

Studies of Novel Water-Soluble Colored Polyesters Containing Azo Moiety

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ABSTRACT: A series of water-soluble colored polyesters (polymeric dyes) were synthesized by interfacial polycondensation reaction of terephthaloyl chloride and various bisazodiols (monomeric dyes) that were derived from diarylidene cyclopentanone and diarylidene cyclohexanone by coupling with various diazonium salts of anthraquinone dyes containing the sodium salts of the sulfonic acid group. All the colored polyesters were characterized by their elemental analysis, IR and UV-visible spectroscopy, viscometry, solubility, and TGA. Color and dyeability of the polymeric dyes are discussed by comparing them with those of the corresponding monomeric dyes. The color fastness of the polymeric dyes show fair to very good fastness to light and very good to excellent fastness to washing, rubbing, perspiration, and sublimation. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 2041–2048, 1998

Key words: water-soluble colored polyester; bis-azodiols; dyeability; fastness

INTRODUCTION

In the past few years chemists have become increasingly interested in preparing polymeric dyes because these dyes have extensive use in the coloration of synthetic resins requiring processing temperatures of 200–350°C and have better bleeding resistance in an alkyd coating and in PVC than the corresponding monomeric dyes.^{1,2} Extensive work has been reported for the polymeric dyes prepared by the polymerization/copolymerization of the dye monomer containing vinyl,³ acryloyl,⁴ and acrylamido^{5,6} groups. Colored resin may be obtained by introduction of inert dyestuff containing at least two functional groups (such as hydroxy,^{7,8} amino, carbonyl, or aminophenol⁹ groups) in the polycondensation reaction. There are few reports about the use of azophenol and arylazo resorcinol as polymerizable dyes with formaldehyde.^{10–12} Green, blue, or purple polymeric dyes are prepared directly

by condensation of N-Ph substituted polyesters, polyethylenimines, and polyurethanes at the backbone with aromatic ketones.¹³ Polymeric dyes from polyallyl amines have been reported as useful for textile dyeing and jet printing inks.¹⁴ Polymeric dyes are also used for nonlinear optics. Miyata and coworkers¹⁵ reviewed polymeric and polymer-dye systems for quadratic nonlinear optics in comparison with inorganic materials.

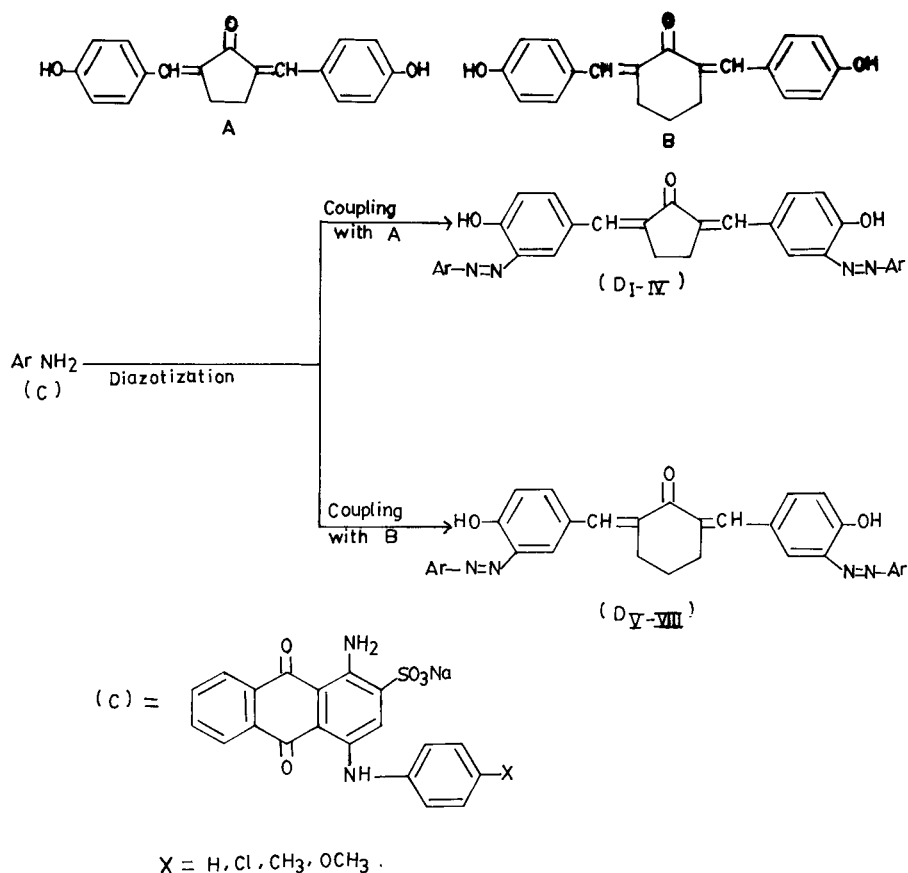
Only limited attention has been given to water-soluble polymeric dyes,^{16,17} even though materials of this type could be extremely useful in a variety of applications. In the present work an attempt was made to introduce an azo anthraquinone moiety that contained sodium salts of the sulfonic acid group to prepare thermally stable water-soluble colored polyesters.

