

Polymeric Dyes Based on Thiadiazole Derivatives

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Abstract: A series of polymeric dyes were synthesized by free radical addition polymerization of monomeric dyes. The 2-amino-5-mercapto-1,3,4-thiadiazole was diazotized and coupled with various N-arylmaleimides to give monomeric dyes. All the polymeric dyes were characterized by elemental analysis, infrared spectroscopy, visible absorption spectroscopy, viscometry, and thermogravimetric analysis. Color and dyeing properties of the polymeric dyes were discussed by comparing them with those of the corresponding monomeric dyes. The dyeing performance of these dyes was assessed on nylon fiber. These dyes were found to give various color shades with good to very good depth and levelness on the fiber. The dyeing of the monomeric dyes showed moderate fastness to light and good to excellent fastness to washing, perspiration and sublimation and their corresponding polymeric dyes showed excellent fastness properties. The dye bath exhaustion and fixation on nylon fiber has been found to be good.

Keywords: 2-amino-5-mercapto-1,3,4-thiadiazole, N-arylmaleimide, Polymeric dyes, Dyeing, Nylon

Introduction

Aminothiadiazoles were among the first heterocyclic diazo components for disperse dyes to be described in the literature[1]. Such heterocyclic amines have been used commercially to produce brilliant red polyester dyes. Depending on the substituent in the diazo component and the coupler used, brilliant in the scarlet to bluish-red dyes are obtained[2-11]. These dyes however still do not quite match the brightness of anthraquinone dyes. The great number of patent applications for structures with various substituents proved the versatility of 2-amino-1,3,4-thiadiazole derivatives [12-16]. However, these heterocycles have fallen short of expectations as far as commercial exploitation is concerned.

The search for more readily available sources of colouration over the last century led to the development of synthetic pigments and dyes. This search in turn fathered modern industrial chemistry. Today a new class of materials, polymeric colourants, has gained recognition and applicability as an alternative to these classical methods of colouration. The marriage of polymer and dye chemistries enables the chemist to design unique materials that exploit the best characteristics of both pigments and dyes.

The origins of polymeric dyes are no doubt lost in antiquity along with the name of the first chemist to synthesise one. In the broadest sense of the word, a polymeric dye is a "high-molecular weight" coloured compound composed of a number of repeating units. This type of definition would include Aniline Black, a black dye discovered over a century ago. The broad definition of polymeric dye given above would also include many polymers, synthetic or natural, soluble or cross-linked, since few of these compounds are stark white. In 1964 Kuhn disclosed the first example of polyoxyalkylene

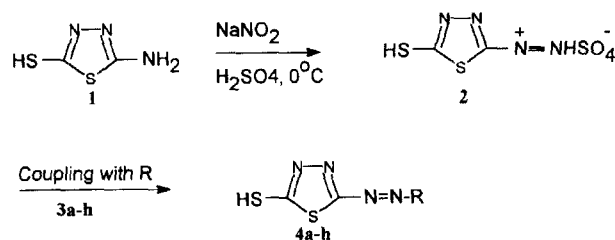
polymeric colorants that fulfill acquired performance requirements such as complete removal of fugative tints and no influence on the final shade of the fiber[17,18]. These large, highly water-soluble molecules could not penetrate the fibers surface and could be readily washed away during normal aqueous dyeing and finishing.

Polymeric colorants offer the advantage of allowing tunability in a range of physical properties such as solubility, absorption, migration, and viscosity. They do not sublime, are non-abrasive, and generally have low toxicity. The range of possible product offered by the joining of the fields of polymer chemistry and color chemistry is virtually inexhaustible. New examples are frequent in many journals of chemical literature of research, which associated with the various applications of polymeric colorants[19-40]. There are reviews that summarize the area[41,26].

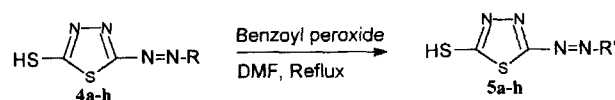
The term polymeric colorants are finding application in a wide variety of technologies. Their applications are dependent on their higher molar mass. In the broad sense, the term macromolecular colorants are defined as a group of intermediate or high molar mass compounds that may also be thought of as being intrinsically or structurally colored polymers, i.e. possessing inherent properties[42], polymeric dyes[31] and polymeric pigments[43]. Each of these terms is somewhat limited in its application.

