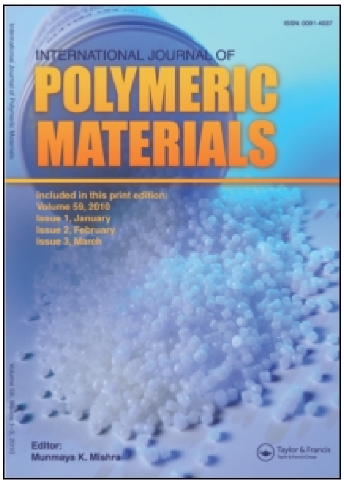

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Synthesis, Characterization and Dyeing Behavior of Oligomeric Trimethylolmelamine-1-naphthol Acid Azo Dyes

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The synthesis of oligomeric acid azo dyes ***A-1*** *to* ***A-11*** *was carried out by coupling reaction of trimethylolmelamine-1-naphthol oligomer* **A***, respectively, with diazonium salts of p-aminobenzoic acid, sulphanilic acid and nine different amino naphthalene sulphonic acid derivatives. The chemical structures of the novel coupling oligomer* **A** *and all the oligomeric acid azo dyes* ***A-1*** *to* ***A-11*** *were established by elemental analysis and spectral studies (IR, UV-visible). The number average molecular weight ($\overline{M}n$) of oligomer* **A** *was estimated by nonaqueous conductometric titration. The dyeability of all of the dyes on wool, silk and nylon fabrics was assessed by exhaustive dyeing, producing attractive shades varying from purple to off-white brown fabrics. The dyeing behavior was evaluated in terms of washing fastness and light fastness properties. It was observed that these novel oligomeric acid azo dyes exhibited attractive brilliant shades with excellent washing fastness and moderate light fastness properties.*

Keywords: acid azo dyes, dyeability, fastness properties, oligomer, oligomeric dyes

INTRODUCTION

The recent trends of research and development in the field of azo dyes are to enhance the dye-fiber affinity and colorfastness properties in textiles dyeing. In general, two chemical approaches used for improving these properties are either to introduce the polar group into the dye molecule or to increase the molecular size of the dye molecule. Abraham Ravve [1] has used phenol-formaldehyde oligomer, coupled with diazotized anthranilic acid to obtain red polymeric azo dye, which

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can be used as a coloured thermosetting resin. On the other hand, Stamler et al. have used novolak phenolic resin for a macromolecular dye preparation to be utilized for dyeing wool, silk, viscose and polyamide fiber [2]. On the basis of these reports, the present work comprises systematic study of synthesis, characterization and dyeing behavior of a series of eleven polymeric acid azo dyes derived from the coupling reaction of a phenolic oligomer, namely trimethylolmelamine-1-naphtol oligomer **A**, with different diazonium salts of aromatic aminobenzene and aminonaphthalene sulphonic acid. Further, perusal of literature has envisaged extensively use of trimethylolmelamine in textile industries for improvement of properties such as flame resistance, heat resistance, finishing agents, for crease proofing of cotton, as a crosslinking agent in fireproofing cotton and polyester, and to improve dyeability of silk [3–8] because of its higher dye fiber affinity. Nevertheless, the study of triazine-based oligomers in the synthesis of azo dyes has not received significant attention except sparse reports [9,10]. Consequently, in the present work efforts have been made to use oligomer **A** as a coupling component in the synthesis of a series of polymeric acid azo dyes. For this purpose the oligomer **A** coupler was prepared by the polycondensation of trimethylolmelamine (TMM) with 1-naphthol in the presence of base catalyst. It was characterized by estimation of its number average molecular weight ($\overline{M}n$), elemental analysis and spectral study (IR, UV-visible). Then, a coupling reaction of **A** was carried out, respectively, with eleven different diazonium salt of 4-aminosulphonic acid [Sulphanilic Acid], p-Aminobenzoic acid, 2-aminonaphthalene-1-sulphonic acid [Tobias Acid], 2-aminonaphthalene-6-sulphonic acid [Bronner's Acid], 1-aminonaphthalene-5-sulphonic acid [Laurent Acid],1-aminonaphthalene-8-sulphonic acid [Peri Acid], 6-amino-1-naphthol-3-sulphonic acid [J-Acid], 1-amino-2-naphthol-4-sulphonic acid [Gamma Acid], 1-amino-2-naphthol-4-sulphonic acid, 8-amino-1-naphthol-3,6-disulphonic acid [H-Acid], 8-amino-1-naphthol-5,7-disulphonic acid [Chicago Acid], to yield polymeric acid azo dyes (**A-1** to **A-11**).

