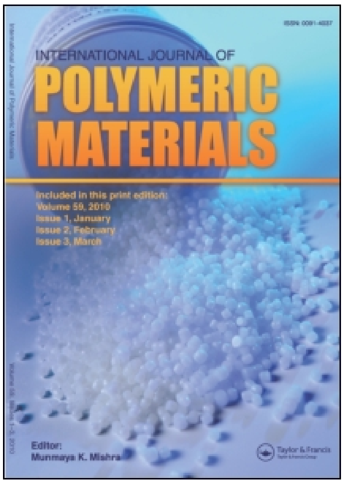

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Hari R. Maradiya[a]; Vithal S. Patel[b]
[a] V.P. and R.P.T.P. Science College, Sardar Patel University, Vallabh Vidyanagar, Gujarat State, India [b] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat State, India

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N-ARYLMALEIMIDE BASED MONOMERIC AND POLYMERIC DYES FOR CELLULOSE TRIACETATE FIBER

Hari R. Maradiya
V.P. and R.P.T.P. Science College, Sardar Patel University,
Vallabh Vidyanagar, Gujarat State, India

Vithal S. Patel
Department of Chemistry, Sardar Patel University,
Vallabh Vidyanagar, Gujarat State, India

A series of monomeric dyes has been prepared by diazotization of 2,6-dibromo-4-nitroaniline and coupled with various N-arylmaleimides. The monomeric dyes were characterized by elemental analysis and IR spectra. The polymeric dyes have been prepared by free radical polymerization of monomeric dyes. They were characterized by IR spectral studies, intrinsic viscosity, molecular weight by vapor pressure osmometry, thermogravimetry analysis and elemental analysis. The purity of all the dyes were checked by thin layer chromatography and they have also been applied on cellulose triacetate fiber as a disperse dye. All the dyes were found to give various color hues with good to very good depth and levelness on the fiber. The percentage dye bath exhaustion and fixation on fiber have been found to be good to very good. The 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, 2,6-dibromo-4-nitroaniline, disperse dyes, monomeric, polymeric, cellulose triacetate

INTRODUCTION

Before about 1955, cellulose acetate fiber was dyed with the classical disperse dyes, which have comparatively simple chemical structure and molecular weight of about 250–300. The 1950s also witnessed a growing

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Address correspondence to Hari R. Maradiya, V.P. and R.P.T.P. Science College, Sardar Patel University, Vallabh Vidyanagar, 388 120, Gujarat State, India. E-mail: mardiahari@usa.net

demand for dyes of improved washing fastness on acetate fiber. These products, which had to be specially developed, have more complex constitutions and substantially higher molecular weight than earlier disperse dyes.

Azo disperse dyes are by far the most important class of dyes, comprising over 50% of total world dyestuffs production. They have achieved this prominence for the several reasons like they are about twice the strength of anthraquinone dyes, the second most important class of dyes; they are usually easy to prepare in a multi-purpose chemical plant from cheap, readily available starting materials; they cover the whole shade range; and they have good fastness properties. The first two features make azo dyes cost effective against most dye classes, but particularly anthraquinone dyes, they tend to be duller in hue and generally can not equal the excellent light fastness of such dyes, especially in the blue hue area. However, dyestuff chemists have been making intensive efforts since 1970 to replace anthraquinone dyes in order to enhance the brilliancy of the tinctorially very strong azo dyes, using specific intermediates, largely from azobenzene derivatives, which are technically equivalent in certain respects, and therefore commercially interesting.

2,6-dibromo-4-nitroaniline enjoys a special status as the dyes obtained reach the level of anthraquinone dyes with respect to their general fastness properties and are extremely bright, their brilliant hues being comparable to those of the anthraquinone type. Furthermore, azo dyes of such benzonoid series have a high tinctorial strength, good levelness and heavy depths [1 – 3]. The major trend has been an attempt produce dyes of improved sublimation fastness and this was achieved either by incorporating a polar group or by simply increasing the molecular size. Increases in molecular weight are normally introduced through a coupling component, although more recently diazo components have increased in size [4].

The term polymeric colorant is useful because it can define textiles that are colored through covalent coupling with reactive dyes. In the broad sense, the term macromolecular colorants include intrinsically or structurally colored polymers, *i.e.*, possessing inherent properties [5], self-colored polymers [6, 7] polymeric dyes [8] and polymeric pigments [9]. Each of these terms is somewhat limited in its application.

