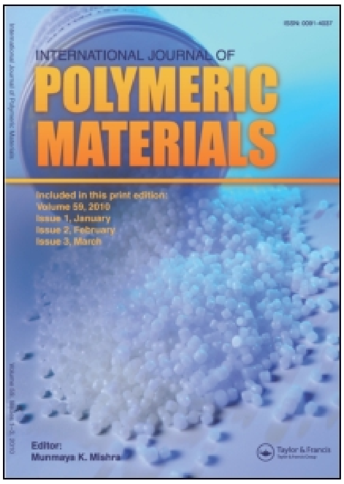

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H. R. Maradiya[a]; V. S. Patel[b]
[a] V.P. and R.P.T.P. Science College, Vallabh Vidyanagar, Gujarat, India [b] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

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Thiophene Based Monomeric and Polymeric Disperse Dyes for Hydrophobic Fibres

H. R. MARADIYA[a,]* and V. S. PATEL[b]

[a]V. P. and R. P. T. P. Science College, Vallabh Vidyanagar-388 120, Gujarat, India; [b]Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, Gujarat, India

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Eight monomeric dyes have been prepared by coupling 2-amino-3-carbethoxy-4,5-dimethylthiophene with various N-phenylmaleimides. Polymeric dyes have been prepared by free radical polymerization of monomeric dyes and they are characterized by IR spectra, Intrinsic viscosity, molecular weight by Vapour Pressure Osmometry, thermogravimetry analysis and elemental analysis. The monomeric dyes have been also characterized by IR spectral studies and elemental analysis. All the dyes were applied as a disperse dyes on nylon and polyester fibres. The dyed fibres showed fair to good fastness to light on nylon and fair fastness on polyester. The washing, rubbing, perspiration and sublimation fastness properties of the dyed fibres has been found to be very good to excellent.

Keywords: 2-Amino-3-carbethoxy-4,5-dimethylthiophene; Disperse dyes; Thermogravimetric analysis (TGA); Vapour Pressure Osmometry (VPO); Infra-Red (IR) spectra; Intrinsic viscosity; Monomeric; Polymeric; Free radical polymerization; Nylon fibre; Polyester fibre

INTRODUCTION

A major advance was made by the research group of J. B. Dickey *et al.*, of Eastman Kodak in the 1950 in heterocyclic azo dyes [1]. A recent important development is the resurgence of interest in dyes

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*Corresponding author.

derived from 2-aminothiophene derivatives [2–4]. The dyes derived from thiophene have many advantages such as the colour deepening effect as an intrinsic property of thiophene ring, small molecular structure leading to better dyeability and intrinsic conjugation.

Monomeric dye is a polymerizable dye which contains a polymerizable group normally ethylene type double bond is present, while polymeric dyes are those which contain a polymeric moiety in them and possessing inherent properties. Their applications are markedly dependent on their relative high molar mass. Thus, polymeric dyes are useful polymers or oligomers as well as useful dyes of unique importance of their high tinctorial power. Their utilization has been possible because of certain essential dyes properties such as fast leveling on fibres, fastness to light, fastness to wet treatment, low sublimation rate and very good thermal and chemical resistancy.

The colour fastness of the coloured fibre is related to the chemical structure, molecular size of dye molecule and physical characteristics of the fibre itself. Giles has given some very useful information on the relationships between dye structure, fibre structure and external condition and behaviour of the coloured fibres on exposure to light, heat, gaseous impurities and wash [5]. Also another important point is that, the most of the organic dyes are carcinogenic and more or less are toxic. In order to improve the fastness properties as well as reduce the toxicity by increasing the size of the dye molecules. The molecular size of the dye molecule can be increased by polymerization reaction. This reaction has been made use of in the synthesis of polymeric dyes.

Only a few researchers have reported the use of various N-phenylmaleimides as a coupling component to prepare coloured compounds for various applications [6–9]. As no report seems to be available in literature to synthesized the monomeric dyes by coupling various N-phenylmaleimides with diazotized 2-aminothiophene derivatives. In view of above, it was consider worthwhile to prepared monomeric dyes using various N-phenylmaleimides and polymeric dyes from the monomeric dyes by polymerization. The dyeing performance of these dyes on nylon and polyester fibres has been assessed.

EXPERIMENTAL

Materials

All the chemicals used were of commercial grade. They were further purified by crystallization.