EXPERIMENTAL

Materials

Terephthaloylchloride (Aldrich) was recrystallized from *n*-hexane [melting point (mp) 83–

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[I \rightarrow IV][V \rightarrow VIII]**Scheme 1** The synthesis of monomeric dyes.

84°C]; 2,5-bis(4-hydroxybenzylidene)cyclopentanone and 2,6-bis(4-hydroxybenzylidene)cyclohexanone were synthesized as described in the literature.¹⁸ The azoaryl compounds used were synthesized in our laboratory.¹⁹ Sodium hydroxide was of analytical grade. All other chemicals were of high purity and were further purified by standard methods.²⁰

Synthesis of Monomeric Dyes

2,5-Bis[4-hydroxy(3-azoaryl)benzylidene]-cyclopentanone (D_{I-IV})

These dyes were prepared by diazotizing the compounds (I–IV) and coupling with 2,5-bis(4-hydroxybenzylidene)cyclopentanone in alkaline medium as described below.

Concentrated sulfuric acid (16 g) in a small beaker was cooled in a ice bath, dry powdered

sodium nitrite (0.01 mol, 0.69 g) was added to it very slowly with stirring, and the temperature was kept below 5°C. After addition of sodium nitrite the stirring was continued for half an hour and the beaker was transferred to a water bath. When the temperature of the mixture had reached that of bathwater (25°C), very gradual heating was started and continued until the temperature reached 70°C. The contents were then stirred at this temperature until all the sodium nitrite was dissolved. The final clear solution was cooled in an ice bath to about 5–10°C. Amino aryl compounds [1-amino-4-aryl amino anthraquinone-2-sulfonic acid] (0.01 mol) were added very slowly to it with stirring. A cooled diazo mixture was stirred for 1 h at below 5°C. Crushed ice (10 g) was then added and excess nitrous acid was removed by adding urea. The resulting diazo solution was used for the subsequent coupling reaction.

2,5-Bis(4-hydroxybenzylidene)cyclopentanone

Table I Characteristic Parameters of Colored Monomers

Compound No.	λ_{\max} (in nm) (log ϵ)	Yield (%)	mp ^a (°C)	Molecular Formula	Elemental Analysis		
					%C Found (Calcd)	%H Found (Calcd)	%N Found (Calcd)
D _I	550 (3.663)	86	>330	C ₅₉ H ₃₆ O ₁₃ N ₆ Na ₂ S ₂	62.08 (61.78)	3.91 (3.14)	7.45 (7.32)
D _{II}	515 (3.932)	90	>325	C ₅₉ H ₃₄ O ₁₃ N ₆ Cl ₂ Na ₂ S ₂	58.95 (58.27)	3.15 (2.79)	6.75 (6.91)
D _{III}	565 (3.749)	90	>335	C ₆₁ H ₄₀ O ₁₃ N ₆ Na ₂ S ₂	63.00 (62.35)	3.68 (3.40)	7.04 (7.15)
D _{IV}	520 (3.561)	89	>330	C ₆₁ H ₄₀ O ₁₅ N ₆ Na ₂ S ₂	60.91 (60.69)	3.48 (3.31)	6.82 (6.96)
D _V	550 (3.766)	92	>330	C ₆₀ H ₃₈ O ₁₃ N ₆ Na ₂ S ₂	60.83 (62.06)	3.81 (3.27)	7.15 (7.24)
D _{VI}	525 (3.490)	89	>335	C ₆₀ H ₃₆ O ₁₃ N ₆ Cl ₂ Na ₂ S ₂	59.89 (58.58)	3.94 (2.92)	6.41 (6.83)
D _{VII}	535 (3.555)	90	>330	C ₆₂ H ₄₂ O ₁₃ N ₆ Na ₂ S ₂	61.77 (62.62)	3.94 (3.53)	6.41 (7.07)
D _{VIII}	530 (3.690)	92	>340	C ₆₂ H ₄₂ O ₁₅ N ₆ Na ₂ S ₂	60.00 (60.98)	3.25 (3.44)	7.33 (6.88)

