

Studies of Novel Monomeric and Polymeric Azo Disperse Dyes

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ABSTRACT: A series of polymeric dyes were synthesized by free-radical addition polymerization of monomeric dyes that were derived from diazotized 2-amino-3,5-bis-(ethoxycarbonyl)-4-methylthiophene by coupling with various *N*-arylmaleimides. All the polymeric dyes were characterized by elemental analysis, IR and visible spectroscopy, viscometry, and TGA. Color and dyeability of the polymeric dyes are discussed by comparing them with those of the corresponding monomeric dyes. All the dyes have been found to give various color shades with good to very good depth and levelness on the fiber. The dyeing of the monomeric dyes shows good fastness to light and very good to excellent fastness to washing, perspiration, sublimation, and solvents. The corresponding polymeric dyes show excellent fastness properties. The percentage dyebath exhaustion and fixation on the fiber have been found to be good to very good (60–90%). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1380–1389, 2002; DOI 10.1002/app.10276

Key words: polymeric dyes; monomeric dyes; 2-amino-3,5-bis (ethoxycarbonyl)-4-methylthiophene; cellulose triacetate; fastness

INTRODUCTION

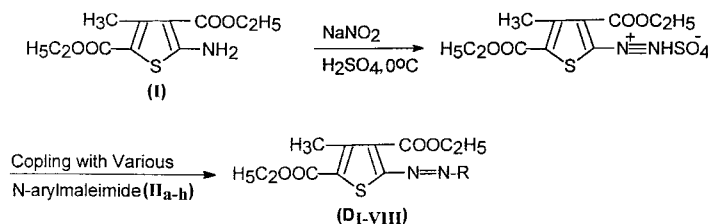
In the last three decades, innovations in azo dye chemistry based on heterocyclic systems have been made as a result of intensive studies stimulated by the mounting need for bright blue dyes. Most heteroarylazo dyes of technical interest for application to textiles are derived from diazo components consisting of five-membered rings containing one sulfur heteroatom and to which a diazotisable amino group is directly attached. Systems of this kind are capable of providing red to blue disperse dyes that meet the rigorous technical and economic requirements demanded of them by both manufacturer and user.

Kuhn disclosed the first example of polymeric colorants that fulfill the required performance requirements in 1964.^{1,2} These large, highly water-soluble molecules could not penetrate the fiber surface and could readily wash away during normal aqueous dyeing and finishing. The motivation for development of this exciting new class of materials is to overcome the deficiencies of both dyes and pigments in particular applications.

Polymeric colorants offer the advantage of allowing a range of physical properties, such as solubility, absorption, migration, and viscosity, that are tunable. They do not sublime, are non-abrasive, and generally have low toxicity. The range of products possible offered by the joining of the fields of polymer chemistry and color chemistry is virtually inexhaustible. New examples frequent many journals of chemical literature that summarize the area.^{2–7} Guthrie covered the liter-

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Scheme 1 Synthesis of monomeric dyes.

ature up to 1990 with an emphasis on color within the context of practical applications. He accurately described these materials.^{8,9}

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. 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. Thus, polymeric dyes are useful polymers or oligomers as well as useful dyes of unique importance due to their tinctorial strength.^{10,11} Their utilization has been possible because of certain essential dye properties such as fast leveling on the 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 number of researchers have reported the use of various *N*-arylmaleimides as coupling components to prepare polymeric azo disperse dyes for nylon, cellulose triacetate and polyester,^{12–15} silk and wool fibers,^{16,17} and UV stabilization.¹⁸ Considerable advances have been progressively made in the chemistry and technology of this class of dyes, so that not only polyamide and polyester but other types of fiber could also be dyed by a similar class of dyes. The present authors carried out work in this direction.^{13–15,19–22} The present article comprises the synthesis of monomeric dyes by coupling with various *N*-arylmaleimides with diazotized 2-amino-3,5-bis(ethoxycarbonyl)-4-methylthiophene. The resulting monomeric dyes were polymerized by free-radical addition polymerization and their dyeing performance on cellulose triacetate fiber were assessed. The entire research work is summarized in Schemes 1 and 2.