Procedures

Synthesis of 2-Amino-3-carbethoxy-4,5-dimethylthiophene (I)

The title compound was synthesized by the method reported in literature [10].

Synthesis of Various N-phenylmaleimides (III_{a-h})

These compounds were synthesized by the method reported in literature [11].

Preparation of 2-(p-N-phenylmaleimide)-azo-3-carbethoxy-4,5-dimethylthiophene (IV_a)

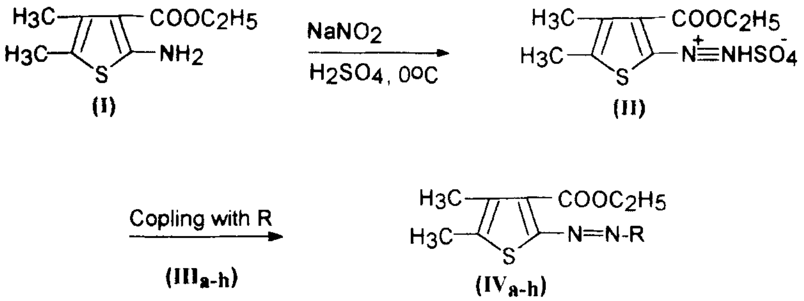
Synthesis of title compound comprises two steps.

(a) Diazotization of 2-amino-3-carbethoxy-4,5-dimethylthiophene Dry sodium nitrite (1.38 g, 0.02 mol) was added in parts over a period of 30 minutes to 98% H_2SO_4 (2.00 g, 0.02 mol) with stirring below 65°C, the resulting solution was treated dropwise at 5–20°C with the mixture of propionic acid and acetic acid (20 ml, 3 : 17). The resulting nitrosyl sulfuric acid mixture was cooled to 0°C and compound **I** (3.98 g, 0.02 mol) was added in portions and stirred for 2 hours at 0–5°C. The excess nitrous acid (the presence tested by starch-iodide paper) was decompose with the required amount of urea. The clear diazonium salt solution (**II**) thus obtained was used for subsequent coupling reaction.

(b) Coupling of Diazonium Salt Solution with N-phenylmaleimide (III_a) N-phenylmaleimide (**III_a**; 3.46 g, 0.02 mol) was dissolved in acetic acid (10 ml) and cooled at 0°C. Freshly prepared diazonium salt solution (**II**) was added dropwise to well-stirred over a period of 2 hours, keeping the temperature below 5°C. The reaction mixture was stirred for 45 minutes at 0–5°C, maintaining the pH at 4.0–4.5 by the help of 10% sodium acetate solution. The reaction mass was then diluted with water (100 ml), filtered, washed and dried in an oven, at 50°C. The product (**IV_a**) thus obtained was crystallized from DMF, yield 80%, m.p. 135°C. The purity of the product was checked by TLC using ethylacetate-benzene (1 : 4) as solvent system. The same procedure was used for the preparation of compounds **IV_{b-h}** using various substituted N-phenylmaleimides (**III_{b-h}**). The whole process for synthesis is drawn in the Scheme-I. The characterization data of **IV_{a-h}** are given in Table I.

Free Radical Addition Polymerization

2-(p-N-phenylmaleimide)-azo-3-carbethoxy-4,5-dimethylthiophene (**IV_a**, 0.766 g, 0.002 mol) and 0.002 g benzoyl peroxide were dissolved in dry benzene (50 ml) and refluxed at 80°C. The solid product start to separate after 30 minutes. The reaction further reflux for 6 hours



Where R is N-phenylmaleimide (III_{a-h}) coupling components

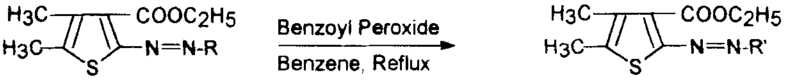
SCHEME I

TABLE I Characterization data and percentage exhaustion of monomeric dyes (**IV**$_{a-h}$)