A monomeric dye is a polymerizable dye that contains a polymerizable group, normally through an ethylenic type double bond in the dye molecule. Polymeric dyes may be defined through their application as polymer and dyes, which possess suitably inherent properties. They are soluble in the medium in which they are applied or in the substrate with which they form a composite. Thus, polymeric dyes are useful polymers or oligomers as well as dyes of unique importance due to their tinctorial strength[41,44]. Their utilization has been possible because of certain essential dye

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Scheme 1. Synthetic scheme of monomeric dyes 4a-h.



Scheme 2. Synthetic scheme of polymeric dyes 5a-h.

properties such as fast levelling on fiber, fastness to light and wet treatment, low sublimation rate and very good thermal and chemical resistance.

The literature survey reveals that only a limited researcher have reported the use of various N-arylmaleimides as a coupling components to prepare various azo disperse dyes [45-47]. Earlier we had studied the dispersed dyes base on various N-arylmaleimides coupling components[48-52]. The encouraging results[53,54] prompted us to extend our study on 1,3,4-thiadiazole moiety. In this article, we wish to report the synthesis of monomeric dyes by coupling with various N-arylmaleimides with diazotized 2-amino-5-mercapto-1,3,4-thiadiazole. The resulting monomeric dyes were polymerized by free radical addition polymerization and their dyeing performances on nylon fiber have been assessed. The entire research work is summarized in Schemes 1 and 2.

Experimental

Materials and Methods

All of the chemicals used were of commercial grade and were further purified by standard method[55]. Elemental analyses of all the dyes were carried out on Carlo Erba Elemental Analyser. Infra-red spectra were recorded in KBr pellets on a Perkin-Elmer model 983 spectrophotometer. The visible spectra were recorded on Carl Zeiss UV/VIS Specord Spectrophotometer. All the polymeric dyes were characterized by intrinsic viscosity measurement in DMF at $35 \pm 0.05^\circ\text{C}$ with an Ubbelohde suspended level viscometer. The molecular weight determination was found in dioxane at 50°C using Vapour Pressure Osmometer, Hewlett Packard model 3028. Thermogravimetric analyse (TGA) of all the polymeric dyes were carried out on a Du Pont model 951 thermogravimetric analyzer in air at a heating rate of $10^\circ\text{C}/\text{minute}$.

Preparation of 2-amino-5-mercapto-1,3,4-thiadiazole 1

The title compound was synthesized by the method reported in the literature[56].

Preparation of Various N-arylmaleimide Coupling Components 3a-h

These compounds were prepared by the general method reported in the literature[57].

Synthesis of Monomeric Dye 4a

The synthesis of the monomeric dyes 4a comprises two steps.

Diazotization of 2-amino-5-mercapto-1,3,4-thiadiazole 1

Dry sodium nitrite (1.38 g; 0.02 mol) was added in parts over a period of 30 minutes to 98% sulphuric acid (1.1 ml; 0.02 mol) with stirring below 65°C . The resulting solution was treated dropwise at $5-20^\circ\text{C}$ with the mixture of propionic acid and acetic acid (20 ml, 3:17). The resulting nitrosylsulphuric acid mixture was cooled to 0°C and compound 1 (2.66 g; 0.02 mol) was added in portions and stirred for 2 hours at $0-3^\circ\text{C}$. The excess nitrous acid (given positive test on starch-iodide paper) was decomposed with the required amount of urea. The clear diazonium salt solution 2 thus obtained was used for subsequent coupling reaction as exemplified below.

