Synthesis, Characterization and Application of Some Polymeric Dyes Derived From Monoazo Disperse Dyes

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Abstract: *In this study, Some Monoazo disperse dyes namely, 4-arylazoaminophenols (AAPs) were synthesized via diazotization and coupling reactions and later, polycondensation of these dyes with formaldehyde in the presence of aqueous oxalic acid was carried out. The resulting polymeric dyes namely, (4-arylazoaminophenol-formaldehyde)s (PAAP-F)s as well as their low-molecular weight precursors were characterized by yield, melting point, color, solubility, viscosimetry, Proton Nuclear Magnetic Resonance spectroscopy, UV-visible spectroscopy and Infra red spectroscopy. Their dyeing performance on nylon and polyester were assessed using standard methods. The products were obtained in good yield and had low melting points The dyes were found to be soluble in chloroform and acetone, some were found to dissolve in ethanol and methanol, and generally insoluble in water. The dyeing on nylon and polyester had yellow shades with moderate to good light and wash fastness. Their rubbing fastnesses on nylon and polyester were very good. Polymerizations of the monomeric dyes on dyed nylon and polyester have also been carried out. The dyeing properties of the monomeric and polymeric dyes were compared with the dyes polymerized in situ on nylon and polyester and the fastness properties were found to increase on polymerization and even better with the dyes polymerized inside the fibers.*
Key words: Color fastness, Disperse dye, Nylon, Polymeric dye, Polyester.

I. Introduction

From prehistoric times people have been fascinated by the colors of nature, and have attempted to duplicate these in their artifacts, usually for aesthetic, religious or purely functional purposes. For thousands of years they could achieve the desired effects only by isolating naturally occurring colorants, such as certain minerals, or the pigments to be found in plants and animal species [1].The modern era of Color Chemistry began in 1856 when William Henry Perkins synthesized the first "coal tar" dye which he called mauve. Since that time many thousands of colorants have been synthesized to color everything from textiles to food. A number of classes of dyestuffs and pigments have been synthesized over the years to address the particular needs of various applications [2]. Today a new class of materials, polymeric colorants, has gained recognition and applicability as an alternative to the classical methods of coloration using dyes and pigments. The marriage of polymer and dye chemistries enables the chemist to design unique materials that exploit the best characteristics of both dyes and pigments. The motivation for the development of this existing new class of materials is performance. Polymeric dyes (colorants) are chromophores that have polymeric chains attached to them [3].

II. Materials and Methods

2.1 Reagents
All the reagents used in this research were of laboratory grade obtained from Sigma-Aldrich and used as received. The formaldehyde was used as 37% aqueous solution of technical grade.

2.2 Instruments
The melting points were determined using Gallenkamp electro-thermal melting point apparatus, intrinsic viscosities were measured in acetone using Ostwald viscometer. Absorbance was taken using Shimadzu 1601 Spectrophotometer in the region 200-800nm.^{1}H-NMR spectra were recorded on Jeol JNM-LA400 FT-NMR system.

2.3 Synthesis of Diazonium Salt Solutions
The diazo components were diazotized using similar procedure adopted by [4]. Using a 400ml beaker, 0.06 mole of each diazo component was dispersed in 20ml of distilled water which stands in an ice-bath. To this was added 10ml of concentrated HCl over a period of two minutes while the dispersion was stirred with magnetic stirrer. The temperature of the ice-bath was maintained at between 0-5^{0}C by addition of common salt (NaCl). 4.3g (0.06 mol.) of sodium nitrite was dissolved in 20ml distilled water in a 50ml beaker. The resulting solution was added drop-wise to the stirred suspension over a period of one hour to attain complete diazotization.

2.4 Azo Coupling of Diazonium salts

0.06 moles of each coupling component was suspended in 20ml distilled water contained in a 250ml beaker at 0-5^{0}C in an ice-bath. Solution of the diazonium salt was added drop-wise to the coupling component over a period of 10 minutes with gentle but continuous stirring. The stirring was continued for further 45 minutes as the dye crystals precipitated. The precipitated dyes were filtered and washed with water and then recrystallized.

2.5 Polycondensation of Monomeric Dyes with Formaldehyde

0.05 moles of each monomeric dye was suspended in 50ml distilled water and then 0.5ml of 37% w/v formaldehyde solution and 0.5g oxalic acid were added. The reaction mixture was gradually heated to 90-95^{0}C and maintained at that temperature for 1hour. The reaction mixture was cooled, filtered and washed with water till the filtrate was neutral. Finally, it was washed with 20ml methanol and air-dried [5].