N-o.	*Coupling component*	*Yield*	*m.p.*[a]	*Molecular*	*Mol.*	*λmax*[b]		*Elemental analysis, (%)*				*Exhaustion, (%)*	
								Found (Calc.)					
IV	(*R*)	(%)	(°*C*)	*formula*	*Wt.*	(*nm*)	*log ε*	*C*	*H*	*N*	R_f	*Nylon*	*Polyester*
a	N-Phenylmaleimide	80	135	$C_{19}H_{17}N_3O_4S$	383	495	3.53	59.40 (59.53)	4.29 (4.43)	10.75 (10.96)	0.85	87	80
b	N-m-Nitrophenyl-maleimide	83	109	$C_{19}H_{16}N_4O_6S$	428	530	3.53	53.10 (53.27)	3.60 (3.73)	12.89 (13.08)	0.83	89	82
c	N-m-Chlorophenyl-maleimide	78	127	$C_{19}H_{16}N_3O_4SCl$	417.5	520	3.38	54.40 (54.61)	3.70 (3.83)	9.90 (10.05)	0.88	83	78
d	N-m-Tolylmaleimide	75	145	$C_{20}H_{19}N_3O_4S$	397	530	3.44	60.30 (60.45)	4.60 (4.78)	10.40 (10.57)	0.86	55	47
e	N-o-Nitrophenyl-maleimide	81	103	$C_{19}H_{16}N_4O_6S$	428	525	3.52	53.07 (53.27)	3.62 (3.73)	12.85 (13.08)	0.89	81	78
f	N-o-Chlorophenyl-maleimide	85	152	$C_{19}H_{16}N_3O_4SCl$	418	520	3.68	54.42 (54.54)	3.74 (3.82)	9.87 (10.04)	0.93	89	79
g	N-o-Tolylmaleimide	88	145	$C_{20}H_{19}N_3O_4S$	397	520	3.92	60.35 (60.45)	4.60 (4.78)	10.42 (10.57)	0.93	90	75
h	N-o-Methoxyphenyl-maleimide	74	109	$C_{20}H_{19}N_3O_5S$	413	530	3.20	58.00 (58.11)	4.50 (4.60)	10.00 (10.16)	0.82	90	80

[a] Melting points carried out by open capillary method and are uncorrected.
[b] Determine in DMF.

and cooled at room temperature. The solid product $V_{a'}$ was filtered and dried in a vacuum at 75°C. The yield was 85%. The same procedure was used for the preparation of compound $V_{b'-h'}$. The whole process for synthesis is drawn in the Scheme-II. The characterization data of $V_{a'-h'}$ are given in Table II.

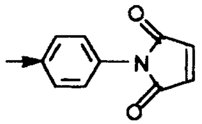


(IV_{a-h}) ($V_{a'-h'}$)

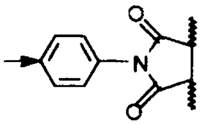
Where R' is poly-N-phenylmaleimide moiety.

SCHEME II

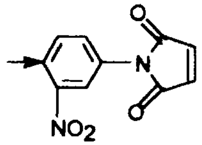
R R'

a. 

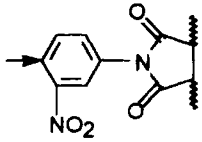
N-phenylmaleimide

a'. 

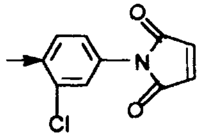
Poly-N-phenylmaleimide

b. 

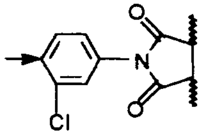
N-m-nitrophenylmaleimide

b'. 

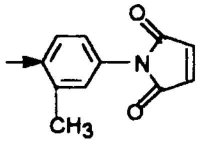
Poly-N-m-nitrophenylmaleimide

c. 

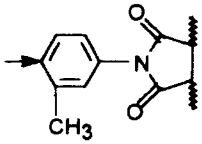
N-m-chlorophenylmaleimide

c'. 

Poly-N-m-chlorophenylmaleimide

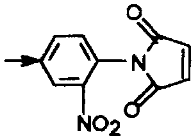
d. 

N-m-tolylmaleimide

d'. 

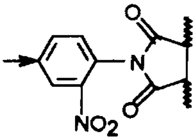
Poly-N-m-tolylmaleimide

e.



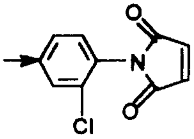
N-o-nitrophenylmaleimide

e'.



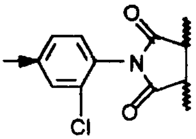
Poly-N-o-nitrophenylmaleimide

f.



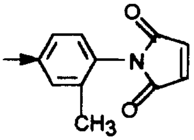
N-o-chlorophenylmaleimide

f.'