Coupling of Diazonium Salt Solution 2 with N-Phenylmaleimide 3a

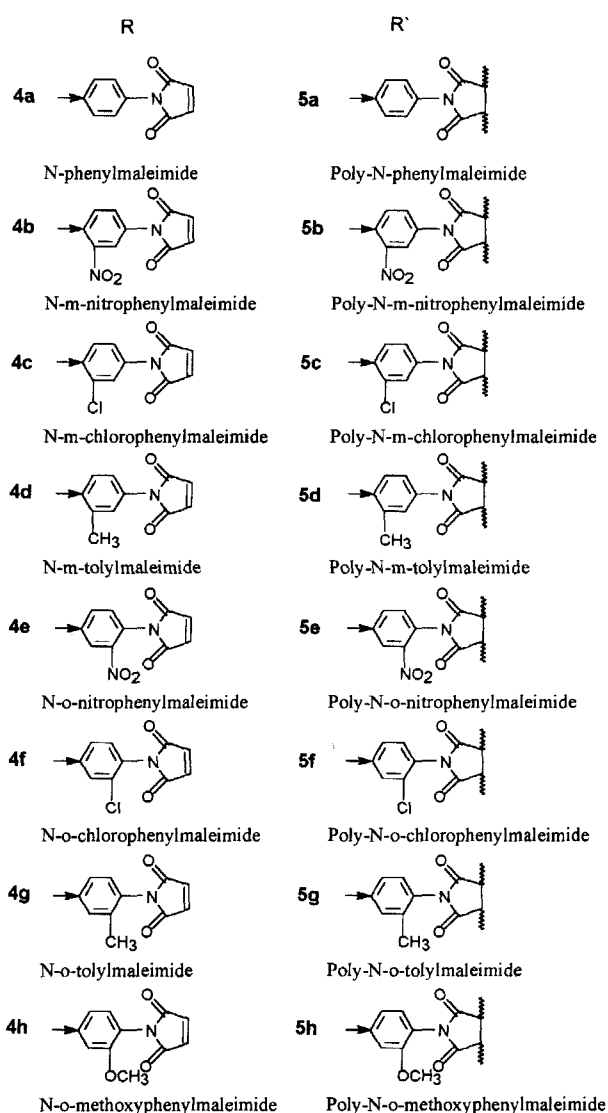
The N-phenylmaleimide 3a (3.46 g; 0.02 mol) was dissolved in 10 ml acetic acid and cooled at 0°C . Freshly prepared diazonium salt solution 2 was added dropwise to this well-stirred solution over a period of 2 hours, keeping the temperature below 5°C . The reaction mixture was stirred for 45 minutes at $0-3^\circ\text{C}$, maintaining the pH at 4-5 by the help of 10% sodium acetate solution. The reaction mass was then diluted with 100 ml water, filtered, washed, and dried in an oven at 50°C . The dye 4a thus obtained was recrystallized from a minimum amount of DMF.

The same procedure was repeated for the preparation of the dyes 4b-h using various N-arylmaleimides 3b-h. The synthetic scheme is shown in Scheme 1. Characterization data for dyes 4a-h are given in Table 2.

Synthesis of Polymeric Dyes 5a-h

The synthesis of the polymeric dyes 5a-h was carried out by free radical polymerization of the monomeric dyes 4a-h using benzoyl peroxide as an initiator in dry benzene. A typical synthesis was described below. The synthetic scheme is shown in Scheme 2. The characterization data for polymeric dye 5a-h are given in Table 3.

A clean dry three-necked flask equipped with a mechanical stirrer (2000 rpm/minute) was charged with a mixture of the monomeric dye 4a (0.02 mol), dry benzene (50 ml) and benzoyl peroxide (0.002 g). The reaction mixture was refluxed at 80°C . The solid product started to separate after 30 minutes. The reaction was further refluxed for 6 hours, and then cooled to room temperature. The solid product was



filtered off, washed with petroleum ether (60-80°C) and dried under reduced pressure.

Dyeing Method

Dyeing at 90-135°C temperature and high pressure (24-30 psi) is a convenient method for dyeing nylon fiber in the laboratory. A laboratory model glycerin-bath high-temperature beaker dyeing machine was used. A paste of finely powder dye (40 mg) was prepared with dispersing agent Dodamol (80 mg); wetting agent Tween-80 (5 mg) and water (1 ml) in a ball mill for 10 minutes. To this paste, water (99 ml) was added with stirring and the pH was adjusted to 4.5-5 using acetic acid. This dye suspension (100 ml) was added to a beaker provided with a lid and a screw cap. Before closing the lid and tightening the metal cap over the beaker, a wetted pattern of nylon fiber was rolled into the beaker. The beaker was then placed vertically on the rotatory carrier inside the

tank and the clamp plate firmly tightened. The rotatory carrier was then allowed to rotate in the glycerin-bath, the temperature of which was raised to 110°C (for nylon fiber) at the rate of 2°C/minute. The dyeing was continued for 1 hour under pressure. After cooling for 1 hour, the beaker was removed from the bath and washed with water. The pattern was thoroughly washed with hot water at 50°C, and then with cold water, and finally dried at room temperature.