2.6 Dyeing of Nylon and Polyester

High temperature dyeing was carried out using a similar method reported by [5].

2.7Polycondensation of Monomeric Dyes on Dyed Nylon and Polyester

After dyeing, the dyed fabrics were rinsed with water, squeezed and introduced into 100ml of water containing 0.5ml of 37% w/v formaldehyde and 0.5g oxalic acid. The temperature was allowed to rise gradually to 90-95 and maintained for 1hr. After cooling, the fabrics were washed with water and treated with 0.2% w/v detergent solution in water at 80^{0}C for 30 minutes. After washing with water, the fabrics were dried at room temperature [5].

2.8 Characterization

The following characterization techniques were employed:

2.8.1 UV-Visible Spectroscopy

The electronic spectra were measured by means of a Shimadzu 1601 Spectrophotometer in the region 200–800nm. [6].

2.8.2 Fourier Transformed Infra-red (FT-IR) Spectroscopy

The sample prepared were characterized using KBr disc sampling method. The discs were prepared by grinding the samples (2% by weight) with KBr which was then compressed in to a disc and were analyzed FTIR Spectrometer (Perkin Elmer model) [7].

2.8.3 Proton Nuclear Magnetic Resonance (^{1}H-NMR) Spectroscopy

^{1}H-NMR spectra were recorded on a Joel Lambda 400 MHz Nuclear Magnetic Resonance spectrometer. An appropriate quantity of the sample was weighted and dissolved in a vial in deuterated DMSO containing tetramethyl silane (TMS) as internal standard. Using a pipette; the liquid was transferred through the pipette filler into the NMR tube and the spectra were recorded. FT-IR yields information about the arrangement of pendants groups such as alkyl, phenyl, etc.

2.8.4 Determination of Melting Point and Solubility

The melting points were determined with Gallenkamp melting point apparatus.
The solubility of each sample was tested in a variety of solvents which include: water, ethanol, methanol, chloroform, carbon tetrachloride, n-hexane, ethyl acetate, petroleum ether, acetone and N,N-dimethyl formamide (DMF). 5cm^3 of each solvent was added to about 0.1g of the sample in a test tube and shaken vigorously. The solubility was carefully observed and recorded.

2.8.5 Dilute Solution Viscometry (DSV)

Viscosity measurements were conducted at 30^{0}C using Ostwald Viscometer as described by [8].

2.9 Color Fastness Properties
2.9.1 Fastness to Light

The light fastness properties of the dyed samples were assessed using the standard methods (B.S 1006). It was carried out on an artificial light fastness tester MK1 fitted with mercury-tungsten (MBTF) 500 watt lamp. The samples were exposed together with blue wool standards for about 96hrs and assessed.
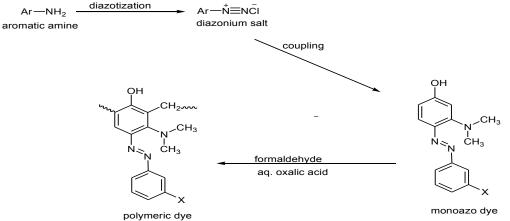
2.9.2 Fastness to washing
    The fastness to washing of the dyed samples was assessed using a similar method adopted by [9].

2.9.3 Fastness to Rubbing
    A piece of the dyed fabric was rubbed on a plane dry white cloth and then a wet white cloth. The staining of the white cloth was observed and assessed [9].

III.   Results and Discussions

    The proposed synthetic scheme for the polymeric dyes and their low-molecular weight precursors is outlined below:

When, X = H: Dye A_1 [poly (4-hydroxy-2-N,N-dimethylphenylazo-3'-nitrobenzene)]   When, X = NO$_2$: Dye D_1 [poly (4-hydroxy-2-N,N-dimethylphenylazobenzene)]

Figure 1: Synthesis of Simple and Polymeric Dyes

Table 1: Yield, Color and Melting Point of the Dye Samples

Dye	Yield (%)	Color	M/Pt. (^{0}C)
B	83.0	Orange	110-112
C	67.2	Orange	76-80
E	77.4	Yellow	85-90
B_1	70.5	Orange	138-143
C_1	52.0	Orange	130-132
E_1	38.9	Yellow	138-142

    The percentage yields for the synthesized dyes are good 89.5% and 48% for the monomeric dyes A and D respectively and 53% for the corresponding polymeric dyes (A_1 and D_1). All the dyes were yellow in color, with the polymeric dyes having deeper shades. The dyes were of low melting points, 78-80^{0}C, 80-84^{0}C for the monomeric dyes A and D respectively and 128-130^{0}C and 96-101^{0}C for the corresponding polymeric dyes A_1 and D_1 respectively.