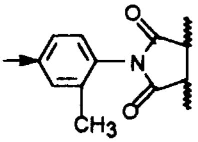
Poly-N-o-chlorophenylmaleimide

g.



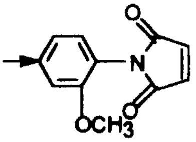
N-o-tolylmaleimide

g'.



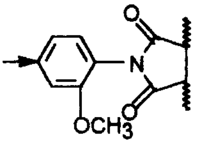
Poly-N-o-tolylmaleimide

h.



N-o-methoxyphenylmaleimide

h'.



Poly-N-o-methoxyphenylmaleimide

MEASUREMENTS

Visible spectra were recorded on CARLZEISS UV/VIS SPECORD Spectrophotometer. A Perkin Elmer model 983 recording infrared spectrophotometer was used for infrared spectra of the compound in KBr pellets. The C, H, N contents were estimated by means of Carlo Erba C, H, N, S, P elemental analyzer (Italy). All the polymeric dyes ($V_{a'-h'}$) were characterized by Intrinsic viscosity measurement in DMF at 35±0.05°C with a Ubbelohde viscometer. The molecular weight determination was found in dioxane at 50°C using vapour pressure osmometer, Hewlett Packard model 3028, thermogravimetry analysis (TGA) has been carried out using Du Pont model 950 thermogravimetric analyzer in air at a heating rate of $10\,\mathrm{K\,min^{-1}}$. The fastness to light, sublimation and perspiration was assessed in

TABLE II Characterization data and percentage exhaustion of polymeric dyes ($\mathbf{V}_{a'-h'}$)

No.	*Various poly-N-phenyl-maleimide moiety*	*Yield*		*Intrinsic viscosity*[b]	*λ max*		*Elemental analysis, (%)*			*Exhaustion, (%)*	
							Found (Calc.)				
V	*R′*	%	*Mol.Wt.*[a]	[*η*], (*dL/g*)	(*nm*)	*log ε*	*C*	*H*	*N*	*Nylon*	*Polyester*
a′	Poly-N-phenylmaleimide	85	4.2×10^3	0.023	485	4.06	59.00 (59.22)	4.09 (4.41)	9.92 (10.82)	60	51
b′	Poly-N-m-nitrophenyl-maleimide	90	3.3×10^3	0.040	515	4.33	52.89 (53.02)	2.90 (3.00)	12.50 (13.08)	43	40
c′	Poly-N-m-chlorophenyl-maleimide	92	4.2×10^3	0.032	510	4.23	54.06 (54.28)	3.62 (3.80)	9.50 (10.04)	48	44
d′	Poly-N-m-tolylmaleimide	87	4.0×10^3	0.019	480	4.52	60.01 (60.15)	4.59 (4.76)	9.92 (10.42)	40	32
e′	Poly-N-o-nitrophenyl-maleimide	86	4.4×10^3	0.071	480	4.35	52.87 (53.02)	2.92 (3.00)	12.62 (13.08)	51	31
f′	Poly-N-o-chlorophenyl-maleimide	91	5.2×10^3	0.052	450	4.33	54.02 (54.28)	3.60 (3.80)	9.20 (10.00)	40	35
g′	Poly-N-o-tolylmaleimide	85	3.9×10^3	0.047	425	4.24	60.00 (60.15)	4.55 (4.76)	10.00 (10.40)	48	42
h′	Poly-N-o-methoxyphenyl-maleimide	89	4.0×10^3	0.068	440	4.06	57.76 (57.83)	4.50 (4.57)	9.25 (10.10)	50	45

[a] Determine in dioxane.
[b] Determine in DMF.

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.

DYEING METHOD

The polyester and nylon fibres were treated at pH 5–6 (adjusted with acetic acid) for 15 minutes at 60°C.

A laboratory model glycerin-bath high-temperature beaker-dyeing machine was used. A paste of 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. To this paste, water (99 ml) was added with stirring and the pH was adjusted to 4 using acetic acid. Dye (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 polyester/nylon fibre 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 glycerine-bath, the temperature of which was raised to 130°C for polyester fibre and 110°C for nylon fibre at the rate of 2°C/min. The dyeing was continued for 60 minutes under pressure. After cooling for 1 hour, the beaker was removed from the bath and washed with water. The pattern was washed several times with cold water. The dyed pattern was further treated with a solution of detergent (0.2 g) and sodium carbonate (0.1 g) in water (100 ml) at 80°C for 30 minutes. The pattern was then washed thoroughly with water and dried at room temperature.