EXPERIMENTAL

Materials

All the chemicals used were of commercial grade. They were further purified by standard methods.²³ 2-Amino-3,5-bis(ethoxycarbonyl)-4-methylthiophene (**I**) was prepared by the process reported in the literature.²⁴ The various *N*-arylmaleimides (**II_{a-h}**) were prepared by following the method described in the literature.²⁵

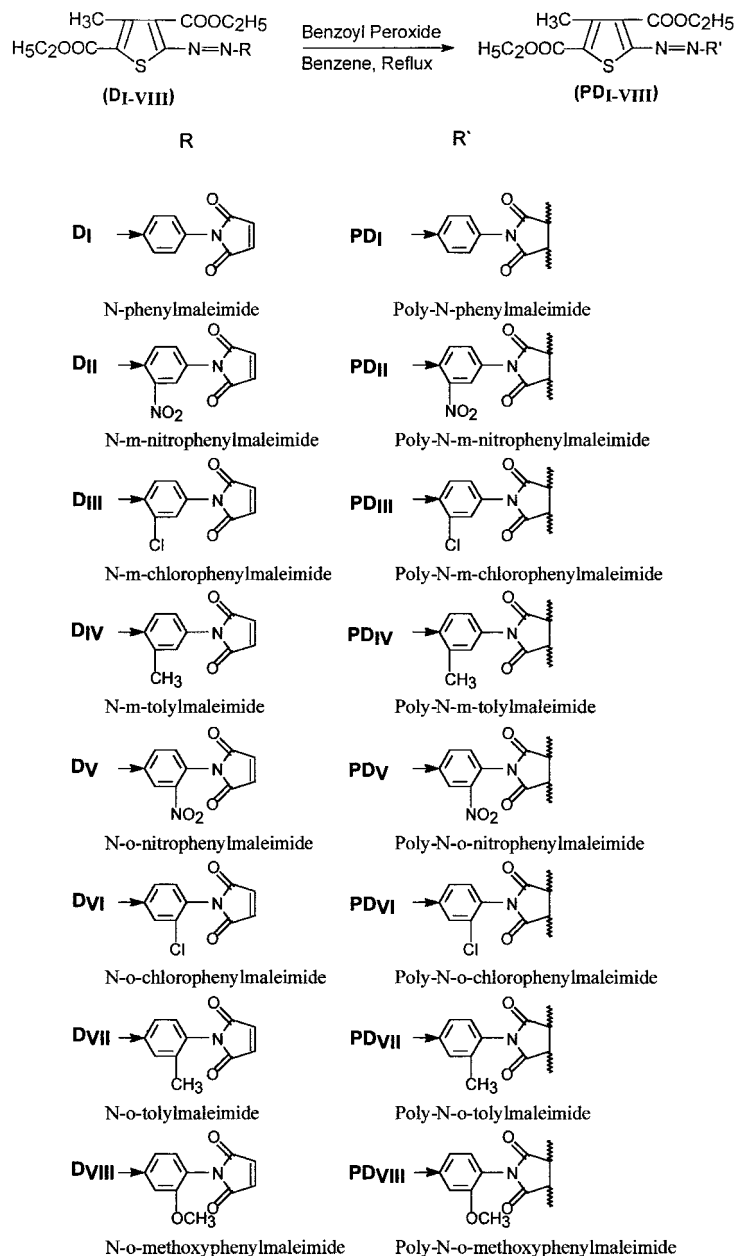
Synthesis of Monomeric Dye (**D_{I-VIII}**)

2-(*p*-*N*-Arylmaleimide)-azo-3,5-bis(ethoxycarbonyl)-4-methylthiophene (**D_{I-VIII}**)

These dyes were prepared by diazotization of 2-amino-3,5-bis(ethoxycarbonyl)-4-methylthiophene (**I**) and coupled with various *N*-arylmaleimides (**II_{a-h}**). A typical synthesis was as described below. The whole process for the synthesis of the monomeric dyes (**D_{I-VIII}**) is drawn in Scheme 1. The characterization data of the monomeric dyes (**D_{I-VIII}**) are given in Table I.