A monomeric dye is a polymerizable dye that contains a group, normally polymerizable through an ethylenic type double bond in the dye molecule. Polymeric dyes may be defined through their applications which are markedly dependent on their relative high molar mass. As such, 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 as well as useful dyes due to their tinctorial power [8] and properties such as fast levelling on fiber, fastness to light and wet treatment, low sublimation

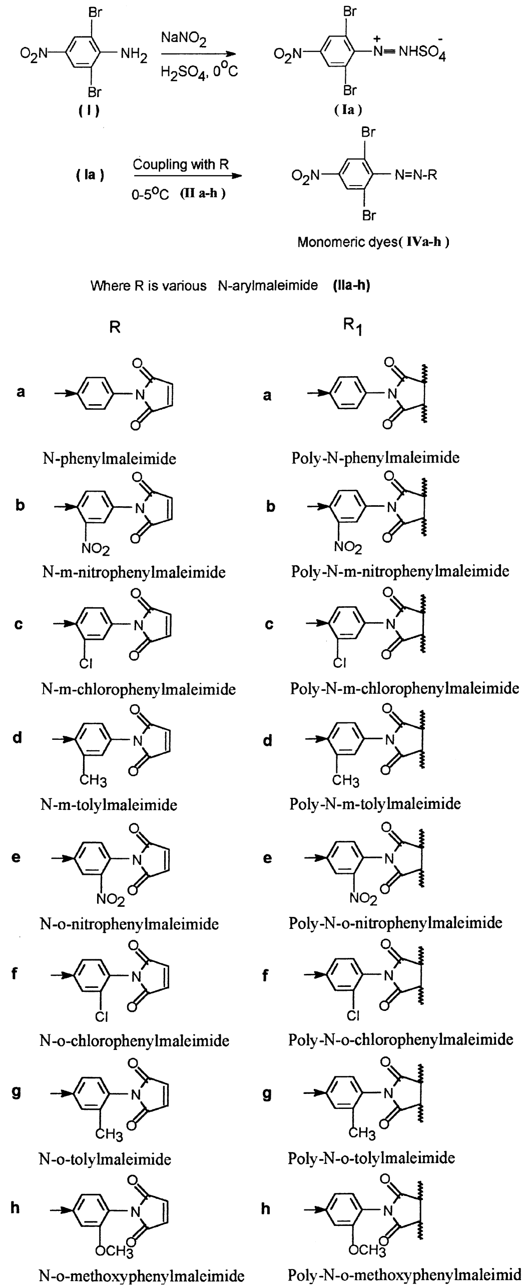

FIGURE 1 Synthesis of monomeric dyes (**IVa–h**).

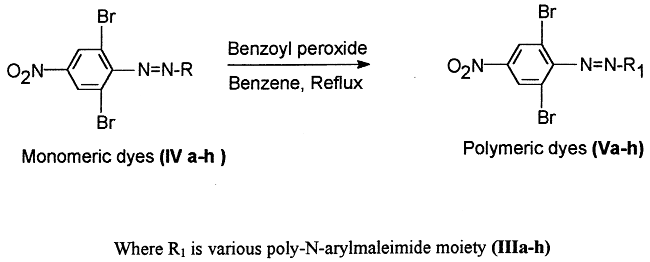

FIGURE 2 Synthesis of polymeric dyes (**Va–h**).

rate and very good thermal and chemical resistance. The color fastness of the coloured fiber is related to the chemical structure, molecular size of dye molecule and the physical characteristics of the fiber itself. Giles [10] given some very useful information on the relationship between dye structure, fiber structure and external conditions and behavior of the colored fiber upon exposure to light, heat, gaseous impurities and washing. Also, another important point is that most of the organic dyes are carcinogenic and more or less toxic. In order to improve the fastness properties as well as reduce the toxicity, attempts to increase the size of the dye molecule were made [11].

A literature survey reveals that only a few researchers have reported the use of various N-arylmaleimides as coupling components to prepare polymeric azo disperse dyes for nylon and polyester [12–15], silk and wool fibers [16, 17] and UV stabilization [18]. Considerable advance have been made in the chemistry and technology of these dyes so that not only polyamide and polyester but other types of fibers could be dyed by them. The present authors have carried out work in this direction [13–15]. In furthering this work [15], the present paper comprises the synthesis of monomeric dyes by coupling with various N-arylmaleimides with diazotized 2,6-dibromo-4-nitroaniline. The resulting monomeric dyes were polymerized by free radical addition polymerization and their dying performance on cellulose triacetate fiber have been assessed. The entire research work is summarized in Figures 1 and 2.