RESULTS AND DISCUSSION

The reaction Schemes-I and II represent the synthesis of monomeric and polymeric dyes respectively. All the monomeric dyes (IV_{a-h}) and polymeric dyes ($V_{a'-h'}$) were characterized by infrared spectra and elemental analysis.

The typical IR spectra and TG curves of selected dyes are shown in Figures 1 and 2 respectively.

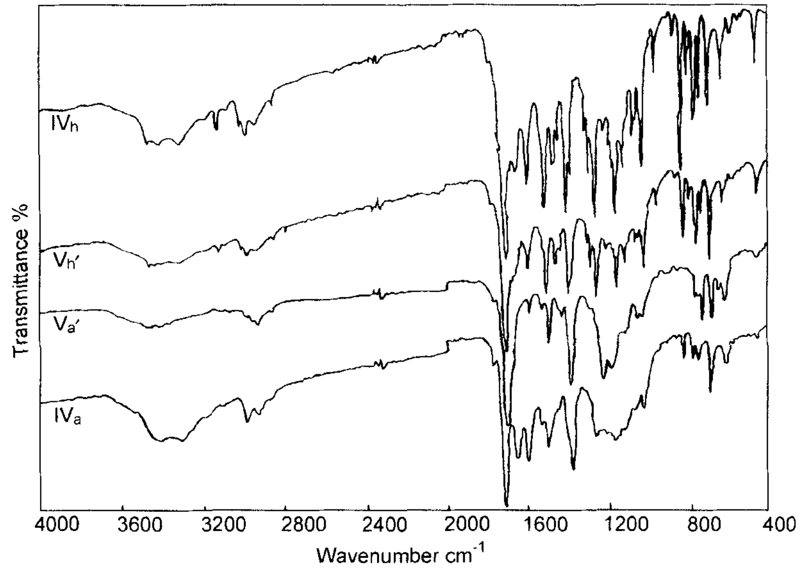


FIGURE 1 IR spectra of dyes IV_a, $\mathrm{V}_{a'}$, $\mathrm{V}_{h'}$ and IV_h.

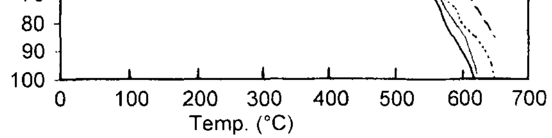


FIGURE 2 TG thermogram of polymeric dyes $\mathrm{V}_{a'}$(—), $\mathrm{V}_{h'}$(—), $\mathrm{V}_{b'}$(· · ·) and $\mathrm{V}_{c'}$(- - -).

The IR spectra of dyes $\mathrm{IV}_{a\ h}$ showed characteristics band at 3085–3200 cm^{-1} (C—H stretching of N-phenylmaleimide ring), 1580–1595, 825–835$_s$ and 945–955$_w$ cm^{-1} (C$=$C conjugated with C$=$O). These bands are disappears in dye $\mathrm{V}_{a'-h'}$. The bands at 1700–1721 cm^{-1} (stretching of C$=$O), 630–680 cm^{-1} (inplane deformation vibration of C=O), 570–580 cm^{-1} (outplane deformation of C=O), 820–860 cm^{-1} (para disubstituted phenyl ring), 1585–1605 cm^{-1} (—N=N—), 1530–1480 cm^{-1} (ester group), 1371$_s$ and 1350$_s$. cm^{-1} (—C—N—C) stretching being asymmetrical and symmetrical respectively. In dyes $V_{a'-h'}$ the saturated tertiary carbon atoms of the N-phenylmaleimide back bone would be expected to show some different C—H stretching.

