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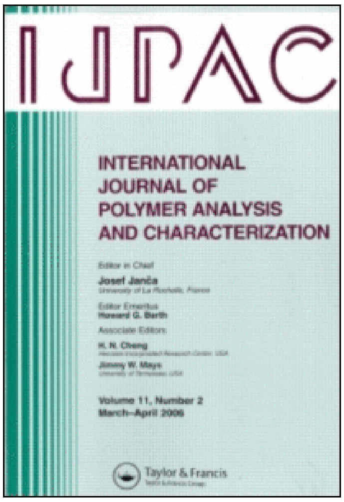

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Thiadiazole-Based Monomeric and Polymeric Dyes for Cellulose Triacetate Fiber

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Thiadiazole-Based Monomeric and Polymeric Dyes for Cellulose Triacetate Fiber

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A series of monomeric dyes was prepared by diazotization of 2-amino-5-mercapto-1,3,4-thiadiazole and coupled with various N-arylmaleimides. The polymeric dyes were prepared by free radical polymerization of monomeric dyes and characterized by IR, intrinsic viscosity, molecular weight by vapor pressure osmometry, thermogravimetry analysis, and elemental analysis. The monomeric dyes were also characterized by elemental analysis and IR spectra. The purity of all the dyes were checked by thin layer chromatography and by application on cellulose triacetate fiber as disperse dyes. All the dyes were found to give various color shades with good-to–very good depth and levelness on fiber. The percentage dyebath exhaustion and fixation on fiber was found to be good-to–very good. The dyeing of monomeric dyes showed very good fastness properties, and their corresponding polymeric dyes showed excellent fastness to light, washing, perspiration, solvent resistance, and sublimation.

Keywords: N-arylmaleimides; 2-amino-5-mercapto-1,3,4-thiadiazole; Disperse dyes; Monomeric dyes; Polymeric dyes; Cellulose triacetate

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Aminothiadiazoles were among the first heterocyclic diazo components for disperse dyes to be described[1]. Dyes derived from 2-amino-1,3,4-thiadiazole are of technical interest for the production of brilliant red shades. Depending on the various substituents in the diazo component and the coupler used, these dyes exhibit brilliant scarlet to bluish red color[2–4]. Commercial success has been achieved with 2-amino-5-ethylthio-1,3,4-thiadiazole in the replacement of red anthraquinone-based dyes[5]; a dye from this diazo component, C.I. Disperse Red 338, has the only structure of this type that has been disclosed to date[6]. Thiadiazole classes of diazo components were extensively studied over the past ten years[7–11] because of their brightness and good light fastness on hydrophobic fibers. They also exhibit generally excellent performance to wet fastness on polyester fiber. These, however, still do not quite match the brightness of the anthraquinone dyes. The great number of patent applications for structures with various substituents bears witness to the versatility of 2-amino-1,3,4-thiadiazole derivatives[12–15]. However, this heterocycle has fallen short of expectations as far as its commercial application is concerned.

The search for more readily available sources of coloration 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 colorants, has gained recognition and applicability as an alternative to these classical methods of coloration. 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 origin of polymeric dyes is no doubt lost in antiquity along with the name of the first chemist to synthesize one. In the broadest sense of the word, a polymeric dye is a “high–molecular weight colored 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. The motivation for the development of this exciting new class of materials is to overcome the deficiencies of both dyes and pigments in specific applications.

Polymeric colorants offer the advantage of allowing a range of physical properties like solubility, absorption, migration, and viscosity to be tunable. They do not sublime, are nonabrasive, and generally have low toxicity. The range of products possible by combining polymer chemistry and color chemistry is virtually inexhaustible. New examples appear frequently in the chemical literature[16–20].

