
PD7	5	4-5	5	3-4	4-5
PD8	5	4	4-5	3	4-5
PD9	5	4-5	5	2-3	4-5
PD10	5	4-5	5	2-3	5

as significant, since they represent the overall nature of the TGA curve.

The T_0 ranged from 200 to 262.5 °C, the T_{10} ranges from 255 to 343 °C and T_{max} ranged from 400 to 500 °C. The values of IPDT and the activation energy (E) for the degradation process were in the range of 427.5-540 °C and 23.4-30.2 kJ.mol⁻¹ respectively. The data are given Table 3.

Dyeability of monomeric dyes—The monomeric dyes were applied on nylon and polyester fibres. The dyeing was carried out in an acidic solution using the method described earlier⁹. The dyeing conditions were as: Dyestuff: 2% (to cloth); Material liquor ratio 1:50, Temperature: 90 °C for nylon and 130 °C for polyester; Time: 1h.

After dyeing, the cloth was soaped as usual. The shade variations in the nylon and polyester fibres are shown in Table 4.

Data of fastness properties (Table 4) show that the light fastness ranged from fair to good for both the fibres. The washing and rubbing fastness were good to excellent and the perspiration and sublimation fastness were very good to excellent.

Bleeding properties—The results of the bleeding test (Table 5) show that the coloured polyesters have excellent fastness to water, excellent to very good fastness to ethanol, butanol + xylene (1:9) and acetone, and fair to good fastness to cellosolve solvent.

Conclusions

The coloured polyesters synthesized from bis-azo diols containing an azoaryl group in the backbone

were found to be thermally stable. The activation energy of the thermal degradation was in the range of 23.4-30.2 kJ.mol⁻¹. Due to the structure complexity, coloured polyesters prepared from 2,9-di(2-dimethyl-*p*-hydroxy benzyl)-5a,10b-dihydro benzofuro [2,3-b] benzofuran are found to be more stable compared to polyesters prepared from 7,7'-dihydroxy-4,4,4',4'-tetramethyl-2,2'-spirobis [chroman]. Coloured polyesters have excellent fastness to water, excellent to very good fastness to ethanol, butanol + xylene (1:9) and acetone, and fair to good fastness to cellosolve solvent.

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