EXPERIMENT

Materials

All the chemicals used were of commercial grade. They were further purified by crystallization and distillation. 2,6-dibromo-4-nitroaniline (**I**) was prepared by a process reported in literature [19]. The various N-arylmaleimides (**IIa–h**) were prepared by following the literature [20].

TABLE 1 Characterization data, percentage exhaustion, and fixation of monomeric dyes (**IVa–h**) on cellulose triacetate fiber

	Coupling								*Element analysis, (%)*				
No.	*component*	*Yield*	*m.p.*[a]	*Molecular*	*Mol.*	*λmax*[b]		R_f	*Found (Calc.)*				
IV	(*R*)	(%)	(°*C*)	*formula*	*Wt.*	(*nm*)	*logε*	*Value*[c]	*C*	*H*	*N*	*Exhaustion* (%)	*Fixation* (%)
a	N-Phenylmaleimide	85	182	$C_{16}H_8N_4O_4Br_2$	479.8	410	3.81	0.92	39.62 (40.01)	1.20 (1.66)	11.42 (11.67)	86	82
b	N-*m*-Nitrophenylmaleimide	72	172	$C_{16}H_7N_5O_6Br_2$	524.8	425	3.86	0.96	35.80 (36.58)	1.00 (1.33)	12.69 (13.33)	79	76
c	N-*m*-Chlorophenylmaleimide	82	160	$C_{16}H_7N_4O_4ClBr_2$	514.3	415	3.79	0.90	36.49 (37.33)	1.10 (1.36)	10.60 (10.88)	83	81
d	N-*m*-Tolylmaleimide	79	178	$C_{17}H_{10}N_4O_4Br_2$	493.8	415	3.82	0.85	40.38 (41.31)	1.89 (2.02)	11.02 (11.34)	88	85
e	N-*o*-Nitrophenylmaleimide	75	192	$C_{16}H_7N_5O_6Br_2$	524.8	435	3.83	0.80	36.10 (36.58)	1.19 (1.33)	13.02 (13.33)	85	80
f	N-*o*-Chlorophenylmaleimide	85	203	$C_{16}H_7N_4O_4ClBr_2$	514.3	406	3.79	0.83	37.08 (37.33)	1.18 (1.36)	10.70 (10.88)	74	72
g	N-*o*-Tolylmaleimide	70	186	$C_{17}H_{10}N_4O_4Br_2$	493.8	426	3.69	0.87	41.01 (41.31)	1.89 (2.02)	11.08 (11.34)	86	81
h	N-*o*-Methoxyphenyl-Maleimide	72	168	$C_{17}H_{10}N_4O_5Br_2$	509.8	440	3.73	0.81	39.86 (40.01)	1.82 (1.96)	10.79 (10.98)	90	85

[a] Melting points carried out by open capillary method and are uncorrected.
[b] Determine in DMF.
[c] Measured in ethyl acetate–benzene (1 : 4).

TABLE 2 Characterization data, percentage exhaustion, and fixation of polymeric dyes (**Va–h**) on cellulose triacetate

No. V	*Various poly-N-arylmaleimide* (R_1)	*Yield* (%)	*Mol. Wt.*[a]	*Intrensic viscosity*[b] $[\eta]$, (dL/g)	λmax (nm)	$\log\varepsilon$	R_f *value*[c]	*Element analysis*, (%) *Found* (*Calc.*)			*Exhaustion* (%)	*Fixation* (%)
								C	*H*	*N*		
a	Poly-N-phenyl-maleimide	80	3.8×10^3	0.024	525	4.15	0.90	39.68 (39.85)	1.56 (1.66)	11.52 (11.62)	78	72
b	Poly-N-*m*-nitro-phenylmaleimide	85	3.6×10^3	0.019	520	4.40	0.92	36.31 (36.44)	1.22 (1.32)	13.10 (13.28)	72	69
c	Poly-N-*m*-chloro-phenylmaleimide	78	4.2×10^3	0.030	518	4.35	0.86	37.01 (37.18)	1.23 (1.35)	10.72 (10.84)	79	72
d	Poly-N-*m*-tolyl-maleimide	83	4.1×10^3	0.015	510	4.14	0.82	41.01 (41.14)	1.91 (2.01)	11.18 (11.29)	83	78
e	Poly-N-*o*-nitrophenyl-maleimide	75	4.2×10^3	0.032	525	4.61	0.79	36.31 (36.44)	1.24 (1.32)	13.16 (13.28)	82	76
f	Poly-N-*o*-chloro phenylmaleimide	72	3.9×10^3	0.022	530	4.22	0.80	37.00 (37.18)	1.24 (1.35)	10.71 (10.84)	72	68
g	Poly-N-*o*-tolyl-maleimide	88	4.3×10^3	0.017	515	4.10	0.82	41.00 (41.14)	1.93 (2.01)	11.20 (11.29)	83	75
h	Poly-N-*o*-methoxy-phenylmaleimide	82	3.1×10^3	0.011	540	4.46	0.76	39.72 (39.85)	1.82 (1.95)	10.81 (10.94)	86	80

[a] Determine in dioxane.