Polymeric colorants are finding applications in a wide variety of technologies. Their applications are dependent on their higher molar mass. In the broad sense, the macromolecular colorants are defined as a

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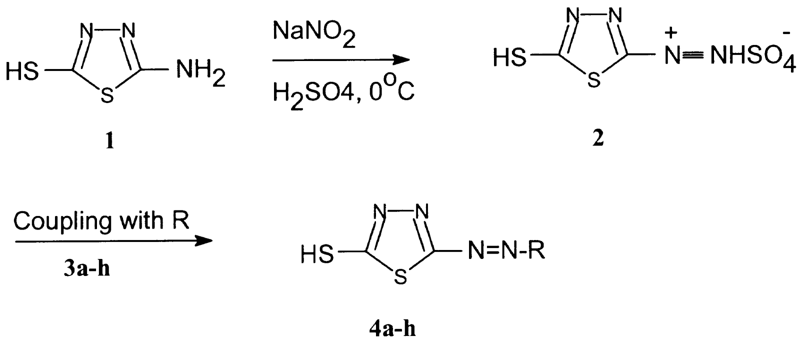
group of intermediate or high molar mass compounds that may also be thought of as being intrinsically or structurally colored, i.e., polymers possessing inherent properties[21], polymeric dyes[22], and polymeric pigments[23]. Each of these terms is somewhat limited in its application.

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 polymers and dyes that 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. There is also the related series of polymeric pigments, although the distinction between polymeric dyes and polymeric pigments is not clear. One can think of a dye as a virtually isolated chromogen and the pigment as an agglomeration of chromogens. Polymeric dyes are useful polymers or oligomers due to their tinctorial strength[24,25]. Their utilization has been possible because of certain essential dye properties, such as fast leveling on fiber, fastness to light and wet treatment, low sublimation rate, and very good thermal and chemical resistance.

A literature survey reveals that only a limited number of researchers has reported the use of different N-arylmaleimides as coupling components to prepare various azo disperse dyes for nylon and polyester[26], silk and wool fibers[27,28], and UV stabilization[29]. Considerable advances have been made in the chemistry and technology of this class of dyes. Earlier we had studied the dispersed dyes based on various N-arylmaleimides coupling components[30–32]. The encouraging results[33–35] prompted us to extend our study to the 1,3,4-thiadiazole moiety. In this article, we report the synthesis of monomeric dyes by coupling various N-arylmaleimides with diazotized 2-amino-5-mercapto-1,3,4-thiadiazole. The resulting monomeric dyes were polymerized by free radical polymerization, and their dyeing performance on cellulose triacetate fibers assessed. The synthetic effort has been summarized in Schemes I and II.



SCHEME 1 Synthetic scheme for monomeric dyes 4a–h.

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EXPERIMENTAL

Materials

All the chemicals used in dye synthesis were of commercial grade and were further purified by crystallization and distillation. 2-amino-5-mercapto-1,3,4-thiadiazole 1[36] and various N-arylmaleimides 3a–h[37] were prepared by known methods.

Synthesis of Monomeric Dye 4a

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

(a) 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 min to 98% sulphuric acid (1.1 mL; 0.02 mol) with stirring below 65°C. The resulting solution was treated dropwise at 5–20°C with a 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 h at 0–3°C. The excess nitrous acid (giving 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.

(b) 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 h, keeping the temperature below 5°C. The reaction mixture was stirred for 45 min at 0–3°C, maintaining the pH at 4–5 with 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 I. The characterization data for dyes 4a–h are given in Table I.

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TABLE I Characteristic Parameters of Monomeric Dyes 4a–h

Dye no.	Yield (%)	m.p. (°C)	Absorption maxima (λ_{max}) (nm)		log ε	Molecular formula (mol. wt.)	Elemental analysis (%) Found (Calcd.)			R_f value	Exhaustion (%)	Fixation (%)
			λ_{max} in DMF	λ_{max} in conc. H_2SO_4			C	H	N			
4a	81	208–209	480	395	3.36	$C_{12}H_7N_5O_2S$ (317)	45.02 (45.42)	2.10 (2.20)	21.95 (22.80)	0.88	88	83
4b	84	225–227	440	390	3.11	$C_{12}H_6N_6O_4S_2$ (362)	39.10 (39.77)	1.45 (1.65)	23.08 (23.20)	0.82	83	79
4c	72	192–193	450	395	3.29	$C_{12}H_6N_5O_2S_2Cl$ (351.5)	40.46 (40.96)	1.60 (1.70)	19.68 (19.91)	0.90	78	72
4d	78	186–188	430	400	4.10	$C_{13}H_9N_5O_2S_2$ (331)	46.89 (47.12)	2.60 (2.71)	21.00 (21.14)	0.92	88	81
4e	70	217–218	450	400	4.60	$C_{12}H_6N_6O_4S_2$ (362)	39.10 (39.77)	1.45 (1.65)	23.08 (23.20)	0.87	82	76
4f	68	236–237	440	415	3.29	$C_{12}H_6N_5O_2S_2Cl$ (351.5)	40.46 (40.96)	1.60 (1.70)	19.68 (19.91)	0.81	80	74
4g	69	200–201	410	485	4.70	$C_{13}H_9O_2S_2$ (331)	46.89 (47.12)	2.60 (2.71)	21.00 (21.14)	0.84	86	81
4h	71	195–196	450	415	4.47	$C_{13}H_9N_5O_3S_2$ (347)	44.80 (44.95)	2.40 (2.59)	20.06 (20.17)	0.88	79	72