Dry sodium nitrite (1.38 g, 0.02 mol) was slowly added over a period of 30 min with stirring to concentrated sulfuric acid (1.6 g) and heated on a water bath to allow the temperature to increase to 65°C. The solution was then cooled to 5°C and a mixture (20 mL) of acetic acid–propionic acid (17 : 3) was added dropwise with stirring, allowing the temperature to increase to 15°C. The reaction mixture was then cooled to 0–5°C. 2-Amino-3,5-bis(ethoxycarbonyl)-4-methylthiophene (**I**) (5.14 g, 0.02 mol) was added portionwise and stirring was continued at this temperature for 2 h. The excess nitrous acid (the presence tested by starch–iodide paper) was decomposed with the required amount of urea. The clear diazonium salt solution thus obtained was used immediately in the coupling reaction (see Scheme 1).

N-Arylmaleimide compounds (0.02 mol) were dissolved in acetic acid (10 mL), then cooled in an ice bath at 0°C. The diazonium solution previ-



Scheme 2 Synthesis of polymeric dyes.

ously prepared was added dropwise over 30 min with vigorous stirring. The mixture was stirred for further 2 h at 0–5°C; then, the sodium acetate solution (10% w/w) was dropped in slowly until the pH became 4–5. The product was then filtered off, washed with warm and cold water until acid-free, and dried at 50°C in an oven. It was crystallized from a minimum amount of DMF.

Synthesis of Polymeric Dye (PD_{I-VIII})

The synthesis of the polymeric dyes (PD_{I-VIII}) were carried out by free-radical addition polymer-

ization of the monomeric dyes (D_{I-VIII}) with benzoyl peroxide as an initiator in dry benzene. A typical synthesis was described as below. The whole process for synthesis is drawn in Scheme 2. The characterization data of the polymeric dyes (PD_{I-VIII}) are given in Table II.

A cleaned dry three-necked flask equipped with a mechanical stirrer (2000 rpm/min) was charged with a mixture of 2-(*p*-*N*-arylmaleimide)-azo-3,5-bis(ethoxycarbonyl)-4-methylthiophene (D_{I-VIII}) (0.02 mol), dry benzene (50 mL), and benzoyl peroxide (0.002 g). The reaction mixture

Table I Characteristic Parameters of Monomeric Dyes

Monomeric Dye	Yield (%)	Mp ^a (°C)	λ_{\max}^b (in nm) (log ϵ)	Molecular Formula	Mol. Wt	Elemental Analysis			% Exhaustion	% Fixation
						% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)		
D_I	76	107	700 (4.25)	C ₂₁ H ₁₉ N ₃ O ₆ S	441	57.00 (57.14)	4.10 (4.30)	9.40 (9.52)	81	78
D_{II}	79	120	650 (3.91)	C ₂₁ H ₁₈ N ₄ O ₈ S	486	51.78 (51.85)	3.65 (3.70)	11.40 (11.52)	76	72
D_{III}	82	103	550 (3.93)	C ₂₁ H ₁₈ N ₃ O ₆ SCl	475.5	52.80 (52.94)	3.70 (3.78)	8.70 (8.82)	69	65
D_{IV}	70	121	740 (4.42)	C ₂₂ H ₂₁ N ₃ O ₆ S	455	57.52 (58.02)	4.52 (4.61)	9.10 (9.23)	68	63
D_V	77	101	565 (4.14)	C ₂₁ H ₁₈ N ₄ O ₈ S	486	51.75 (51.85)	3.60 (3.70)	11.40 (11.52)	87	81
D_{VI}	72	139	555 (3.93)	C ₂₁ H ₁₈ N ₃ O ₆ SCl	475.5	52.80 (52.94)	3.65 (3.78)	8.70 (8.82)	75	72
D_{VII}	80	126	575 (4.11)	C ₂₂ H ₂₁ N ₃ O ₆ S	455	57.59 (58.02)	4.50 (4.61)	9.10 (9.23)	79	74
D_{VIII}	75	110	570 (3.53)	C ₂₂ H ₂₁ N ₃ O ₇ S	471	55.80 (56.05)	4.30 (4.45)	8.80 (8.91)	70	67

^a Melting points were carried out by the open capillary method and are uncorrected.