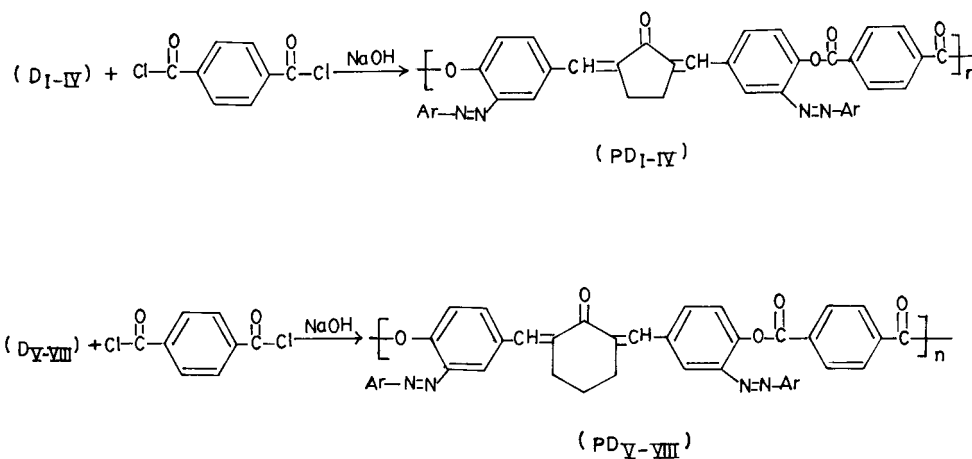
^a All the melting points (mp) are uncorrected.

(0.005 mol, 1.46 g) was dissolved in water (25 mL) containing sodium hydroxide (3 mL, 10% w/v). This solution was diluted by the addition of 25 mL of water and cooled in an ice bath at a temperature below 5°C. Freshly prepared diazo solution was added dropwise to this solution over a period of 2 h while keeping the temperature below 5°C. The pH of the reaction mass was adjusted to 7.5–8.0 by the addition of 10% sodium carbonate solution, and the reaction mixture was further stirred for 4 h at the same temperature.

The product was neutralized by acetic acid then filtered, washed several times with water, dried, and crystallized from acetic acid.

2,6-Bis[4-hydroxy(3-azoaryl)benzylidene]-cyclohexanone (D_{V-VIII})

Adopting the same procedure as above, the title dyes were prepared by diazotizing the compounds (VI–VIII) and coupling with 2,6-bis(4-hydroxybenzylidene)cyclohexanone in alkaline medium.



Scheme 2 The synthesis of polymeric dyes.

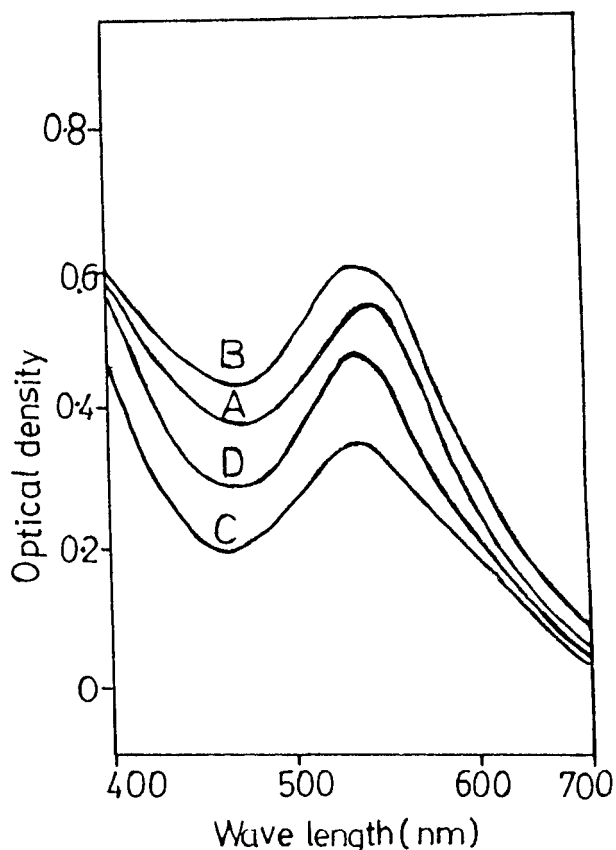


Figure 1 Visible spectra of polymeric and monomeric dyes: (A) monomeric dye D_{II} , (B) polymeric dye PD_{II} , (C) monomeric dye D_V , and (D) polymeric dye PD_V .