3.1 UV-Visible Spectroscopy
    This technique was employed in order to determine the wavelength of maximum absorption (λ_{max}) for the synthesized dyes. Results obtained are presented in the TABLE below.

Table 2: λ_{max} Values for the dye samples

Sample	λ_{max}(nm)	Absorbance
P	402	2.834
Q	457	3.436
R	416	2.916
P_1	462	3.436
Q_1	493	3.524
R_1	438	3.010

The λ_{max} values of the monomeric and polymeric dyes fall between 456-488nm depending upon the nature and position of the substituents. The synthesized dyes all have the same chromophore (i.e –N=N-), so they all have approximately the same λ_{max}. However, the polymeric dyes synthesized, absorbed at slight longer wavelength than the monomeric dyes. Hence there is a bathochromic shift.

The polymeric dyes except A_1 and D_1 were found to have absorption higher than the corresponding monomeric dyes indicating that, little quantity of the polymeric dye can provide sufficient colour that can only be obtained when relatively larger quantity of the monomeric dye is used [10].

3.2 FT-IR Spectroscopy

Identification of the type of functional groups present in a polymer is effectively achieved by IR analysis. From the result obtained, the hydroxyl stretching vibration bands for the dye samples were observed in the region $3436.21 cm^{-1}$, $3398.55 cm^{-1}$ for A and D respectively and $3422.01 cm^{-1}$ and $3398.55 cm^{-1}$ respectively for A_1 and D_1. Bands in the region $1528.82 cm^{-1}$ - $1617.67 cm^{-1}$ were assigned to the –N=N- group. The IR spectra of the monomeric and polymeric dyes are almost identical in their important characteristics. However, the main difference between the IR spectra of the polymeric dyes and those of their low molecular weight precursors is the presence of medium bands at $2901.92 cm^{-1}$ and $2930.07 cm^{-1}$ due to asymmetric (CH_2) methylene bridges in the spectra of polymeric dyes A_1 and D_1 and respectively.

Table 3: Infra-red absorption bands

Sample	Group				
	-OH	-N=N-	C-N	N-H	CH_2
B	$3426.55 cm^{-1}$	$1590.08 cm^{-1}$			
C	$3400.40 cm^{-1}$	$1542.03 cm^{-1}$			
E		$1522.82 cm^{-1}$	$1333.98 cm^{-1}$	$3433.33 cm^{-1}$	
B_1	$3413.97 cm^{-1}$	$1589.84 cm^{-1}$			$2972.57 cm^{-1}$
C_1	$3394.50 cm^{-1}$	$1624.17 cm^{-1}$			$2901.78 cm^{-1}$
E_1		$1529.45 cm^{-1}$	$1259.57 cm^{-1}$	$3370.16 cm^{-1}$	$2927.53 cm^{-1}$

From the result in TABLE 3, the hydroxyl stretching vibration bands for the dye samples except for sample E and E_1, were observed in the region $3394.50 cm^{-1}$ – $3436.21 cm^{-1}$. Bands in the region $1522.82 cm^{-1}$ - $1624.17 cm^{-1}$ were assigned to the –N=N- group. Bands at $1259 cm^{-1}$ and $1333.98 cm^{-1}$ were due to C-N stretching of aromatic amine for E_1 and E respectively. Bands at $3433.33 cm^{-1}$ and $3370.16 cm^{-1}$ of the spectrum of sample E and E_1 respectively, are assignable to the aromatic N-H group. The IR spectra of all monomeric and polymeric dyes are almost identical in their important characteristics. However, the main difference between the IR spectra of the polymeric dyes and those of their low molecular weight precursors is the presence of medium bands at 2901.92 cm^{-1}, $2972.57 cm^{-1}$, $2901.78 cm^{-1}$, $2930.07 cm^{-1}$, and $2927.53 cm^{-1}$ due to asymmetric (CH_2) methylene bridges in the spectra of polymeric dyes A_1, B_1, C_1, D_1 and E_1 respectively.

3.3 [1] H-NMR Spectroscopy

In the ^{1}H-NMR Spectral data of the synthesized dyes were observed Ar-H at $7.16 – 7.44$ ppm as multiples, the *OH* peaks appeared at $2.0 – 3.05$ ppm and the aromatic NH peaks appeared at $3.90 – 4.77$ ppm. The ^{1}H-NMR spectra of the monomeric and polymeric dyes are almost similar in their important characteristics. However, there is appearance of peak at around 2.88 ppm assignable to some traces of $-CH_2-$ in the spectra of the polymeric dyes.