^b Determined in DMF.

Table II Characterization Data and Physical Properties of Polymeric Dyes

Polymeric Dye	Yield (%)	Mol wt ^a	Viscosity ^b (η) dL/g	λ_{\max} (in nm) (log ϵ)	Elemental Analysis			% Exhaustion	% Fixation
					% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)		
PD_I	71	2.4×10^3	0.05	695 (4.82)	56.42 (56.88)	4.05 (4.28)	9.35 (9.48)	72	70
PD_{II}	65	3.3×10^3	0.018	640 (4.66)	51.19 (51.63)	3.49 (3.68)	11.00 (11.47)	73	70
PD_{III}	68	3.5×10^3	0.085	540 (4.33)	52.20 (52.77)	3.46 (3.76)	8.62 (8.76)	65	61
PD_{IV}	74	3.2×10^3	0.032	725 (4.43)	57.30 (57.76)	4.40 (4.59)	9.00 (9.20)	64	60
PD_V	72	4.2×10^3	0.057	560 (4.33)	51.40 (51.63)	3.51 (3.68)	11.40 (11.45)	80	73
PD_{VI}	60	3.8×10^3	0.030	540 (4.17)	52.41 (52.71)	3.48 (3.76)	8.62 (8.76)	70	63
PD_{VII}	70	4.1×10^3	0.086	470 (4.52)	57.49 (57.76)	4.40 (4.59)	9.05 (9.20)	72	68
PD_{VIII}	64	2.5×10^3	0.042	545 (4.13)	55.59 (55.81)	4.21 (4.43)	8.70 (8.85)	67	62

^a Molecular weight by VPO measurement in dioxane.

^b Viscosity in DMF.

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 at 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 estimated 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 Carl Zeiss UV/vis Specord spectrophotometer. All the polymeric dyes were characterized by an 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 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 $10^\circ\text{C min}^{-1}$. The fastness to light, sublimation, perspiration, and organic solvents was assessed in accordance with BS: 1006-1978. The wash fastness test was in accordance with IS:765-1979. Brief details of various fastness tests are mentioned in the literature.¹⁵ The percentage dye bath exhaustion and fixation of the dyes on the fiber were calculated according to the standard method.²⁶

DYEING METHOD

Dyeing Method for Monomeric Dyes

The dyeing of the cellulose triacetate fiber was carried out according to method described below. Dyeing at a 90–135°C temperature and high pressure (24–30 psi) is a convenient method for dyeing cellulose triacetate fiber in the laboratory. A laboratory-model glycerin bath high-temperature beaker dyeing machine was used. A paste of finely powdered dye (40 mg) was prepared with a dispersing agent, Dodamol (80 mg), a 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. The previously mentioned 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 was firmly tightened. The rotatory carrier was then allowed to rotate in the glycerin bath and the temperature was increased to 90°C for the cellulose triacetate fiber at the rate of 2°C min^{-1} . 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 dyed pattern was thoroughly washed with hot water at 50°C and then with cold water and dried at room temperature.

Dyeing Method of Polymeric Dyes

The dyeing method of polymeric dyes is little different from the above dyeing method. The finely powdered polymeric dye (40 mg) was intimately mixed with a suitable dispersing agent, Dodamol (30 mg), and a wetting agent, Tween-80 (20 mg), and DMF (1 mL) in a ball mill for 1 h. This paste was then poured into an aqueous solution of a dispersing agent, Dodamol (20 mg/99 mL). This provides a good dispersion quality. The pH of the resulting disperse solution was adjusted to pH 4.5–5 using acetic acid. The dyeing of cellulose triacetate fiber was carried out at 95°C. The dyeing was continued for 75 min under pressure. After cooling for 1 h, the dyed pattern was removed and washed with hot water at 50°C and then with cold water and dried at room temperature.