Dyeing Method of Polymeric Dyes

Dyeing method of polymeric dyes differed little from the above procedure. The finely powdered polymeric dye (40 mg) was intimately mixed with a suitable dispersing agent Dodamol (30 mg) and wetting agent Tween-80 (20 mg) and DMF (1 ml) in a ball mill for 1 hour, and then this paste was poured into aqueous solution of dispersing agent Dodamol (20 mg/99 ml). This provides good dispersion quality. The pH of the resulting disperse solution was adjusted to 4.5-5 using acetic acid. The dyeing was continued for 75 minutes under pressure. After cooling for 1 hour, the pattern was removed and washed with hot water 50°C, and then with cold water, and dried at room temperature.

Fastness Properties

The fastness to light, sublimation, and perspiration was assessed in accordance with BS:1006-1978. The rubbing fastness test was carried out using crockmeter (Atlas) in accordance with AATCC-1961 and the wash fastness test in accordance with IS:765-1979. The details of various fastness tests were described in the literature[58].

Determination of the Percentage of Exhaustion and Fixation (Dissolution Method)

The dyebath exhaustion percentage (%E) and fixation percentage (%F) of the dyed fiber were determined according to the known method[58].

Result and Discussion

Preparation of Monomeric/Polymeric Dyes

2-amino-5-mercapto-1,3,4-thiadiazole **1** was synthesized from thiosemicarbazide by reacting with carbon disulphide, either with or without base present. The ring closure of the dithiocarboxylate salt occurs upon heating under the reaction conditions. Weak amines, such as compound **1**, required the use of nitrosylsulphuric acid and it was diazotized satisfactorily at 0°C by adding to nitrosylsulphuric acid in acetic acid-propionic acid mixture. The resulting diazonium salt solution **2** was generally used within a few hours since this decomposed on standing, even when cold. Coupling was usually accompanied by some evidence of decomposition; however, by careful addition of the diazonium salt solution **2** at 0-3°C to a solution of the coupler in acetic acid, a 68-84% yield of the dye was usually obtained. To complete coupling

particularly for reactions using nitrosylsulphuric acid in the diazotization, the pH of the reaction mixture was eventually adjusted to approximately 4-5. Thus, an appropriate amount of 10% sodium acetate solution was slowly added below 3°C.

Physical Property of Dyes

In order to determine the end point of diazotization, it was found useful to check the presence of unreacted diazo component on thin layer chromatography (T.L.C.). Thus, when unreacted diazo component no longer persisted on T.L.C., the diazotization was ended. Subsequent coupling reaction took place readily upon the addition of the resulting diazonium salt solution **2** continuously to the solution of the coupling component **3a-h** in acetic acid.

The purified dyes were all found to have satisfactory elemental analyses. All the dyes required purification to eliminate contaminants arising from diazo decomposition and/or coupling components used. The purity of the dyes was checked by T.L.C. using ethyl acetate:benzene (1:4) as the solvent system. When adsorbed onto silica chromatography plates, each dye produced a single colour spot. All the recrystallized dyes exhibited well-defined melting point characteristic of pure compounds. It would be premature to attempt to explain in detail their relative values, because of the complex dependence of the melting points on a number of factors (e.g., polarity, geometry, size and molecular interaction.).

The results of intrinsic viscosities and the number average molecular weights of the polymeric dyes are given in Table 3. The data of the viscosity measurement of polymeric dyes ranged from 0.015 to 0.092 dl/g which indicate that the polymeric dyes are of low molecular weight ranging from 2.5×10^3 to 4.8×10^3 . The appreciable steric hindrance of the double bond of N-arylmaleimide ring is taken as responsible for their low polymerization tendency.