[b] Determine in DMF.

[c] Measure in ethyl acetate–benzene (1 : 4).

Synthesis of Monomeric Dye (IVa–h)

The synthesis of the monomeric dyes (**IVa–h**) were carried out by diazotization of 2,6-dibromo-4-nitroaniline (**I**) and coupling with varies N-arylmaleimide (**IIa–h**). A typical synthesis was described in literature [15]. The whole process for synthesis is drawn in Figure 1. The characterization data of **IVa–h** are given in Table 1.

Synthesis of Polymeric Dye (Va–h)

The synthesis of the polymeric dyes (**Va–h**) were carried out by free radical addition polymerization of monomeric dyes (**IVa–h**), using benzoyl peroxide as initiator in dry benzene. A typical synthesis was described in literature [15]. The whole process for synthesis is drawn in Figure 2. The characterization data of **Va–h** are given in Table 2.

MEASUREMENTS

The C, H and N contents of all the dyes were estimated using an element 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 intrinsic viscosity measurement in DMF at $35 \pm 0.050°C$ using a Ubbelohde viscometer. The molecular weight was determined in dioxane at 50°C using vapor pressure osmometer, Hewlett Packard model 3028. Thermogravimetric analysis (TGA) of all the polymeric dyes was carried out on a dupont model 950 thermogravimetric analyzer in air at a heating rate of $10\,\mathrm{K\,min^{-1}}$.

FASTNESS PROPERTIES

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 literature [15].

EXHAUSTION AND FIXATION STUDY

The percentage dye bath exhaustion and fixation of the dyes on fiber were calculated according to a standard method [21].

DYING METHOD

The dying of the cellulose triacetate fiber was carried out according to a method describe in the literature [15].

RESULTS AND DISCUSSION

Figures 1 and 2 are representative of the synthesis of monomeric and polymeric dyes, respectively.

Typical IR spectra of dyes **IVc**, **IVd**, **Vc**, and **Vd** are shown in Figure 3. They reveal that the 1,2-ethylenic bond of maleimide ring is identified by the band at 1620 cm^{-1} which is due to the stretching vibration of the C=C conjugated with C=O. The unsaturation is also indicated by the C—H stretching vibrations which appear at 3100 and 850 cm^{-1}. The band at 680 cm^{-1} is an out-plane – deformation vibration characteristics of CH=CH. These bands disappear in polymeric dyes. The pair of bands at 1740 and 1760 cm^{-1} are due to the stretching vibration of C=O. The band appearing at 635 cm^{-1} can be attributed to an in-plane-deformation vibration of the C=O and at 550 cm^{-1} to an out-plane-deformation vibration of the C=O. The bands at 1380 and 1350 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 1510 cm^{-1} is due —N=N— stretching vibration. The bands at 2850 cm^{-1}, 640 – 690 cm^{-1} and 1390 – 1450 cm^{-1} are due to C—H bending vibration 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 —N_2 group.

The data of intrinsic viscosity and the molecular weight of the polymeric dyes are given in Table 2. The data indicate that the polymeric dyes are of low molecular weight ranging from 3.1×10^3 to 4.3×10^3. The appreciable steric hindrance of the double bond of N-arylmaleimide ring is taken as responsible for their low polymerization tendency.

Thermogravimetric investigations were carried out in the range from 25°C to 650°C, at heating rate of 10 $Kmin^{-1}$ in an air. Typical thermograms of polymeric dyes **Vb**, **Vc**, **Vd** and **Ve** are shown in Figure 4. In order to determine the thermal stability trend, TGA parameters such as T_0 (temperature of the onset of decomposition) and T_{10} (temperature for a 10% weight loss) were calculated. The higher the values of T_0 and T_{10}, the higher will be the thermal stability of polymeric dyes [22]. All the polymeric dyes have good thermal stability and degrade in a single step. The polymeric dyes **Vc** and **Vd** have better thermal stability compared to other dyes.