RESULTS AND DISCUSSION

The typical IR spectra of selected dyes, **D_{III}**, **D_{IV}**, **PD_{III}**, and **PD_{IV}**, are shown in Figure 1. 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 1620 cm^{-1} is due to the stretching vibration of C=C, which is conjugated with C=O. The unsaturation is also indicated by the C—H stretching vibrations, which appear at 3100 and 850 cm^{-1} and due to the out-of-plane-deformation vibration. The band at 680 cm^{-1} is an out-of-plane-deformation vibration characteristic of CH=CH. These bands disappear in polymeric dyes. The pair of bands at 1700 and 1721 cm^{-1} are due to the stretching vibration of C=O. The

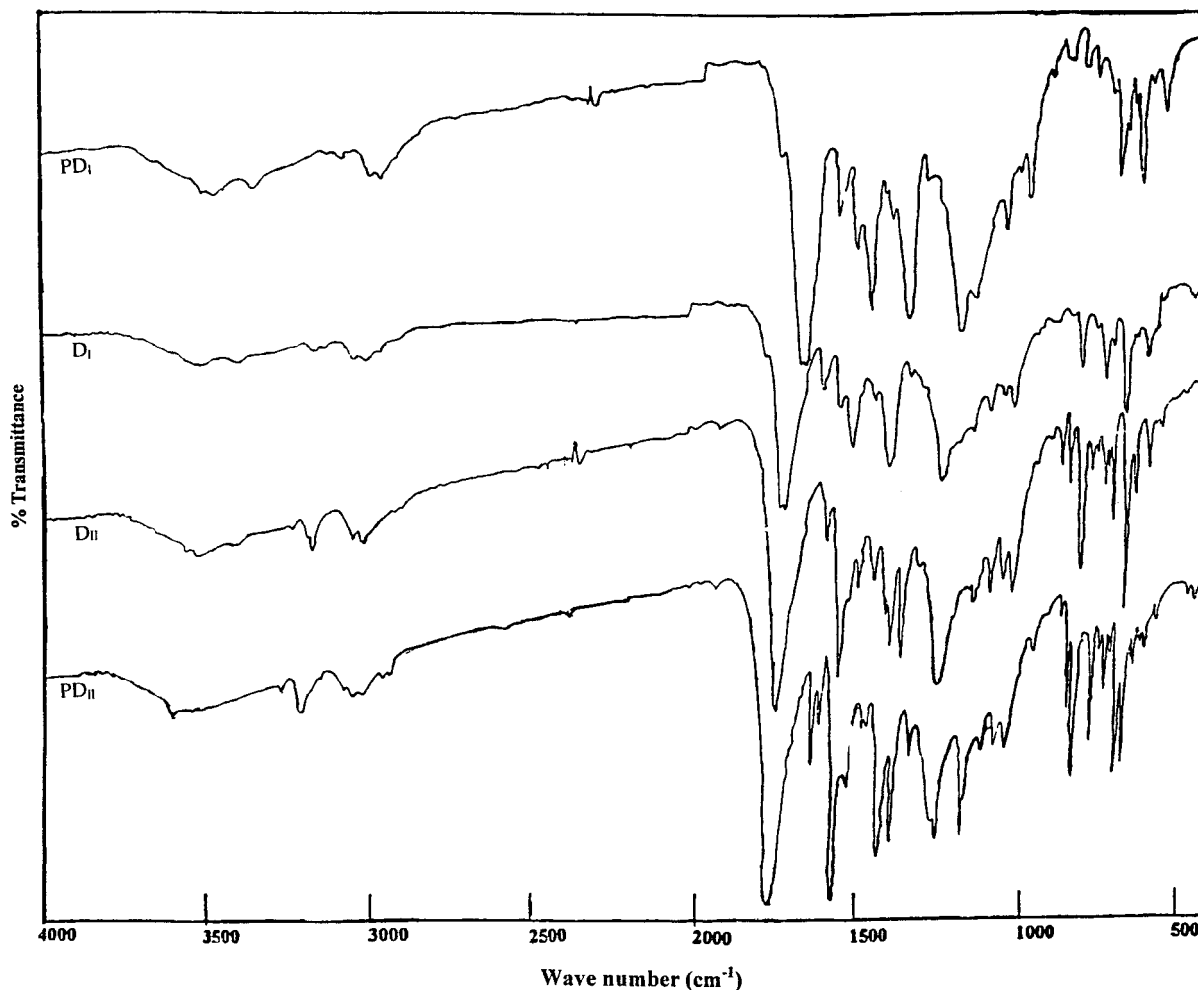


Figure 1 Infrared spectra of monomeric and polymeric dyes, D_{III} , D_{IV} , PD_{III} , and PD_{IV} .

band appearing at $630\text{--}680\text{ cm}^{-1}$ can be attributed to an in-plane-deformation vibration of $C=O$, and that at $570\text{--}580\text{ cm}^{-1}$, to an out-of-plane-deformation vibration of the $C=O$. The bands at 1350 and 1371 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 1570 cm^{-1} ; that at $1575\text{--}1585\text{ cm}^{-1}$ is due a $-N=N-$ stretching vibration. The band around $1480\text{--}1530\text{ cm}^{-1}$ is due to an ester group. The bands at 2850 , $640\text{--}700$, and $1390\text{--}1450\text{ cm}^{-1}$ are due to a $C-H$ bending vibration of $-OCH_3$, $C-Cl$, and $C-CH_3$ stretching vibrations, respectively. The band at $1320\text{--}1360\text{ cm}^{-1}$ is due to symmetric stretching of the $-NO_2$ group.