Infra-red Spectra of Dyes

The IR spectra of the dyes reveals that the 1,2-ethylenic bond of the maleimide ring can be identified by the stretching vibration of C-H. The band appearing at 1585 cm^{-1} is due to the stretching vibration of the C=C, which is conjugated with C=O. The unsaturation is also indicated by the C-H stretching vibrations which appears at $3085\text{-}3200$ and $820\text{-}832 \text{ cm}^{-1}$ (out-of-plane-deformation vibrations). The band at 675 cm^{-1} is an out-of-plane-deformation vibration characteristics of CH=CH. These bands disappear in polymeric dyes. The pair of bands 1710 and 1725 cm^{-1} are due to the stretching vibration of the C=O. The band appearing at $625\text{-}675 \text{ cm}^{-1}$ can be attributed to an in-plane-deformation vibration of the C=O and that at $575\text{-}585 \text{ cm}^{-1}$ to an out-of-plane-deformation vibration of the C=O. The bands at 1350 and 1375 cm^{-1} are due to a stretching vibration of C-N-C, the first being asymmetrical and the second symmetrical. The band of the

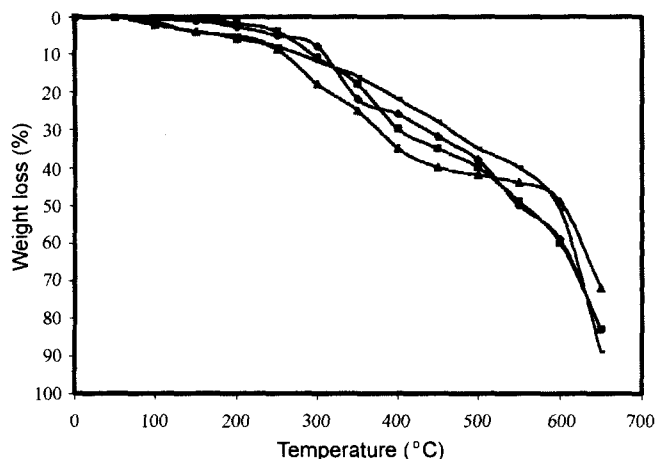


Figure 1. TGA curves of polymeric dyes: ● 5b, ■ 5f, ▲ 5g, ◆ 5h.

skeletal C-C bond appear at 1575 cm^{-1} , and the band at $1580\text{-}1585 \text{ cm}^{-1}$ is due to -N=N- stretching vibration. The strong characteristics band at $600\text{-}660 \text{ cm}^{-1}$ and $675\text{-}700 \text{ cm}^{-1}$ are due to S-H stretching vibration of the mercapto group, and 1070 cm^{-1} due to -C-N stretching. The band around $1480\text{-}1530 \text{ cm}^{-1}$ is due to an ester group. The bands at 2850 cm^{-1} , $700\text{-}640 \text{ cm}^{-1}$ and $1390\text{-}1450 \text{ cm}^{-1}$ are due to C-H bending vibration of -OCH₃, C-Cl and C-CH₃ stretching vibration respectively. The band at $1320\text{-}1360 \text{ cm}^{-1}$ is due to symmetric stretching of the -NO₂ group.

Thermogravimetric Study

Thermogravimetric investigations were carried out for the polymeric dyes in the range from 25°C to 650°C, at heating rate of 10°C/minutes in an air oxidation decomposition. The typical TGA curves for the selected polymeric dyes **5b**, **5f**, **5g** and **5h** are shown in Figure 1. In order 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_a) of the degradation process were calculated by Doyle's

Table 1. TGA parameters of polymeric dyes **5a-h**

Dye no.	T_{10}	T_{max}	IPDT (°C)	E_a (KJ/mol)
5a	239	458	336.8	20.82
5b	256	510	329.9	19.96
5c	270	520	350.2	19.10
5d	282	530	380.6	19.00
5e	287	536	382.6	21.30
5f	292	540	345.8	18.90
5g	288	506	352.7	18.20
5h	298	518	361.5	20.10

[59] and Broido's[60] methods.

T_0 and T_{10} are the two main criteria used to indicate the thermal stability of the polymeric dyes. The higher the values of T_0 and T_{10} , the higher will be the thermal stability [61]. 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_{10} ranged from 239 to 298°C, and T_{max} ranged from 458 to 540°C. The values of IPDT and the overall activation energy E_a for the degradation process was in the range of 329.9°C to 382.6°C and 18.2 to 21.3 KJ/mol, respectively (Table 1).