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 is described below. The synthetic scheme is shown in Scheme 2. The characterization data for polymeric dyes 5a–h are given in Table II.

A clean, dry three-necked flask equipped with a mechanical stirrer (2000 rpm/min) 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 min. The reaction was further refluxed for 6 h, and then cooled to room temperature. The solid product was filtered off, washed with petroleum ether (60–80°C), and dried under reduced pressure.

Measurements

The C, H, and N contents of all the dyes were measured using an elemental analyzer made by Carlo Erba, Italy. The IR spectra of all the dyes were scanned in KBr pellets on a Perkin-Elmer 983 spectrophotometer. The visible spectra of all dyes were recorded on a Carl Zeiss uv/vis spectrophotometer. All polymeric dyes were characterized by intrinsic viscosity measurements in DMF at 35 ± 0.05°C with an Ubbelohde viscometer. The molecular weight determination was made in dioxane at 50°C using a vapor pressure osmometer (Hewlett-Packard model 3028). Thermogravimetric analysis (TGA) of all the polymeric dyes was carried out on a DuPont model 951 thermogravimetric analyzer in air at a heating rate of 10°C/min. The fastness to light, sublimation, perspiration, and organic solvents was assessed in accordance with BS:1006-1978. The wash fastness test was carried out in accordance with IS:765-1979. The details of various fastness tests are given in the literature[31]. The percentage dyebath exhaustion and fixation of the dyes on fiber were also calculated according to the standard method described in the literature[38].

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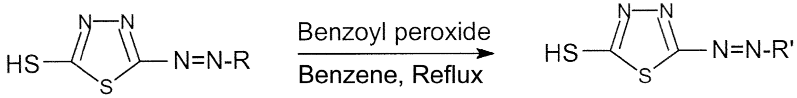

5a-h

SCHEME 2 Synthetic scheme for polymeric dyes 5a–h.