All the eleven polymeric acid azo dyes were characterized for their chemical structure elucidation, and dyeing behavior on nylon, wool and silk fabrics.

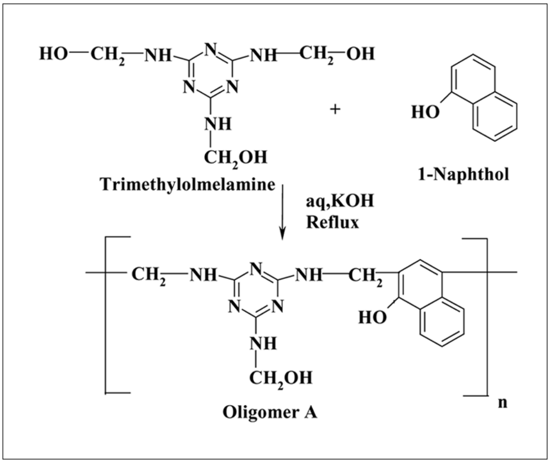
EXPERIMENTAL

Materials and Synthesis

1-naphthol, p-aminobenzoic acid, sulphanilic acid, and aminonaphthalene sulphonic acids were used after purification. All other chemicals were of laboratory grade and were used without further purification. The starting material of oligomer **A**, trimethylolmelamine, was prepared by condensation of melamine with formaldehyde in the presence of base catalyst in good yield by a method reported in the literature [11]. The optimum reaction conditions were established by performing a polycondensation reaction of trimethylolmelamine with 1-naphthol using various molar ratios of trimethylolmelamine to 1-naphthol and different proportions of alkali catalyst. Finally, the procedure chosen is described here.

Scheme 1 represents the synthetic protocols of oligomer **A** in which an aqueous methanolic solution of trimethylolmelamine and 1-naphthol in a molar ratio 1:1.5 and the base catalyst KOH (4% of total mass) was refluxed for an hour at temperature 70–75°C. The reaction mixture was cooled and the upper aqueous layer was decanted. The semisolid thus separated was washed several times with water, followed by benzene, to remove alkali and unreacted 1-naphthol, respectively. It was dried at 20°C in vacuo. The yield of oligomer **A** was 80% and its analytical data are given in Table 1.

Scheme 2 represents the synthetic protocol of polymeric acid azo dyes in which reactive oligomer **A** was used as a coupling component and p-aminobenzoic acid, sulphanilic acid and nine different aminonaphthalene sulphonic acids were used as diazonium salt to yield a series of eleven oligomeric acid azo dyes (**A-1** to **A-11**). The percentage yield and analytical data of these dyes are given in Table 2. The general procedure followed in the synthesis is given here.

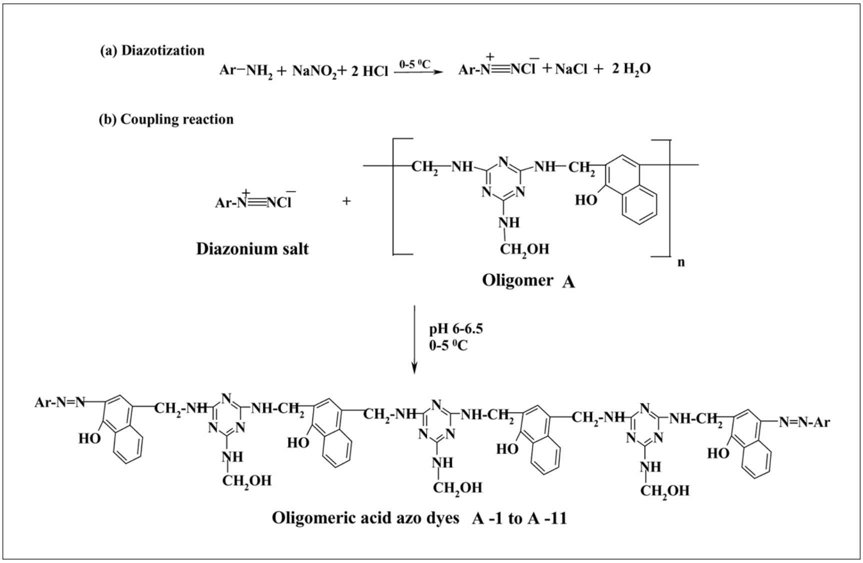


SCHEME 1 Synthesis of trimethylolmelamine-1-naphthol oligomer.