Visible Absorption Spectroscopic Properties of Dyes

Absorption maxima of dyes recorded in DMF solution and

Table 2. Characteristic data, elemental analysis, intensities, exhaustion and fixation properties of monomeric dyes **4a-h**

Dye no.	Yield (%)	m.p. (°C)	Absorption maxima (λ_{max})		log ϵ (DMF)	Molecular formula (Mol. wt.)	Elemental analysis (%)			R_f value	(%E)	(%F)
			λ_{max}/nm (DMF)	λ_{max}/nm (Conc. H ₂ SO ₄)			Found (Require)					
							C	H	N			
4a	81	208-209	480	395	3.36	C ₁₂ H ₇ N ₅ O ₂ S (317)	45.02 (45.42)	2.10 (2.20)	21.95 (22.80)	0.88	72	81
4b	84	225-227	440	390	3.11	C ₁₂ H ₆ N ₆ O ₄ S ₂ (362)	39.10 (39.77)	1.45 (1.65)	23.08 (23.20)	0.82	80	85
4c	72	192-193	450	395	3.29	C ₁₂ H ₆ N ₅ O ₂ S ₂ Cl (351.5)	40.46 (40.96)	1.60 (1.70)	19.68 (19.91)	0.90	86	85
4d	78	186-188	430	400	4.10	C ₁₃ H ₉ N ₅ O ₂ S ₂ (331)	46.89 (47.12)	2.60 (2.71)	21.00 (21.14)	0.92	83	80
4e	70	217-218	450	400	4.60	C ₁₂ H ₆ N ₆ O ₄ S ₂ (362)	39.10 (39.77)	1.45 (1.65)	23.08 (23.20)	0.87	73	78
4f	68	236-237	440	415	3.29	C ₁₂ H ₆ N ₅ O ₂ S ₂ Cl (351.5)	40.46 (40.96)	1.60 (1.70)	19.68 (19.91)	0.81	78	83
4g	69	200-201	410	485	4.70	C ₁₃ H ₉ O ₂ S ₂ (331)	46.89 (47.12)	2.60 (2.71)	21.00 (21.14)	0.84	68	81
4h	71	195-196	450	415	4.47	C ₁₃ H ₉ N ₅ O ₃ S ₂ (347)	44.80 (44.95)	2.40 (2.59)	20.06 (20.17)	0.88	81	80

Table 3. Characteristic data, elemental analysis, intensities, exhaustion and fixation properties of polymeric dyes **5a-h**

Dye no.	Yield (%)	Mol. wt.	Viscosity (η) dl/g	Absorption maxima (λ_{max})		log ϵ (DMF)	Elemental analysis (%)			R_f value	(%E)	(%F)
				λ_{max}/nm (DMF)	λ_{max}/nm (Conc. H ₂ SO ₄)		Found (Require)					
							C	H	N			
5a	76	4.8×10 ³	0.092	475	391	3.18	45.65 (45.71)	2.10 (2.22)	22.10 (22.22)	0.82	68	63
5b	80	3.6×10 ³	0.057	436	380	3.06	39.90 (40.00)	1.52 (1.66)	23.22 (23.33)	0.80	75	70
5c	81	3.2×10 ³	0.048	442	386	3.19	41.05 (41.20)	1.60 (1.71)	19.82 (20.02)	0.86	80	73
5d	77	2.8×10 ³	0.052	426	392	4.02	47.30 (47.41)	2.60 (2.73)	21.12 (21.27)	0.85	76	71
5e	74	2.7×10 ³	0.068	442	385	4.50	45.60 (45.71)	2.12 (2.22)	22.08 (22.22)	0.81	70	67
5f	78	3.4×10 ³	0.076	432	405	3.20	39.88 (40.00)	1.56 (1.66)	23.20 (23.33)	0.80	71	66
5g	81	3.1×10 ³	0.039	403	470	4.60	41.10 (41.20)	1.58 (1.71)	19.80 (20.02)	0.76	64	61
5h	75	2.5×10 ³	0.015	445	408	4.20	45.10 (45.21)	2.48 (2.60)	20.10 (20.28)	0.79	75	71

concentrated sulphuric acid are shown in Tables 2 and 3. The introductions of electron donating or electron-attracting groups at suitable position on the coupler ring affect the absorption characteristics of the dyes. The dyes, listed in Tables 2 and 3, are reddish-brown to deep brown. The logarithm of molar extinction coefficient ($\log \epsilon$) of the dyes were in the range of 3.06 to 4.70, indicating high intensity of absorption.

