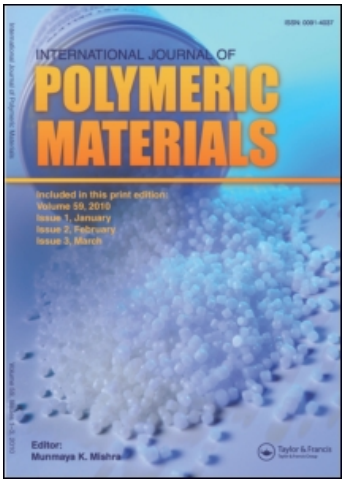

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Polymerizable Dyes Part II

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Polymerizable Dyes Part II

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Arylene bisazo resorcinol dyes IIIa–e were prepared and polycondensed with formaldehyde in the presence of aqueous oxalic acid. The resulting polymeric dyes IVa–e were characterized by yield, melting point, colour, elemental analysis and visible and IR spectroscopy. The thermal properties of polymeric dyes were examined by thermogravimetric analysis. Their dyeing performance on nylon and polyester was assessed. The dyeing on nylon and polyester had yellow, orange, red and brown shades with moderate to good, light and wash fastness. Polymerization of bisazo dyes IIIa–e with formaldehyde on dyed nylon and polyester have also been carried out. The dyeing properties of polymeric dyes were compared with the dyes polymerized on nylon and polyester.

KEY WORDS Arylene bisazo resorcinol polymerizable dyes, polymeric dyes, light and wash fastness.

INTRODUCTION

In continuation of our earlier communication,[1] the present work comprises the synthesis, characterization and dyeing performance on nylon and polyester of various arylene bisazo resorcinol (IIIa–e) and their polycondensates with formaldehyde IVa–e. Polymerization of bisazo dyes IIIa–e on dyed nylon and polyester was also carried out and their dyeing properties were compared with those of polymeric dyes IVa–e (Scheme I).

RESULTS AND DISCUSSION

The yield of various bisazo dyes IIIa–e and their polymeric dyes IVa–e ranging from 60 to 80%. All the simple bisazo dyes IIIa–e were yellow, orange, red or brown. The polymeric dyes IVa–e were deep orange, red or brown.

The bisazo dyes were soluble in common organic solvents, the polymeric dyes were soluble only in DMF. The polymeric dyes do not melt up to 300°C.

The IR spectra (not shown) of all the simple bisazo and polymeric dyes are almost identical in their important characteristics. However, the main difference between the IR spectra of bisazo dyes and their corresponding polymeric dyes is the appearance of medium bands at 2920 and 2850 cm^{-1} due to (asymmetric and

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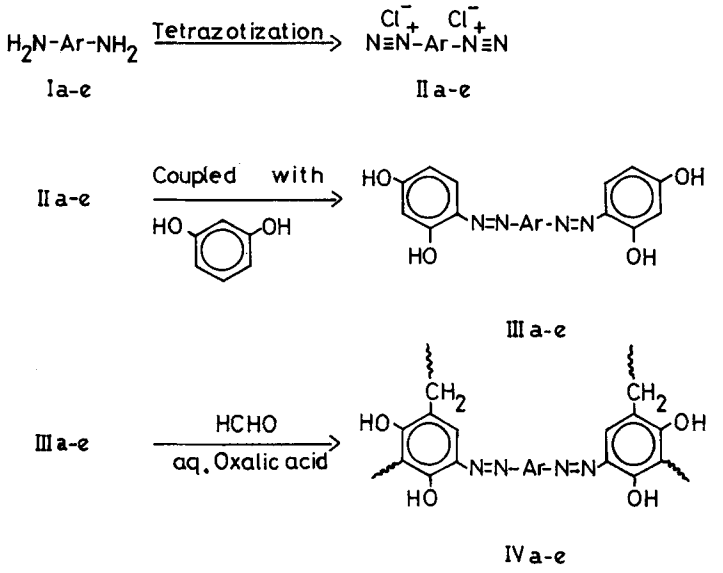

Diamine (I)	—Ar—
a	—Ph*—
b	—Ph-Ph—
c	—Ph-CH_2-Ph—
d	—Ph-O-Ph—
e	—Ph-S(=O)(=O)-Ph—

Where,

—Ph*— = 1,3-Phenylene

—Ph— = 1,4-Phenylene

SCHEME I Synthesis of bisazo dyes and their polymers.

symmetric ν_{CH_2}) methylene bridge in the spectra of polymeric dyes. However, the broad band at 3200 to 3600 cm^{-1} due to hydroxy group in the IR spectra of bisazo dyes becomes much broader in the IR spectra of polymeric dyes. This may be due to less intermolecular hydrogen bonding.