TABLE 1 Analytical Data of Oligomer **A**

Physical data			
Color	Brown		
Physical state	viscous liquid		
Molecular formula of repeat unit	$C_{16}H_{16}N_6O_2$		
Molecular weight of repeat unit	324 gm/mole		
Elemental composition			
	% C	% H	% N
Calculated	59.26	4.93	25.92
Found	59.86	4.82	25.21
Number average molecular weight ($\overline{\mathrm{M}}$n)*	1069 gm/mole		
Degree of polymerization	Dp = 3		
IR Features			
Naphthol, methylol			
O–H stretching	3335 cm^{-1}		
C–O stretching	1010 (m) cm^{-1}		
Methylene bridge (–CH_2–)			
–CH_2 stretching	2921 cm^{-1}		
Triazine ring			
N–H stretching (Secondary amino group)	3250 (w) cm^{-1}		
C–H stretching	1150 (s) cm^{-1}		
N–H In Plane bending	1450 (w or s) cm^{-1}, 1576 (s) cm^{-1}		
Out of Plane bending	815 (w) cm^{-1}		

*$\overline{\mathrm{M}}$n was estimated by nonaqueous conductometric titration.



SCHEME 2 Synthetic protocol of oligomeric acid azo dyes **A-1** to **A-11**.

TABLE 2 Analytical Data of Oligomeric Acid Azo Dyes

Dye no.	Diazonium compound	No. of azo group	% Yield	Fusing temp. range°C	No. ave. molecular weight^a ($\overline{\text{M}}$n)	λmax (nm)	Absorbance^b (A)	log €	Elemental analysis calc. (found) % C	% H	% N	% S
A-1	4-amino sulphonic acid	1.90	70	139–145	1500	476	0.296	4.413	56.00 (55.62)	4.26 (4.23)	20.50 (19.30)	4.26 (4.29)
A-2	4-amino benzoic acid	2.01	72	128–133	1428	476	0.292	4.415	58.82 (59.02)	4.48 (4.56)	21.50 (20.13)	– –
A-3	2-amino naphthalene-1-sulphonic acid	2.00	69	136–146	1600	486	0.356	4.551	58.50 (58.63)	4.31 (4.40)	19.20 (19.50)	4.00 (4.12)
A-4	2-amino naphthalene-6-sulphonic acid	1.95	78	129–136	1600	493	0.292	4.465	58.50 (58.35)	4.31 (4.23)	19.20 (18.50)	4.00 (4.18)
A-5	1-amino naphthalene-5-sulphonic acid	1.88	74	140–149	1600	498	0.270	4.431	58.50 (58.74)	4.31 (4.28)	19.20 (19.65)	4.00 (4.26)
A-6	1-amino naphthalene-8-sulphonic acid	1.99	65	126–136	1600	517	0.250	4.397	58.50 (58.45)	4.31 (4.35)	19.20 (18.29)	4.00 (3.96)
A-7	6-amino-1-naphthol-3-sulphonic acid	2.10	79	144–156	1632	496	0.400	4.610	57.35 (58.03)	4.22 (4.20)	18.80 (18.45)	3.92 (4.06)
A-8	1-amino-2-naphthol-4-sulphonic acid	1.97	76	130–142	1632	502	0.268	4.436	57.35 (57.69)	4.22 (4.15)	18.80 (19.01)	3.92 (3.78)

(*Continued*)

TABLE 2 Continued

Dye no.	Diazonium compound	No. of azo group	% Yield	Fusing temp. range°C	No. ave. molecular weight[a] ($\overline{M}n$)	λmax (nm)	Absorbance[b] (A)	log €	Elemental analysis calc. (found)			
									% C	% H	% N	% S
A-9	8-amino-1-naphthol-3, 6-disulphonic acid	1.84	72	146–153	1792	511	0.300	4.702	52.23 (53.01)	3.85 (4.02)	17.10 (17.52)	7.14 (7.65)
A-10	1-amino-2 naphthaol sulphonic acid	1.92	81	134–148	1632	448	0.450	4.485	57.35 (57.24)	4.22 (4.13)	18.80 (18.96)	3.92 (3.56)
A-11	8-amino-1-naphthol-5, 7-disulphonic acid	1.94	72	140–152	1792	432	0.262	4.467	52.23 (53.26)	3.85 (3.95)	17.10 (17.23)	7.14 (6.98)

[a] No. Average Molecular weight $\overline{M}n$ calculated on the basis of oligomer **A** and molecular weight of two moles of aromatic diazonium component.

[b] Concentration of dye solution 1.6×10^{-2} mg/ml.