Exhaustion and Fixation Study

Table 2 show that the exhaustion and fixation of the monomeric dyes on nylon fiber are higher than those of corresponding polymeric dyes (Table 3). The polymeric dyes have larger molecular size and tend to have interactions with the fiber. Nylon fiber is crystalline and hydrophobic and has a highly regular molecular structure. Consequently, diffusion of the polymeric dye within the fiber proceeds slowly under the given dyeing conditions thereby affecting the exhaustion value. The polymeric dyes exhaust smoothly onto the fiber when applied from a stable dispersion under dyeing condition and provide satisfactory colour shade with slightly lower depths. The uptake of disperse dyes by nylon fiber takes place via progressive adsorption of the small concentration of the dye in solution that is always present in an aqueous dispersion. The substantivity of the dye, which determines its tendency to partition in favour of the fiber,

depends on factors such as molecular size, geometry and (in particular) the polarity of the molecule. During the dyeing process, the fiber is in the glass-like state below about 80°C and inaccessible to aqueous solutions of dye. When the glass-to-rubber transition temperature is reached, the fiber immediately becomes readily dyeable.

Dyeing Properties

All the disperse dyes were applied at 2% depth on nylon fiber. No problem was encountered in preparing satisfactory dispersions when the monomeric dyes were milling with dispersing agent. Polymeric dyes were more resistance to milling than the monomeric dyes owing to the nature of their crystals; however, they also gave satisfactory dispersion when they were ground in ball mill using DMF and Dodamol. The dispersing agent has dual function: they facilitate the breakdown of aggregated dyes particles during milling and act as a stabilising agent for the dispersion of the dye in the dye-liquor. For stability the amount of dispersing agent must be maintained above a certain minimum. The dispersing agent also promotes levelling and, in particular, prevents surface deposition of the dye, which may result in poor fastness to light. Levelling by migration of the absorbed dye is virtually impossible. Careful control of the temperature in the transition region is therefore essential. However, even under the most carefully controlled conditions, it is difficult

Table 4. Result of dyeing and various fastness properties of monomeric dyes 4a-h

Dyes no.	Shade on nylon	Fastness to						
		Light	Rubbing		Washing	Perspiration		Sublimation
			Dry	Wet		Acid	Alkaline	
4a	Dark yellow	3-4	5	5	5-4	5	5	5
4b	Dark brown	4-3	5	5	5	5	5	5
4c	Yellow	4-3	5	5-4	5	5	5	5
4d	Yellow	4-5	4-5	5-4	5-4	5	5	5
4e	Brown	3-4	5	5	5	5	5	3-4
4f	Reddish yellow	4-3	5	5	5	5	5	5
4g	Yellowish orange	4-5	5	5	5	5	5	4-5
4h	Deep brown	3-4	5	5-4	5	5	5	5

Table 5. Result of dyeing and various fastness properties of polymeric dyes 5a-h

Dyes no.	Shade on nylon	Fastness to						
		Light	Rubbing		Washing	Perspiration		Sublimation
			Dry	Wet		Acid	Alkaline	
5a	Brownish yellow	8	5	5	5	5	5	5
5b	Reddish orange	8	5	5	5	5	5	5
5c	Yellowish brown	8	5	5	5	5	5	5
5d	Reddish brown	8	5	5	5	5	5	5
5e	Yellow	8	5	5	5	5	5	5
5f	Brownish yellow	8	5	5	5	5	5	5
5g	Reddish brown	8	5	5	5	5	5	5
5h	Brown	8	5	5	5	5	5	5

to achieve complete uniformity at the temperature of the material. Therefore, it is essential that the dispersing agent act as a retarder.

All the fastness properties shown in Tables 4 and 5 are interrelated since they depend, among other things, on the rate of diffusion of dye in the fiber. This rate is a function of the geometry of the dye molecule and depends on molecular weight. The concentration of the dye in the fiber appeared to be the most influential factor in the fastness of the dyes. For example, the variation of light fastness of dye with their concentration in the substrate is partly a function of their particle size (which varies with change in concentration). In any system where particles are formed from a liquid phase, they appear in a random range of sizes. Moreover, their average size increases with concentration. Strickly speaking, this will be met only in dye systems that are molecularly dispersed, but it is likely also to occur with dyes dispersed in a medium.