The syntheses of the monomeric dyes (D_{I-VIII}) are shown in reaction Scheme 1.

All the monomeric dyes were characterized by their melting point, elemental analysis, and IR and UV-visible spectroscopy. The data regarding mp, percent yield, elemental analysis, and maximum absorbance (λ_{max}) are listed in Table I.

Synthesis of Water Soluble Colored Polyesters (Polymeric Dyes PD_{I-VIII})

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 2,5-bis[4-hydroxy(3-azoaryl)benzylidene]cyclopentanone (D_{I-IV})/2,6-bis[4-hydroxy(3-azoaryl)benzylidene]cyclohexanone (D_{V-VIII}) (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 100 mL of water was also intro-

duced. After mixing, terephthaloyl chloride (0.01 mol) dissolved in methylene chloride (25 mL) was added over a 2-min period at 25°C and vigorously stirred. After the complete addition of acid chloride, stirring was continued for 1 h whereby a highly colored solid separated out. The solid was filtered off, washed with 20% sodium chloride, and dried under reduced pressure (reaction Scheme 2).

Measurements

A Perkin-Elmer 983 recording IR spectrophotometer was used for IR spectra of the sample in KBr pellets. Visible spectra were recorded on a Carlzeiss UV/VIS Specord spectrophotometer. Intrinsic viscosity of the colored polyesters was measured in DMF at $30 \pm 0.05^\circ\text{C}$ with 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 $10^\circ\text{C}/\text{min}$ in N_2 atmosphere. Fastness to light, sublimation, and perspiration were assessed in accordance with BS 1006-1978. The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC-1961, and the wash fastness test was in accordance with IS 765-1979.

RESULTS AND DISCUSSION

UV-visible spectra and IR spectra of polymeric dyes were observed. The results obtained are shown in Figures 1 and 2 where they are compared with the corresponding monomeric dyes.

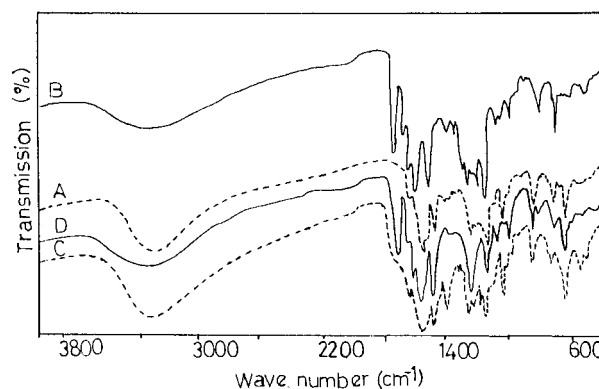


Figure 2 Infrared spectra of polymeric and monomeric dyes: (A) monomeric dye D_{II} , (B) polymeric dye PD_{II} , (C) monomeric dye D_V , and (D) polymeric dye PD_V .

Table II Physical Properties of Water Soluble Colored Polyesters

Polymeric Dye	Viscosity (η) (dL/g)	λ_{\max} (in nm)		Yield (%)	Elemental Analysis		
		DMF ^a	Water ^a		%C Found (Calcd)	%H Found (Calcd)	%N Found (Calcd)
PD _I	0.130	535	525	90.4	62.61 (63.00)	3.13 (2.97)	6.25 (6.58)
PD _{II}	0.157	500	505	92.1	60.83 (59.77)	2.83 (2.67)	6.57 (6.24)
PD _{III}	0.482	520	510	95.5	63.89 (63.49)	3.24 (3.22)	6.33 (6.44)
PD _{IV}	0.310	515	520	90.8	62.85 (61.97)	3.12 (3.14)	6.84 (6.28)
PD _V	0.323	540	550	91.7	64.01 (63.25)	3.12 (3.10)	6.65 (6.51)
PD _{VI}	0.233	505	515	89.6	61.07 (60.04)	3.58 (2.79)	6.44 (6.18)
PD _{VII}	0.317	525	530	93.2	63.89 (63.73)	3.51 (3.33)	6.16 (6.37)
PD _{VIII}	0.410	515	525	91.1	62.10 (62.22)	3.55 (3.25)	6.98 (6.22)

^a Visible spectra (λ_{\max}) were measured in either DMF or water.