The reverse diazotization method was used to diazotize all the aminonaphthalene sulphonic acids [12] but the diazotization of aminonaphthalene sulphonic acid derivatives not containing phenolic (–OH) group ortho to amino group was carried out in the absence of copper sulphate.

In diazotization, to a cooled aqueous solution of aromatic aminosulphonic acid (0.01 mol) and copper sulphate (0.2 g) was slowly added a solution of sodium nitrite (2 ml, 5 N) with continuous stirring at temperature 0–5°C, to yield a yellow-colored solution containing a few coarse particles. The solution was filtered and treated with concentrated hydrochloric acid to achieve complete precipitation of diazonium salt. It was immediately used for the subsequent coupling reaction, in which the above diazonium salt solution of aromatic aminosulphonic acid was added dropwise with continuous stirring to the cooled methanolic solution of oligomer **A** (0.05 mol) at temperature 0–5°C. After completion of the reaction, the solution was acidified with dilute hydrochloric acid to precipitate the dye. It was filtered off and air-dried. In some cases, the acidification of the dye solution did not precipitate the dye completely; then sodium chloride was added and digested for 30 min to achieve complete precipitation of the dye.

MEASUREMENTS

The number of azo groups ($-N{=}N-$) in the dye was estimated by redox titration of each of the oligomeric dye with a standard solution of stannous chloride following the method reported in the literature [13]. The number average molecular weight ($\overline{M}n$) of oligomer **A** was determined by nonaqueous conductometric titration using pyridine as solvent and standard solution of sodium methoxide as a titrant base according to the procedure reported in the literature [14–16]. Finally, number average molecular weight ($\overline{M}n$) of all the dyes was calculated by the summation of number average molecular weight ($\overline{M}n$) of oligomer **A** and molecular weight of this respective diazonium salt. Micro-analytical data for C, H, N, or S were obtained on a Carlo Erba CHN Analyzer (Italy). Infrared spectra were recorded as KBr pellets on a Nicolet-400D FTIR Spectrophotometer. UV-visible spectra were recorded on a Shimadzu-20 Spectrophotometer by using a spectroscopic grade DMF ethanol at concentration 1.6×10^{-2} mg/ml of the dye.

Dyeing Procedure

The wool, nylon and silk fabrics were treated at pH 5–6 (adjusted with acetic acid) for 15 min at 60°C. A laboratory model glycerinbath high-temperature metallic beaker-dyeing machine was used. A paste of dye (40 mg) was prepared with dispersing agent Dodamol (80 mg), wetting agent Tween-80 (5 mg) and water (1 ml) in a beaker. To this paste, water (160 ml) was added with stirring and the pH was adjusted to 4 using acetic acid to give the dyeing solution. This solution was then transferred to a metallic beaker provided with a lid and a screw cap. Before closing the lid and tightening the metal cap over the beaker, a pretreated patch of fabric 2 g of wool, silk, and nylon) was rolled into the beaker. The beaker was then placed vertically on the rotatory carrier inside the tank and the clamp plate was firmly tightened. The rotatory carrier was then allowed to rotate in the glycerin bath. The temperature of the bath was raised to 95, 100, and 110°C, respectively, for silk, wool, and nylon fabrics at the rate of 2°C/min. The dyeing was continued for 60 min under pressure. After cooling for an hour, the beaker was removed from the bath and washed thoroughly with water. The mother liquor after dyeing was collected and used further for exhaustion study. The dyed pattern was washed several times with cold water followed by detergent (0.2 g) and sodium carbonate (0.1 g) in water (100 ml) at 80°C for 30 min. Finally it was washed thoroughly with water and dried at room temperature. The dyeing behavior of these dyes was examined by studying the percentage dye bath exhaustion and fixation of the dye on fabric according to a standard method [17]. The color fastness of all the dyed fabrics to washing and light were tested according to the Indian standards [18].

RESULTS AND DISCUSSION

The procedure presented in the experimental part was the result of an optimization process. Polycondensation of trimethylolmelamine with 1-naphthol using 1:1.5 molar ratios assumes 1-naphthol as two end groups in the bake-bone chain of oligomer **A**. This was further confirmed from the analytical data of a number of azo groups present in all the oligomeric dyes. The results of elemental analysis of oligomer **A** and oligomeric dyes **A-1** to **A-11** were in agreement with calculated values. The estimated number average weight ($\overline{\mathrm{M}}\mathrm{n}$) of oligomer **A** reported in Table 1 suggested the presence of three repeat units in **A**. Consequently, the number average molecular weight ($\overline{\mathrm{M}}\mathrm{n}$) of the dyes **A-1** to **A-11** would be the sum of ($\overline{\mathrm{M}}\mathrm{n}$) of oligomer **A** and two moles of the corresponding aromatic diazonium component.