The results of the intrinsic viscosities and the number-average molecular weight of the poly-

meric dyes are given in Table II. The data of the viscosity measurement of the polymeric dyes ranged from 0.018 to 0.086 dL g^{-1} , which indicates that the polymeric dyes are of low molecular weight ranging from 2.4×10^3 to 4.2×10^3 . The appreciable steric hindrance of the double bond of the N -arylmaleimide ring is taken as being responsible for their low polymerization tendency.

Thermogravimetric Study

Thermogravimetric investigations were carried out for the polymeric dyes in the range from 25 to 650°C , at a heating rate of $10^\circ\text{C min}^{-1}$ in an air-oxidation decomposition. The typical TGA curves for the selected polymeric dyes, PD_{IV} , PD_V , PD_{VII} , and PD_{VIII} , are shown in Figure 2. To determine the thermal stability trend, thermo-

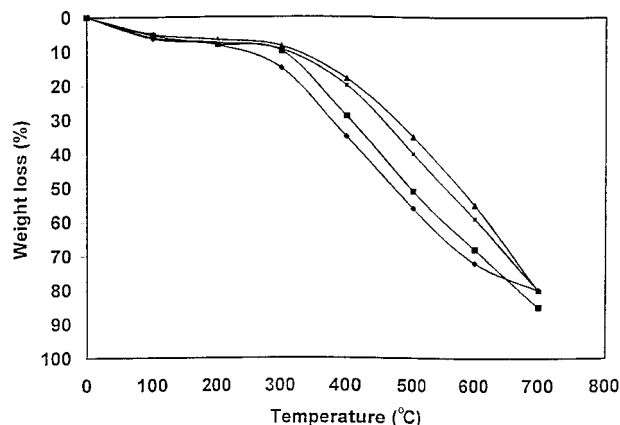


Figure 2 Thermogravimetric curves: (—◆—) PD_{IV} ; (—■—) PD_{V} ; (—▼—) PD_{VII} ; (—■—) PD_{VIII} .

gravimetric 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's²⁷ and Broi-do's²⁸ 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.²⁹ 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 235 to 300°C, and T_{max} ranged from 405 to 522°C. The values of IPDT and the overall activation energy E_a for the degradation process was in the range of 397–483°C and 11–28 kJ mol⁻¹, respectively (Table III). All the polymeric dyes have good thermal stability and degrade in a single step. The polymeric dye PD_{V} has better thermal stability compared to the other dyes.