The λ_{max} values of the bisazo dyes and their polymeric dyes falls between 390–465 nm depending upon the nature of the substituent. Comparison of the λ_{max} values of the bisazo dyes and their corresponding polymeric dyes reveals that some of the polymeric dyes show a bathochromic shift, that is they absorb at a slightly longer wavelength than the corresponding bisazo dyes.

As there is no practical value of $\overline{Mn}$ and viscometric study of the produced polymers, the data of $\overline{Mn}$ & [η] are not presented. However, the viscometric behaviour of the solution of polymeric dyes in DMF does not obey the relation found by Huggins, but show the behaviour of polyelectrolyte according to the empirical relation (1) for the reduced viscosity of solution containing linear polyelectrolyte.

TABLE I

Characterization of bisazo resorcinol dyes [IIIa–e]

Compound	Yield %	Colour	Nitrogen (%) calcd.	found
III a	76	Brown	16.00	15.86
III b	79	Orange	13.14	13.02
III c	72	Red	12.72	12.60
III d	69	Orange	12.66	12.54
III e	74	Red	11.42	11.36

$$\frac{\eta sp}{C} = \frac{A}{1 + B \cdot \sqrt{C}} \tag{1}$$

Where A and B are constant characteristics of each sample. The data are not presented.

Examination of thermograms (not shown) of the polymeric dyes shows that up to 250°C the dyes are quite stable and show negligible weight loss. The thermograms above 350°C are very similar to each other. At 500°C the dyes show 35 to 60% weight loss.

The examination of the results of the dyeing properties of all the bisazo dyes and polymeric dyes reveals that they gave yellow, orange, red or brown shade. However, polymerization on nylon and polyester resulted in attractive hues. The light fastness of the bisazo dyes on nylon is poor (2–3) to good (4–5) and on polyester it varies from moderate (3–4) to good (4–5). The light fastness of the polymeric dyes on nylon is poor (2–3) to moderate (3–4) and on polyester it is moderate (3–4) to good (4–5). The wash fastness of the bisazo dyes on nylon is moderate (3–4) to good (4–5) and on polyester it is good (4–5) to very good (5–6). The wash fastness of the polymeric dyes on nylon and polyester is not better than that of the corresponding bisazo dyes. However, the light and wash fastness on nylon and polyester increases after polymerization of the bisazo dyes on nylon and polyester as follows:

1. The light fastness of the bisazo dyes IIIa–e on nylon is (2–3) to (4–5) which increases to (2–3) to (5–6) and on polyester it is (3–4) to (4–5) which increases to (4–5) to (5–6).

2. The wash fastness of the bisazo dyes IVa–e on nylon is (3–4) to (4–5) which increases to (4–5) to (5–6) and on polyester it is (4–5) to (5–6) which increases to (5–6).

Comparison of fastness properties of the polymeric dyes with the corresponding bisazo dyes polymerized on nylon and polyester reveals that the fastness properties improve significantly on polymerization on nylon and polyester.

TABLE II

Characterization and dyeing properties of IIIa-e

Bisazo dye	Yield %	Shade on N&W	Shade on PE	Nitrogen % calc.	Nitrogen % found	λ_{max} (nm)	log ε	Dyeing Properties: Nylon L.F.	Nylon W.F.	Wool L.F.	Wool W.F.	polyester L.F.	polyester W.F.
IIIa	76	O	O	16.00	15.82	465	4.29	2-3	3-4	3-4	4	4-5	5
IIIb	79	R	R	13.14	12.99	442	4.35	3-4	3-4	4-5	4	4-5	5
IIIc	72	R	O	12.72	12.57	410	4.73	4	4	4-5	4	4-5	5
IIId	69	O	O	12.67	12.48	450	4.46	3-4	3	3-4	5	4-5	5
IIIe	74	O	O	11.42	11.33	450	4.44	3-4	3-4	4-5	5	3-4	5