Only a slight difference in the λ_{\max} value was observed for the polymeric dyes compared to the corresponding monomeric dyes. The data regarding the λ_{\max} values are furnished in Tables II and I, respectively.

The IR spectra of all the polyesters (Fig. 2) 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 the ester linkage at 1745–1755 cm^{-1} , the carbonyl (C=O) group of the cyclopentanone/cyclohexanone at 1680–1695 cm^{-1} , and the C=C groups at 1580–1600 cm^{-1} . In the 1280–1300 cm^{-1} region, a band was observed due to C—H stretching, and in the 1200–1250 and 1030–1040 cm^{-1} regions asymmetric SO₂ and symmetric SO₂ stretching bands were observed in all cases. The other characteristic absorptions of various compounds also showed the following signals:

- C—Cl stretching at 625–640 cm^{-1} (PD_{II}, PD_{VI}),
- C—CH₃ stretching at 1390–1450 cm^{-1} (PD_{III}, PD_{VII}),
- C—H bending of —OCH₃ at 2860 cm^{-1} (PD_{IV}, PD_{VIII}).

All the polyesters were found to be soluble in water, methanol, ethanol, and DMF and were insoluble in most of the nonpolar solvents. The intrinsic viscosities of all colored polyesters are listed in Table I. The results of the viscosity measurement of the colored polyesters reveal that the value ranged from 0.130 to 0.482 dL/g, which indicates the formation of low molecular weight polymers.

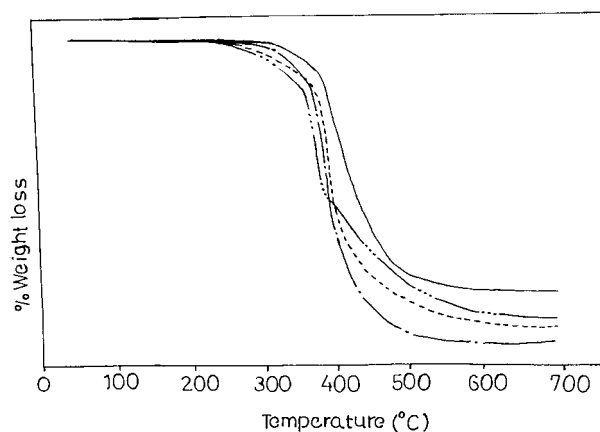


Figure 3 Thermogravimetric curves of colored polyesters (—) PD_{II}, (---) PD_{III}, (- · · -) PD_{VI}, and (· · ·) PD_{VIII}.

Table III Thermal Properties of Water Soluble Colored Polyesters

Polymeric Dye	T_0 (°C)	T_{max} (°C)	IPDT (°C)	E (kJ/mol)	Temperature (°C) for Various Decompositions				
					10%	20%	30%	40%	50%
PD _I	200	375	459.1	24.5	275	350	395	475	372
PD _{II}	300	405	601.0	33.8	372	395	408	415	430
PD _{III}	275	325	472.3	20.3	310	310	330	345	388
PD _{IV}	255	350	538.8	27.2	325	325	345	355	370
PD _V	200	325	452.3	21.7	295	295	315	320	367
PD _{VI}	213	370	580.5	29.6	325	355	363	375	380
PD _{VII}	225	375	572.7	26.8	300	355	380	415	485
PD _{VIII}	250	338	505.1	22.4	325	330	332	345	357

Thermogravimetric Study of Colored Polyesters

Thermogravimetric studies were carried out for the colored polyesters at a heating rate of 10°C/min in N₂ atmosphere. The typical TGA curves for the selected thermograms are shown in Figure 3. Table III summarizes the thermal behavior data of the colored water soluble polyesters. To determine the thermal stability trend, thermogravimetric parameters such as the temperature of the onset of decomposition (T_0), the temperature for 10% weight loss (T_{10}), the temperature of the maximum rate of degradation (T_{max}), the integral procedure decomposition temperature (IPDT), and the activation energy (E) of the degradation process were calculated by Doyle's²¹ and Broido's²² methods.