Dyeing Properties

No problem was encountered in preparing satisfactory dispersions when the monomeric dyes were milled with the dispersing agent. Polymeric dyes were more resistance to milling than were the monomeric dyes owing to the nature of their crystals; however, they give satisfactory dispersion when they were ground in ball mill using DMF and Dodamol. The dispersing agents have a

dual function: They facilitate the breakdown of aggregated dye particles during milling and act as a stabilizing agent for the dispersion of the dye in the dye liquor. To ensure stability, the amount of the 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 results 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 of the temperature of the material. Therefore, the use of the dispersing agent acting as retarder is essential. All the fastness properties shown in Tables IV and V are interrelated since they depend, among other things, on the rate of diffusion of the dye in the fiber. This rate is a function of the geometry of the dye molecule, depending on the molecular weight. The concentration of dye in the fiber appeared to be the most influential factor in the fastness of the dyeing. For example, the variation of light fastness of the dyes with their concentration in the substrate is partly a function of their particle size.

In attempting to trace relationships between the chemical structure and light fastness, it is important to appreciate that there is no absolute value for the light fastness of a dye; the value obtained for given colorant in any fading test depends on many factors, the most important of which are the concentration and/or degree of aggregation of the dye within the fiber; the nature of the fiber in which it is dispersed; and the characteristics of the incident radiation and molecular structure. It is well known that both molecular mass and intermolecular interactions affect the

Table III TGA Parameters of Polymeric Dyes

Polymeric Dye	T_{10}	T_{max}	IPDT (°C)	E_a (kJ mol ⁻¹)
PD_{I}	235	450	337.8	21.37
PD_{II}	260	520	475.4	21.68
PD_{III}	275	498	460.8	21.68
PD_{IV}	275	425	482.9	21.03
PD_{V}	300	522	404.7	25.86
PD_{VI}	283	436	410.8	19.78
PD_{VII}	298	420	397.2	11.08
PD_{VIII}	275	405	420.6	27.71

Table IV Dyeing Properties of Monomeric Dyes

Monomeric Dyes	Shade on Cellulose Triacetate	Fastness to				
		Light	Washing	Perspiration		Sublimation
				Acid	Alkaline	
D_I	Violet	2-3	4-5	4-5	4-5	3-4
D_{II}	Brownish red	2-3	3-4	4-5	4-5	4-5
D_{III}	Reddish brown	2-3	4-5	4-5	4-5	4-5
D_{IV}	Reddish violet	2-3	5-4	4-5	4-5	4-5
D_V	Pinkish violet	2-3	5-4	4-5	5	4-5
D_{VI}	Reddish violet	2-3	4-5	5-4	4-5	4-5
D_{VII}	Reddish brown	2-3	5	5	5-4	4-5
D_{VIII}	Bronze red	2-3	4-5	5-4	4-5	5-4

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 temperature encountered in processing. It has been observed that the vapor pressure of a dye is inversely proportional to its molecular mass and its polarity.³⁰ Some general trend might, therefore, be expected between the sublimation fastness of disperse dyes and their molecular weight and/or the introduction of polar groups into the dye structures. To obtain a satisfactory combination of light and sublimation fastness, a judicious choice of substituents is required. To improve these fastness properties by choosing the proper substituents is very difficult. Thus, a dye of higher sublimation fastness can be achieved by increasing the molar mass, which reduces the volatility of the dyes 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 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 ratings of the cellulose triacetate dyeing was primarily influenced by the depth of the shade. The lower depths of the cellulose triacetate dyeing means that staining was low and color was not lost. Thus, low depths of a shade restricted the occurrence of any staining. Monomeric dyes were much more soluble in cellulose triacetate. This suggests that the higher solubility of these dyes allows heavier depths to be achieved. These dyes had inferior fastness relative to that shown by the polymeric dyes, presumably because of one or more of the factors