Where, O = Orange, R = Red, N = Nylon, W = Wool, PE = Polyester, L.F. = Light Fastness & W.F. = Wash Fastness

TABLE III

Characterization and dyeing properties of Condensates of IIIa–e with formaldehyde [IVa–e]

Polymeric dye	Yield %	Shade on N&W	Shade on PE	Nitrogen % calc.	Nitrogen % found	λ_{max} (nm)	Wt.loss at 300°C %	Dyeing Properties: Nylon L.F.	Nylon W.F.	Wool L.F.	Wool W.F.	Polyester L.F.	Polyester W.F.
IVa	75	O	O	14.97	14.81	464	12	2-3	5-6	2-3	5-6	4-5	5
IVb	73	R	O	12.44	12.35	445	10	2-3	5-6	2-3	5-6	4-5	5
IVc	70	O	O	12.06	11.97	410	14	3-4	5	4-5	5	4-5	5
IVd	69	Y	Y	12.01	11.89	455	18	4-5	4-5	4-5	5-6	3-4	5
IVe	62	O	Y	10.89	10.72	458	09	4	5	3-4	5-6	4	5

Where, O = Orange, Y = Yellow, R = Red, N = Nylon, W = Wool, PE = Polyester,
L.F. = Light Fastness & W.F. = Wash Fastness.

TABLE IV

Dyeing properties of bisazo dyes polymerized on nylon and polyester

Dyes IIIa-e polymerized on nylon and polyester	Shade on		Dyeing Properties			
			Nylon		Polyeser	
	N	PE	L.F.	W.F.	L.F.	W.F.
IIIa	O	Y	2-3	4-5	4	5
IIIb	R	R	3-4	5	4-5	5
IIIc	O	O	5-6	4-5	5-6	6
IIId	O	O	4-5	5	4-5	5-6
IIIe	O	O	4	5-6	4-5	5-6

Where, O = Orange, Y = Yellow, R = Red, N = Nylon, PE = Polyester

L.F. = Light fastness, W.F. = Wash fastness

EXPERIMENTAL

Materials

All the diamines (Scheme I) employed for preparation of tetrazonium salts were laboratory grade. Formalin was used as 37% aqueous solution of technical grade. Resorcinol was used after recrystallization. Polyamide (i.e. nylon 6,6) fabric was obtained from Vareli, Surat, India. Polyester (i.e. polyethylene terphthalate) fabric was obtained from Mafatlal Group, Ahmedabad, India were used for dyeing purposes.

Synthesis of bisazo dyes IIIa–e, their polycondensation with formaldehyde and dyeing of bisazo dyes IIIa–e and their polymeric dyes IVa–e and polymerization of bisazo dyes IIIa–e on dyed nylon and polyester are shown in Scheme I.

Various aromatic diamines (I) (0.5 mol) (listed in Scheme I) were tetrazotized to their tetrazonium salt solution (II) by methods reported earlier.[2,3]

The azo coupling of tetrazonium salts IIa–e to resorcinol and polycondensation of bisazo dyes IIIa–e with formaldehyde were carried out by the method reported in an earlier communication.[1]

Dyeing of bisazo dyes IIIa–e, their polymeric dyes IVa–e and polymerization on dyed nylon and polyester were carried out by the method reported in our earlier communication.[1]

MEASUREMENTS

Melting points of the dyes are uncorrected. Elemental analyses were carried out on C, H, N, O, and S Elemental Analyser, Carlo Erba, Italy. The IR spectra were

scanned in KBr on a Perkin-Elmer 983 Spectrophotometer. The visible spectra were recorded using Backman DU Spectrophotometer. DMF was used as a solvent.

Thermogravimetric analysis of the polymeric dyes were carried out on a DuPont 950 Thermogravimetric Analyser in air at a heating rate of 10°C/min.

Fastness properties of the dyed patterns were measured by the standard process.[4]

CONCLUSIONS

The polymerization of potential bisazo dyes on nylon and polyester leads to brilliancy of shade, very good dye fixation and increase in light and wash fastness.

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