IR spectra of oligomeric dyes **A-1** to **A-11** showed the following characteristic features. Two characteristic absorbance bands at 1595 cm^{-1} and 760 cm^{-1} were attributed azo group (–N=N–) and

TABLE 3 Analytical Data of Dyeing On Fabrics

Oligomeric acid azo dye	% Exhaustion			% Fixation			Light fastness			Wash fastness			Shade observed on dyed fabrics
	W[a]	S[b]	N[c]	W	S	N	W	S	N	W	S	N	
A-1	85.92	84.34	85.39	72.39	74.69	74.69	4	4	5	5	4	5	orange
A-2	86.64	85.3	84.16	80.95	82.05	81.65	5	3–4	5–6	5	4	5	orange
A-3	88.96	87.58	86.19	73.85	76.15	79.34	5	3–4	4	4	3	4	reddish orange
A-4	85.68	84.12	85.68	71.98	74.34	82.69	4	4	4	5	4	5	dark orange
A-5	90.02	88.62	82.46	72.18	74.68	81.68	5	4	4–5	4	4–5	4–5	reddish brown
A-6	89.06	87.49	87.73	73.46	76.98	80.68	4	3–4	5	4–5	4	4–5	brown
A-7	84.91	84.03	83.98	76.46	80.06	81.98	5	4	5	4	3	5	maroon
A-8	87.39	84.63	85.08	76.64	79.46	78.64	5	4	5–6	5	4	4	purple
A-9	83.98	81.61	82.39	75.14	72.06	76.98	4	4	5–6	3	3	5	reddish brown
A-10	82.64	83.98	82.11	73.66	79.61	80.16	5	4	5	5	4	4	light brown
A-11	88.48	86.6	85.66	74.68	78.96	79.43	4	3–4	4	4	4	4–5	reddish brown

[a] W for wool fabric.
[b] S for silk fabric.
[c] N for nylon fabric.

substituted naphthalene ring of 1-naphthol, respectively. The two strong bands in the regions of 1190–1200 cm^{-1} and 1040–1060 cm^{-1} and a weak band at 650 cm^{-1} were characteristic of the sulphonic ($-SO_3H$) group present in the diazonium components of the dye. In conclusion, the results of analysis of **A** oligomer and oligomeric acid azo dyes derived from **A** are in good agreement with the chemical structure shown in Schemes 1 and 2, respectively.

The electronic absorption spectra of all the oligomeric acid azo dyes were recorded in DMF- ethanol solvent at the dye concentration of 1.6×10^{-2} mg/ml. The absorption maxima of these dyes showed their absorption band in the visible region from 430 to 520 nm, reported in Table 2. The structure–property relationship of the diazonium component of acid dye with λ_{max}, absorbance value and color shade was evaluated. The model dyes **A-1** and **A-2** showed almost the same λ_{max} orbance values and orange shade on all the three fabrics. Bathochromic shift ($\Delta\lambda$) of 20–40 nm was observed due to an increase in the aromatic character of the naphthalene ring of dyes **A-3** to **A-9** as compared to that of a phenyl ring in **A-1** and **A-2** dyes. The presence of the sulphonic acid group in the sixth position of the naphthalene ring of **A-4** showed a bathochromic shift compared to **A-3** because of the occurrence of resonance in the ring. In addition to this, a bathochromic shift of $\sim$10 nm was observed in the acid azo dye **A-8** relative to **A-4**, due to the presence of an auxochrome ($-OH$) in **A-8**. Hence, in general, dyes giving bathochromic effect showed A deepening of color upon dyeing the fabric, as expected.

All the dyes were applied as acid azo dyes on wool, silk and nylon fabrics at 2% shade and gave light orange to purple shades (see Table 3) with good levelness, brightness and depth. The percentage dye bath exhaustion and fixation of all dyes on fabrics varied from 80–90% and 70–85%, respectively, depending upon the nature of oligomeric dye. The data of washing fastness and light fastness of these dyes on the fabrics are shown in Table 3. Comparison of these data indicates a very good to excellent fastness properties of these dyes.

CONCLUSION

It can be concluded from the above studies that the improvement of the fastness properties and increasing the molecular size of the dye molecule, by using reactive oligomer as dye precursor leads to attractive brilliant shades with excellent fastness properties.

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