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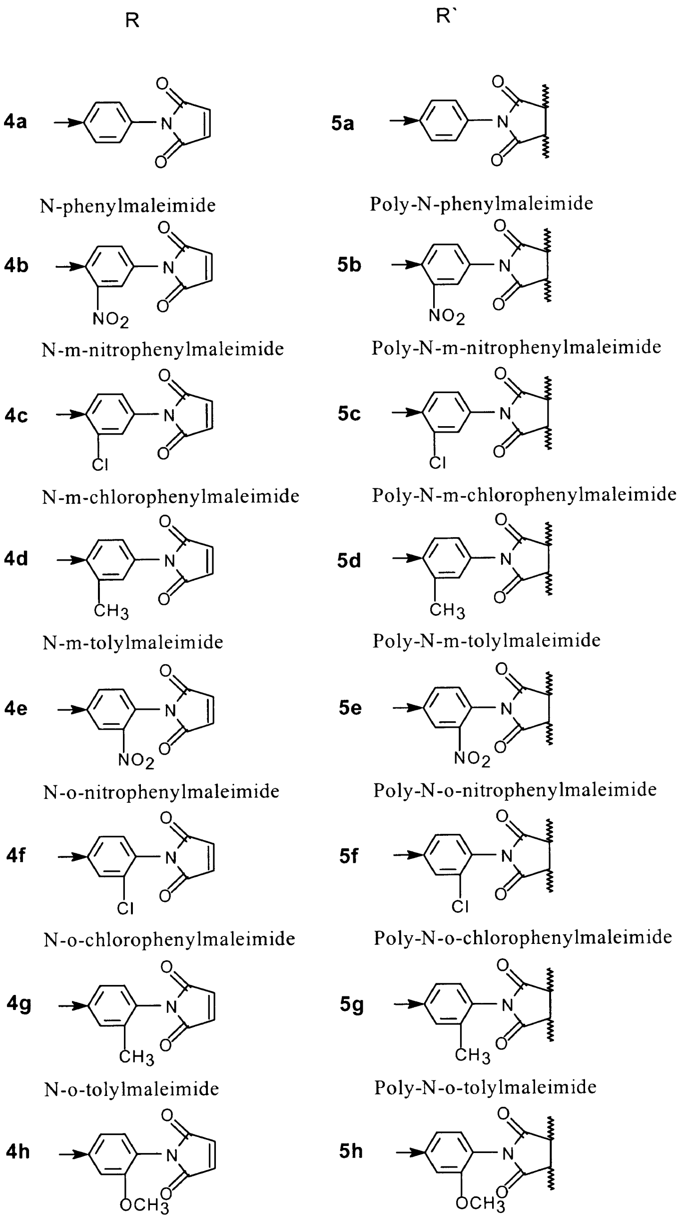

4a N-phenylmaleimide
5a Poly-N-phenylmaleimide
4b N-m-nitrophenylmaleimide
5b Poly-N-m-nitrophenylmaleimide
4c N-m-chlorophenylmaleimide
5c Poly-N-m-chlorophenylmaleimide
4d N-m-tolylmaleimide
5d Poly-N-m-tolylmaleimide
4e N-o-nitrophenylmaleimide
5e Poly-N-o-nitrophenylmaleimide
4f N-o-chlorophenylmaleimide
5f Poly-N-o-chlorophenylmaleimide
4g N-o-tolylmaleimide
5g Poly-N-o-tolylmaleimide
4h N-o-methoxyphenylmaleimide
5h Poly-N-o-methoxyphenylmaleimide

SCHEME 2 Continued.

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TABLE II Characteristic Parameters of Polymeric Dyes 5a–h

				Absorption maxima (λ_{max}) (nm)			Elemental analysis (%) Found (Calcd.)					
Dye no.	Yield (%)	Mol. wt.	Viscosity ($\eta\, dL/g$)	λ_{max} in DMF	λ_{max} in conc. H_2SO_4	log ε	C	H	N	R_f value	Exhaustion (%)	Fixation (%)
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	78	74
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	70	66
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	81	76
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	74	71
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	72	65
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	81	71
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	76	70

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DYEING METHOD

Dyeing Method for Monomeric Dyes

A convenient laboratory method for dyeing cellulose triacetate is to employ high temperature (90–135°C) and high pressure (24–30 psi), using a laboratory dyeing machine with a glycerin bath. A paste of finely powdered 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 min. 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 cellulose triacetate 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 90°C (for cellulose triacetate fiber) at the rate of 2°C/min. The dyeing was continued for 1 h, under pressure. After cooling for 1 h, the beaker was removed from the bath and washed with water. The pattern was thoroughly washed with hot water at 50°C, then with cold water, and finally dried at room temperature.

Dyeing Method of Polymeric Dyes

The dyeing method for 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 h, and then this paste was poured into an 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 4.5–5.0 using acetic acid. The dyeing was continued for 75 min under pressure. After cooling for 1 h, the fiber pattern was removed and washed with hot water 50°C, then with cold water, and finally dried at room temperature.

RESULTS AND DISCUSSION

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. A weak amine, such as compound 1, required the use of nitrosylsulphuric acid, and it was diazotized

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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 it 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.

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 (TLC). Thus, when unreacted diazo component no longer persisted on TLC, 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 TLC using ethyl acetate-benzene (1:4) as the solvent system. When adsorbed onto silica chromatography plates, each dye produced a single color spot. All the recrystallized dyes exhibited well-defined melting points 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 point on a number of factors (e.g., polarity, geometry, size, and molecular interactions).