Polymeric dyes were more resistance to milling than the monomeric dyes; however, they gives satisfactory dispersion when they were ground in ball mill using DMF and Dodamoi®. The polymeric dyes exhaust smoothly onto the fiber when applied from a stable dispersion under dying condition and provide satisfactory color hue with slightly lower depth.

All the disperse dyes were applied at 2% depth on cellulose triacetate fiber. The dyed fiber gave attractive color hue varying from reddish orange to deep brown with good levelness on the fiber (Tabs. 2 and 4). The

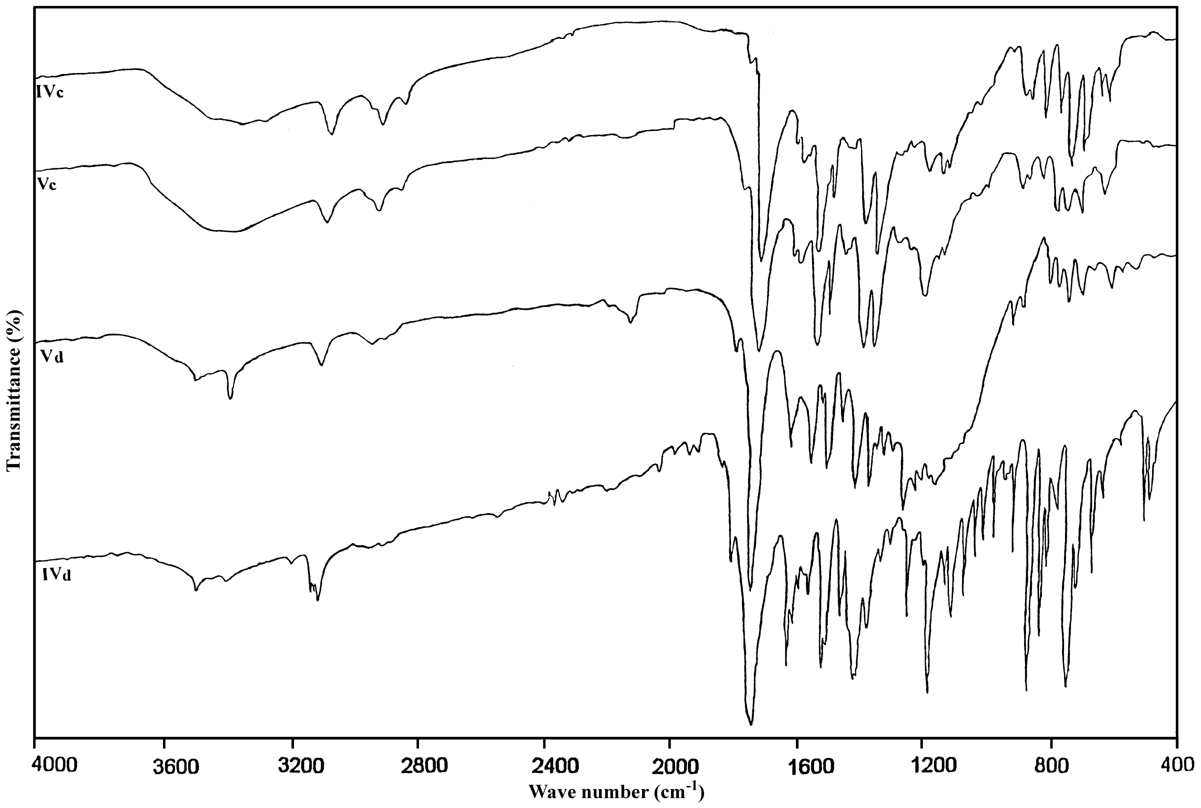

FIGURE 3 IR spectra of dye **IVc**, **IVd**, **Vc**, and **Vd**.

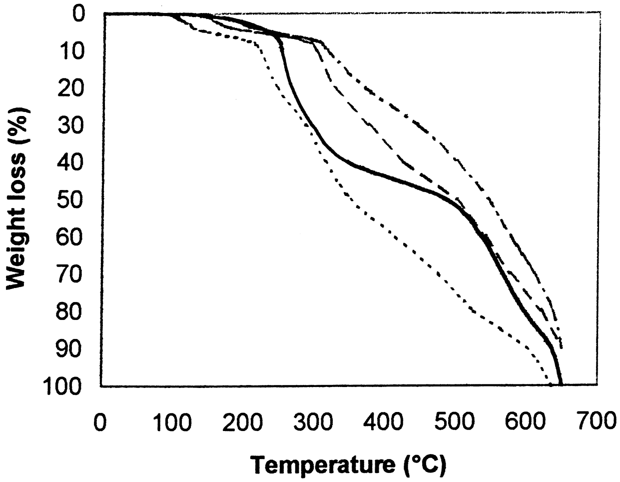

FIGURE 4 TG thermogram of polymeric dye. —5b– – –5c– – – -5d- - - - - -5e.

variation in the hues of dyed fiber is due to the nature and position of the various substituent present on the N-arylmaleimide ring.