3.4 Solubility

The dyes were found to be soluble in chloroform and acetone, some were found to dissolve in ethanol and methanol, and generally insoluble in water. Their insolubility in water may be attributed to their disperse nature.

3.5 Dilute Solution Viscometry (DSV)

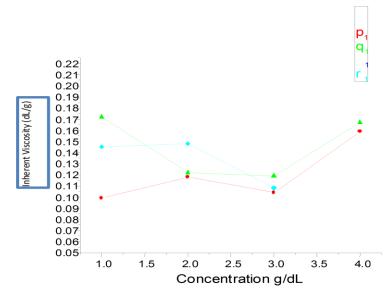The viscosities of the polymer samples are presented in the figures below:

Figure 2: Plots of Inherent Viscosity against Concentration of the Polymeric Dyes
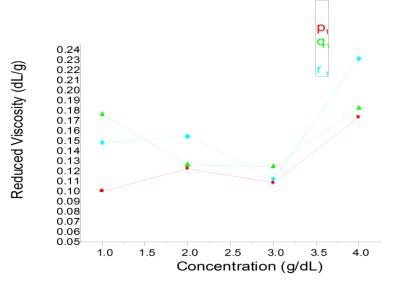

Figure 3: Plots of Reduced Viscosity against Concentration of the Polymeric Dyes

The plots of inherent viscosities of the polymeric dyes obtained are shown in figure 1. The relative positions of these plots give an idea of the viscosity of the samples. The variation in the viscosities of the samples is a direct relation with molecular mass. The plots of reduced viscosity against concentration are shown in figure 2. The intercepts of the plots with the vertical axis correspond to the limiting or intrinsic viscosities of the samples at infinite dilution. These intercepts can be used in combination with appropriate constants in the Mark-Houwink-Sakurada equation to evaluate the viscosity average molar mass M_v. However, the constants k and α, are specific for a polymer/solvent at a given temperature. The samples were of low viscosity and this implies low molecular weight and hence, better ability to penetrate the fibers [11]

3.6 Color Fastness Properties

Fastness properties of dyed fabrics show resistance of the color to external agencies. Wash fastness measures the resistance to laundry treatments while light fastness measures resistance to sunlight [12]. The color fastness properties of polymeric dyes and their low-molecular weight precursors are summarized in table 4.

As indicated in tables 4, the light fastness of the monomeric dyes on both Nylon and Polyester varied from moderate to good. The washing fastness varied from moderate to very good. The wash fastness of the polymeric dyes on both nylon and polyester is not better than those of the corresponding monomeric dyes. However, the light and wash fastness increases after polymerization of the simple dye on nylon and polyester.

Table 4: Color Fastness Properties of the Monomeric, Polymeric and Dyes Polymerized on Nylon and Polyester

Monomeric Dyes						
	Nylon			Polyester		
Dye	Light	Washing	Rubbing	Light	Washing	Rubbing
P	2-3	3-4	4-5	3-4	4-5	4-5
Q	2-3	3	3-4	2-3	4	3-4
R	2-3	4-5	4-5	2-3	4-5	4-5
Polymeric Dyes						
P_1	3-4	4-5	4-5	5	4-5	4-5
Q_1	4-5	4-5	4-5	5	4-5	4-5
R_1	4-5	4-5	4-5	5	4-5	4-5
Polymerized Dyes						
P_2	4-5	4-5	4-5	5	4-5	4-5
Q_2	3-4	3-4	4	4-5	4-5	4
R_2	4-5	4-5	4-5	5-6	5	4-5

The rubbing fastness for the dyes is excellent on both fibers. Generally, those dyes polymerized on the fabrics showed better fastness and more attractive hues. The fastness properties of the synthesized dyes are comparable to those reported by [12] and [13].

IV.   Conclusion

In this study, two polymeric dyes were synthesized via diazotization and coupling   reactions followed by condensation with formaldehyde in the presence of aqueous oxalic acid. The synthesized dyes have been characterized using color, melting point, yield, dilute solution viscometry, UV-visible, proton-nuclear magnetic resonance, and IR spectroscopy. The melting points of the dyes were generally low. The absorbances of the polymeric dyes were found to be higher than those of their low molecular weight precursors. Generally, the dyes have good exhaustion in both the fibers though they exhaust better in nylon than polyester. Their fastness properties on nylon and polyester were good with the polymeric dyes having more brilliant colours generally, the polymerization of potential monomeric dyes on nylon and polyester leads to brilliancy of shade and increase in fastness properties.

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