Table V Dyeing Properties of Polymeric Dyes

Polymeric Dye	Shade on Cellulose Triacetate	Fastness to				
		Light	Washing	Perspiration		Sublimation
				Acid	Alkaline	
PD_I	Reddish brown	8	5	5	5	5
PD_{II}	Red	8	5	5	5	5
PD_{III}	Purple	8	5	5	5	5
PD_{IV}	Brown	8	5	5	5	5
PD_V	Violet	8	5	5	5	5
PD_{VI}	Reddish violet	8	5	5	5	5
PD_{VII}	Reddish brown	8	5	5	5	5
PD_{VIII}	Maroon	8	5	5	5	5

Table VI Bleeding Properties of Polymeric Dyes

Polymeric Dye	Solvent System				
	Water	Ethanol	Toluene	<i>n</i> -Butanol-Xylene (1 : 9)	Cellosolve
PD _I	5	5	5	5-4	4-5
PD _{II}	5	5-4	4-5	4-5	5-4
PD _{III}	5	5-4	5-4	5	5
PD _{IV}	5	5	5-4	5	4
PD _V	5	5-4	5	5-4	4-5
PD _{VI}	5	5-4	5	4	4-5
PD _{VII}	5	5	5-4	5	4
PD _{VIII}	5	5-4	4-5	5-4	5

(e.g., a relatively small molecular mass, which facilitates diffusion out of the sample, higher substantivity for the fiber, as well as a higher initial concentration of the dye that provided a deep sample shade) could have been significant.

All the fastness properties of a dyed fiber of the monomeric dyes (Table IV) range from good to excellent, while dyed fiber of their corresponding polymeric dyes (Table V) shows excellent fastness properties. The improved fastness might be attributed to the highly conjugated system created on the *N*-arylmaleimide as a result of keto/enol tautomerism which may act as an UV absorber.³¹ Table VI indicates the result of the bleeding test. The dyed fiber of the polymeric dyes have 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 can be suggested that the polymeric dyes may react with the cellulose triacetate fiber and are easily soluble under the dyeing condition. Thus, polymeric dyes applied to cellulose triacetate fiber are more resistance to removal by solvent extraction, indicating that polymeric dyes are reactive to the fiber.

Exhaustion and Fixation Study

Table I shows that the exhaustion and fixation of the monomeric dyes on cellulose triacetate fiber is higher than those of their corresponding polymeric dyes (Table II). This may be due to a larger molecular size and, therefore, interaction can take place between the dye molecule and the fiber. Cellulose triacetate fiber is a more crystalline, hydrophobic, and highly regular molecular structure and, consequently, diffusion of the dye

within the fiber proceeds slowly under the given dyeing conditions. Hence, the rate of diffusion of the dye molecules into the fiber is lower, which affects the exhaustion value. The polymeric dyes exhaust smoothly onto the fiber when applied from a stable dispersion under the dyeing condition and provide a satisfactory color shade with a slightly lower depth. The uptake of disperse dyes by cellulose triacetate fiber takes place by progressive adsorption of the small concentration of the dye in a 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 the molecular size, geometry, and, in particular, polarity of the molecule. During the dyeing process, the fiber is in the glasslike state and inaccessible to aqueous solutions of the dye. When the transition temperature is reached, the fiber immediately becomes readily dyeable.

CONCLUSIONS

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

It can be concluded from the above studies that the improvement of the fastness properties with an increase in the molecular size of the dye molecule by a polymerization reaction has been shown. The dyeing from the polymeric colorants

on cellulose triacetate fiber had a relatively low depth shade with an excellent fastness and staining rating.

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