The IR spectra of the dyes reveal 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 that appear at 3085–3200 and 820–832 cm^{-1} (out-of-plane-deformation vibrations). The band at 675 cm^{-1} is an out-of-plane-deformation vibration characteristic 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 625–675 cm^{-1} can be attributed to an in-plane-deformation vibration of C=O and that at 575–585 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 skeletal C-C bond appears at 1575 cm^{-1}, and the band at 1580–1585 cm^{-1} is due to -N=N- stretching vibration. The strong characteristic bands at 600–660 cm^{-1} and 675–700 cm^{-1} are due to –S-H stretching vibrations of the mercapto group, and 1070 cm^{-1} is due to -C-N stretching. The band around 1480–1530 cm^{-1} is due to an ester group. The bands at 2850 cm^{-1}, 700–640 cm^{-1}, and 1390–1450 cm^{-1} are due to C-H bending vibrations of -OCH_3, C-Cl, and C-CH_3 stretching vibration, respectively. The band at 1320–1360 cm^{-1} is due to symmetric stretching of the –NO_2 group.

The data of intrinsic viscosities and the number average molecular weights of the polymeric dyes are given in Table II. The data for the viscosity measurement of the polymeric dyes ranged from 0.015 to 0.092 dL g^{-1}, 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 the low polymerization tendency.

Thermogravimetric investigations were carried out for the polymeric dyes in the range from 25°C to 650°C, at a heating rate of 10°C/min in air atmosphere. Typical TGA curves for the selected polymeric dyes 5a, 5c, 5d, and 5e 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 and the temperature for a 10% weight loss T_{10} were calculated. 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

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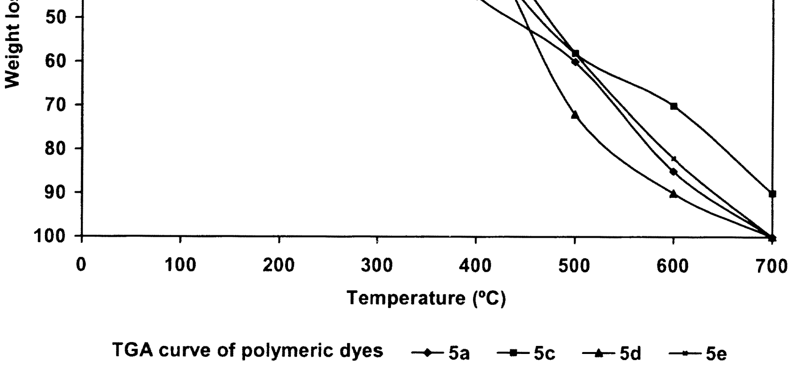

FIGURE 1 TGA curves of polymeric dyes 5a, 5c, 5d, and 5e.

and T_{10}, the higher will be the thermal stability[39]. All the polymeric dyes have good thermal stability and degrade in a single step.

All the disperse dyes were applied at 2% depth on cellulose triacetate fiber. No problems were encountered in preparing satisfactory dispersions when the monomeric dyes were milling with the dispersing agent. Polymeric dyes were more resistant to milling than the monomeric dyes owing to the nature of their crystals; however, they give satisfactory dispersion when they were ground in a ball mill using DMF and Dodamol. The dispersing agent has dual functions: it facilitates the breakdown of aggregated dye particles during milling and acts as a stabilizing 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 leveling and, in particular, prevents surface deposition of the dye, which may result in poor fastness to light. Leveling 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 to achieve complete uniformity at the temperature of the material. Therefore, it is essential that the dispersing agent acts as a retarder.