In attempting to trace the relationships between chemical structure and light fastness, to appreciate that there is no absolute value for the light fastness of a dye; the value obtained for a given colourant in any fading test depends on many factors, the most important of which are: concentration and/or degree of aggregation of dye within the fiber, nature of fiber in which it is dispersed, the characteristics of the incident radiation, and molecular structure. It is well known that molecular mass and intermolecular interactions affect the sublimation fastness property; these factors also appear to influence the volatility of the dyes. Disperse dyes sublime because they are devoid of ionic solubilising groups and therefore have a significant vapour pressure at the temperature encountered during processing. It has been observed that the vapour pressure of a dye is inversely proportional to its molecular mass and its polarity[62]. Some general trend might, therefore, be expected between the sublimation fastness of disperse dyes and their molecular weight of and/or the presence of polar groups on the dye structures. In order to obtain a satisfactory combination of light and sublimation fastness, judicious choice of substituents is required. It is difficult to choose the proper substituents in order to improve the light and sublimation fastness properties. A dye with good light fastness may be achieved by increasing the molar mass, which reduces the volatility of the dye and thus lowers the dye sublimation. The introduction of polar groups can adversely affect the dyeing properties of a dye. The polymeric dyes were slightly less soluble in nylon fiber compared to the monomeric dyes, so that saturation was reached at the application level, slightly restricting the depth of dyeing.

The wash fastness ratings of the nylon dyeing were primarily influence by depth of the shade. The lower depths of the nylon dyeing mean that staining was low which did not lose colour. Thus, the low depths of shade restricted the occurrence of any staining. Monomeric dyes were much

Table 6. Bleeding properties of polymeric dyes **5a-h**

Dye no.	Solvent system				
	Water	Ethanol	Toluene	n-butanol-xylene (1:9)	Cellosolve
5a	5	4	5	5-4	4-5
5b	5	5-4	5-4	4-5	4-5
5c	5	5-4	4-5	5	5-4
5d	5	5-4	5-4	4-5	5-4
5e	5	5-4	5-4	5-4	4-5
5f	5	4-5	4-5	4-5	4-5
5g	5	5-4	5	5-4	5
5h	5	5-4	4-5	5-4	4-5

more soluble in nylon, which suggests that the higher solubility of these dyes allows greater depths to be achieved. These dyes had inferior fastness relative to that shown by the polymeric dyes, presumably because one or more of the factors could have been significant, e.g., a relatively small molecular mass, which facilitates diffusion out of the sample, a higher substantivity for the fiber, as well as a higher initial concentration of the dye that provided a deep sample shade.

All the fastness properties of fiber containing the monomeric dyes (Table 4) range from good to excellent, while dyed fiber with corresponding polymeric dyes (Table 5) shows excellent fastness properties. The improved fastness might be attributed to the highly conjugated system created by the N-arylmaleimide as a result of keto/enol tautomerism which may act as an UV absorber[63].

Table 6 indicates the result of the bleeding test. The dyed fiber with the polymeric dyes has excellent fastness to water, very good to excellent fastness to ethanol, toluene and n-butanol-xylene (1:9), and good to very good fastness to cellosolve solvent. It may be suggested that the polymeric dyes are easily soluble with nylon fiber under the dyeing condition. Thus polymeric dyes applied to nylon fiber are more resistant to removal by solvent extraction.

Conclusion

The disperse dyes containing thiadiazole moiety have been prepared from various N-arylmaleimides as the coupling components. The nitrosylsulphuric acid was needed for satisfactory diazotization of 2-amino-5-mercapto-1,3,4-thiadiazole.

Good yields of all the monomeric and polymeric dyes were obtained. These dyes provide a narrow range of colour shades, and excellent affinity and intensity of colour. The polymeric dyes have low molecular weight. The utilization of these dyes was possible because of certain essential dye properties, such as fast levelling on fiber, excellent fastness to light, wet treatment and sublimation and very good to excellent thermal and chemical resistance.

From the above studies, it is clear that increasing in the molecular size of the dye molecule via polymerization has given improvements of the fastness properties. The polymeric dyes on nylon fiber have a relatively low depth shade with excellent fastness and staining ratings.

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