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.²³ However, T_0 , T_{10} , and T_{max} are single features of the TGA curves. To

obtain the quantitative picture of the relative stability, IPDT values can be regarded as significantly important because they represent the overall nature of the TGA curve.

The T_0 ranged from 200 to 300°C, the T_{10} ranged from 275 to 375°C, and the T_{max} ranged from 325 to 405°C. The values of IPDT and the overall activation energy (E) for the degradation process was in the range of 450–580 ± 2°C and 20–35 ± 2 kJ mol⁻¹, respectively. The data given in Table III indicate that the colored polyesters derived from the monomeric unit containing cyclopentanone are more thermally stable than those derived from the monomeric unit containing cyclohexanone. This may be due to ring size.

Dyeability of Polymeric Dyes/Monomeric Dyes

The polymeric dyes/monomeric dyes were applied on nylon and wool fibers. The dyeing was carried out in an acidic solution using the method de-

Table IV Color of Nylon/Wool Fibers Dyed with Polymeric Dyes and Corresponding Monomeric Azo Dyes

Compound No.	Polymeric Dyes		Compound No.	Monomeric Dyes	
	N	W		N	W
PD _I	Pinkish violet	Pinkish violet	D _I	Brown	Brownish grey
PD _{II}	Purple	Pinkish grey	D _{II}	Wooden brown	Brown
PD _{III}	Ash grey	Grey	D _{III}	Smoke grey	Grey
PD _{IV}	Brownish yellow	Wooden brown	D _{IV}	Brownish yellow	Wooden brown
PD _V	Bluish violet	Reddish violet	D _V	Reddish brown	Violet brown
PD _{VI}	Purple	Light reddish violet	D _{VI}	Purple brown	Purple brown
PD _{VII}	Blue	Bluish violet	D _{VII}	Dark blue	Brownish violet
PD _{VIII}	Pinkish grey	Reddish violet	D _{VIII}	Brown	Brownish grey

N, nylon; W, wool.

Table V Color Fastness of Polymeric Dyes Applied on Nylon and Wool Fibers

Polymer No.	Fastness to													
	Light		Washing		Rubbing				Perspiration				Sublimation	
					Dry		Wet		Acid		Alkaline			
N	W	N	W	N	W	N	W	N	W	N	W	N	W	
PD _I	3	3	5	5	5	5	5	5	5	5	5	5	5	5
PD _{II}	3	3	5	5	5	5	5	5	5	5	5	5	5	5
PD _{III}	3	3	5	5	5	5	5	5	5	5	5	5	5	5
PD _{IV}	3	3-4	4-5	5	5	5	5	5	5	5	5	5	5	5
PD _V	3	3	5	5	5	5	5	5	5	5	5	5	5	5
PD _{VI}	3	3	5	5	5	5	5	5	5	5	5	5	5	5
PD _{VII}	3	3	5	5	5	5	5	5	5	5	5	5	5	5
PD _{VIII}	3	3-4	4-5	5	5	5	5	5	5	5	5	5	5	5

N, nylon; W, wool.

scribed earlier.²⁴ The dyeing conditions were as follows:

dyestuff: 2% (to cloth);
 material liquor ratio: 1 : 50;
 temperature: 90°C for nylon and 60–70°C for wool;
 time: 1 h.

After dyeing the cloth was soaped as usual. For comparison the dyeing was carried out by using the corresponding monomeric dye under the same conditions. Polymeric dyes showed some variation in the shade due to the hydroxyl groups of the monomeric dyes disappearance in the formation of ester groups and also due to the increase in chromophoric groups. The shade variations in the nylon and wool fibers are shown in Table IV.

Data of fastness properties (Table V) shows that the light fastness ranged from fair to good for all the fibers. The washing and rubbing fastness were good to excellent, and the perspiration and sublimation fastness were very good to excellent. The same fastness properties were observed for the corresponding monomeric dyes.

CONCLUSIONS

The water soluble colored polyesters synthesized from bisazodiols containing sodium salts of sulfonic acid containing an azoaryl group in the backbone were found to be thermally stable. The activation energy of the thermal degradation was in

the 20–35 kJ mol⁻¹ range. The polyesters derived from the monomeric unit containing cyclopentanone were more thermally stable than the monomeric unit containing cyclohexanone.

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