All the fastness properties shown in Tables III and IV 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 also 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 its concentration

TABLE III Dyeing Properties of Monomeric Dyes 4a–h

		Fastness to				
				Perspiration		
Dyes no.	Shade on cellulose triacetate	Light	Washing	Acid	Alkaline	Sublimation
4a	Brown	3	4	4–5	4–5	4–5
4b	Reddish brown	3–2	3–4	4	4–5	4
4c	Dark brown	3	4–5	4–5	4–5	4–5
4d	Brown	3	4	4–5	4–5	4–5
4e	Reddish yellow	3	4–5	4	5	4
4f	Brown	3–2	4–5	5	4–5	4–5
4g	Bronze red	3–2	5–4	4	5–4	5–4
4h	Brown	4	4	4–5	4–5	4

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TABLE IV Dyeing Properties of Polymeric Dyes 5a–h

		Fastness to				
				Perspiration		
Dyes no.	Shade on cellulose triacetate	Light	Washing	Acid	Alkaline	Sublimation
5a	Reddish brown	8	5	5	5	5
5b	Red	8	5	5	5	5
5c	Brown	8	5	5	5	5
5d	Reddish brown	8	5	5	5	5
5e	Yellowish brown	8	5	5	5	5
5f	Brown	8	5	5	5	5
5g	Brown	8	5	5	5	5
5h	Reddish yellow	8	5	5	5	5

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in the substrate is partly a function of particle size (which varies with changes in concentration). In any system where particles are formed from a liquid phase, they appear in a range of random sizes. Moreover, their average size increases with concentration. Strictly 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, one needs to appreciate that there is no absolute value for the light fastness of a dye. The value obtained for a given colorant 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 the 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 solubilizing groups and therefore have a significant vapor pressure at the temperatures encountered during processing. It has been observed that the vapor pressure of a dye is inversely proportional to its molecular mass and its polarity[40]. Some general trend might, therefore, be expected between the sublimation fastness of disperse dyes and their molecular weight and/or the presence of polar groups on the dye structures. In order to obtain a satisfactory combination of light and sublimation fastness, a 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 of light fastness may be achieved by increasing the molar mass, which reduces the volatility of the dye and thus lowers the

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dye sublimation. The introduction of polar groups can adversely affect the dyeing properties of a dye. The polymeric dyes were slightly less soluble in cellulose triacetate fiber compared to the monomeric dyes, so that saturation was reached at the application level, slightly restricting the depth of dyeing. The wash fastness rating of the cellulose triacetate dyeing was primarily influenced by depth of the shade. The lower depths of the cellulose triacetate dyeing means that staining was low, which did not lose color. Thus, the low depths of shade restricted the occurrence of any staining. Monomeric dyes were much more soluble in cellulose triacetate, 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 III) range from good to excellent, while dyed fiber with corresponding polymeric dyes (Table IV) 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 a UV absorber[41]. Table V indicates the result of the bleeding test. The fiber dyed 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 may react with cellulose triacetate fiber and are easily soluble under the dyeing condi-

TABLE V Bleeding Properties of Polymeric Dyes 5a–h

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

tion. Thus polymeric dyes applied to cellulose triacetate fiber is more resistant to removal by solvent extraction.

Absorption maxima of dyes recorded in DMF solutions and concentrated sulphuric acid are shown in Tables I and II. As far as absorption maxima are concerned, λ_{max} values are directly proportional to the electron-donating power of the substituents in the N-arylmaleimide ring system. The dyes listed in Tables I and II are reddish-brown to deep brown. The logarithms of molar extinction coefficients (log ε) of the dyes range from 3.11 to 4.71, indicating high intensity of absorption. The introduction of electron-donating or electron-attracting groups at suitable positions on the coupler ring affects the absorption characteristics of the dyes.

Table I shows that the exhaustion and fixation of the monomeric dyes on cellulose triacetate fiber are higher than those of their corresponding polymeric dyes (Table II). The polymeric dyes have larger molecular size and tend to have more interactions with the fiber. Cellulose triacetate 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 color shade with slightly lower depths. The uptake of disperse dyes by cellulose triacetate fiber takes place via progressive adsorption of the low 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 favor 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.

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CONCLUSION

The disperse dyes containing thiadiazole moiety have been prepared from various N-arylmaleimides as the coupling components. 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 color shades and excellent affinity and intensity of color. The polymeric dyes have low molecular weight. The utilization of these dyes was possible because of certain essential dye properties, such as fast leveling 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 the molecular size of the dye molecule via polymerization yielded improvements of the fastness properties. The polymeric dyes on cellulose triacetate fiber have a relatively low depth shade with excellent fastness and staining ratings.

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