Table 1 shows that the exhaustion and fixation of the monomeric dyes on cellulose triacetate fiber is higher than their corresponding polymeric dyes (Tab. 2) which may be due to larger molecular size. Hence the rate of diffusion of the dye molecules into the fiber is lower, which affect the exhaustion value.

A function of the dispersing agent is to promote levelling and, in particular, to prevent surface deposition of dye. All the fastness properties shown in Tables 3 and 4 are interrelated since they depend, among other

TABLE 3 Dying properties of monomeric dyes (**IVa–h**) on cellulose triacetate

		Fastness to				
				Perspiration fastness		
No. **IV**	*Hue on cellulose triacetate*	*Light fastness*	*Washing fastness*	*Acid*	*Alkaline*	*Sublimation fastness*
a	Orange	5–6	4–5	5–4	5–4	4
b	Yellowish orange	5–6	5	4–5	5–4	4
c	Yellow	6–5	5–4	5–4	4–5	5–4
d	Brown	6	4–5	4	4–5	4–5
e	Reddish pink	5–6	4–5	4	4–5	4–5
f	Deep orange	5–6	5	4–5	5–4	4
g	Deep brown	5	5–4	4–5	5	4–5
h	Reddish yellow	5–6	5–4	5–4	4–5	4

TABLE 4 Dying properties of polymeric dyes (**Va–h**) on cellulose triacetate

				Fastness to		
				Perspiration fastness		
No. **V**	*Hue on cellulose triacetate*	*Light fastness*	*Washing fastness*	*Acid*	*Alkaline*	*Sublimation fastness*
a	Brown	8	5	5	5	5
b	Deep red	8	5	5	5	5
c	Light yellow	8	5	5	5	5
d	Dark brown	8	5	5	5	5
e	Reddish pink	8	5	5	5	5
f	Deep brown	8	5	5	5	5
g	Reddish brown	8	5	5	5	5
h	Dark brown	8	5	5	5	5

things, on the rate of diffusion of dye in the fiber, This rate is a function of the geometry of the dye molecule, also depending on molecular weight.

It is well known that molecular mass and intermolecular interactions affect the sublimation fastness property; these factors also influence the volatility of the dyes. It has been observed that the vapor pressure of a dye is inversely proportional to its molecular mass. Thus a dye of high sublimation fastness can be achieved by increasing its molecular mass.

It is suggested that the polymeric dyes react with cellulose triacetate fiber and are easily soluble in the fiber under the dying condition. Thus polymeric dyes applied to cellulose triacetate fiber are more resistance to removal by solvent extraction (Tab. 5). This also indicate that polymeric dyes may react with the fiber.

The fastness properties of dyed fiber of the monomeric dyes (Tab. 3) range from good to excellent, while dyed fibers of their corresponding polymeric dyes (Tab. 4) show excellent fastness properties. The improved

TABLE 5 Bleeding properties of polymeric dyes (**Va–h**) on cellulose triacetate fiber

No.	*Solvent system*				
V	*Water*	*Ethanol*	*Toluene*	*n-butanol-Xylene* (1 : 9)	*Cellosolve*
a	5	5	5	5–4	4–5
b	5	5	4–5	4–5	5–4
c	5	5–4	5–4	5	5
d	5	5	5–4	5	4
e	5	5–4	5	5–4	4–5
f	5	5–4	5	4	4–5
g	5	5	5–4	5	4
h	5	5–4	4–5	5–4	5

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 a UV absorber [23]. Table 5 indicates the result of the bleeding test. The dyed fibers 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.

CONCLUSION

Good yields of all the monomeric and polymeric dyes were obtained. 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, sublimation and very good to excellent thermal and chemical resistancy.

It can be concluded from the above studies that an improvement has been shown of the fastness properties with an increase in the molecular size of the dye molecule. The dying of cellulose triacetate fiber by the polymeric colorants had good depth hue with excellent fastness.

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