The IR spectra of some of the dyes also showed the following characteristic bands:

IV_h, $V_{h'}$: 2850 cm^{-1} (C—H bending of —OCH_3)
IV_b, IV_e, $V_{b'}$, $V_{e'}$: 1320–1360 cm^{-1} (symmetric stretching due to —NO_2 group)
IV_c, IV_f, $V_{c'}$, $V_{f'}$: 640–700 cm^{-1} (C—Cl)
IV_d, IV_g, $V_{d'}$, $V_{g'}$: 1450 and 1390 cm^{-1} (C—CH_3)

Table I shows that the exhaustion of the monomeric dyes IV_{a-h} on nylon and polyester fibres is good to very good while its corresponding polymeric dyes $V_{a'-h'}$ shows fair to fairly good exhaustion on fibres. This may be due to larger molecular size and therefore interaction takes place between dye molecule and fibre. Hence rate of diffusion of the dye molecules into fibre are lower, which affect the exhaustion value. The higher exhaustion on the nylon fibre may be expected due to the relatively open structure of nylon fibre. The data also reveal that the change in absorption value of the dyes is due to both the nature and the position of substituent in the maleimide ring system. The hypsochromic shift is observed with introduction of the electron attracting substituent on the various maleimide moieties in the dyes IV_{b-c} and IV_{e-f}. Also, polymeric dyes $V_{a'-h'}$ shows the hypsochromic shift compare to its corresponding monomeric dyes IV_{a-h}. The data also reveal that the dyes $V_{a'-h'}$ are of low molecular weight ranging from 2.4×10^3 to 4.2×10^3. Thermogravimetric investigations were carried out in the range from 25°C to 650°C, at heating rate of 10 Kmin^{-1} in a static air atmosphere. In order to determine the thermal stability trend, TG parameters such as T_0 (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss) and T_{80} (temperature for 80% weight loss) were calculated and are shown in Table V.

TABLE III Dyeing properties of monomeric dyes ($\mathbf{IV}_{a-h}$)

No.	Fastness to															
							Rubbing				*Perspiration*					
	Shade on		*Light*		*Washing*		*N*		*P*		*N*		*P*		*Sublimation*	
IV	*N*	*P*	*N*	*P*	*N*	*P*	*Dry*	*Wet*	*Dry*	*Wet*	*Acid*	*Alkaline*	*Acid*	*Alkaline*	*N*	*P*
a	Light brown	Cream	3	2–3	5	5	5	5	5	5	5	5–4	5	5	5	5
b	Deep brown	Cream	3–4	2–3	5	5–4	4	5	5	5	5–4	5	5	5	4	4
c	Light brown	Cream	3–4	2–3	5–4	5	5	5	5	5	5	5	5	5	5	5
d	Yellowish brown	Light brown	3	2–3	5–4	5	5	4	5	4	4–5	5	5	5	5	5
e	Yellowish brown	Light brown	3	2–3	5	5–4	5	5	5	5	5–4	5–4	5	5–4	4	4
f	Cream	Cream	3	2–3	5	5–4	5	4	5	4	5	5	5–4	5	5	5
g	Light brown	Cream	3–4	2–3	5	5	5	5	4	5	5	5–4	5	5–4	5	5
h	Light brown	Cream	3–4	2–3	5	5	4	5	5	4	5	5	5	5	4	4

P; Polyester and N; Nylon.

TABLE IV Dyeing properties of polymeric dyes ($V_{a'-h'}$)

	Fastness to														
							Rubbing				*Perspiration*				
No.	*Shade on*		*Light*		*Washing*		*N*		*P*		*N*		*P*		*Sublimation*
V	*N*	*P*	*N*	*P*	*N*	*P*	*Dry*	*Wet*	*Dry*	*Wet*	*Acid*	*Alkaline*	*Acid*	*Alkaline*	*N*	*P*
a′	Cream	Light	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		yellow	5	5	5	5	5	5	5	5	5	5	5	5	5	5
b′	Cream	Light	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		yellow	5	5	5	5	5	5	5	5	5	5	5	5	5	5
c′	Cream	Light	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		yellow	5	5	5	5	5	5	5	5	5	5	5	5	5	5
d′	Cream	Light	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		yellow	5	5	5	5	5	5	5	5	5	5	5	5	5	5
e′	Cream	Light	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		yellow	5	5	5	5	5	5	5	5	5	5	5	5	5	5
f′	Cream	Light	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		yellow	5	5	5	5	5	5	5	5	5	5	5	5	5	5
g′	Cream	Light	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		yellow	5	5	5	5	5	5	5	5	5	5	5	5	5	5
h′	Cream	Light	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		yellow	5	5	5	5	5	5	5	5	5	5	5	5	5	5

P; Polyester and N; Nylon.

TABLE V Temperature characteristics for thermal decomposition of polymeric dyes $(\mathbf{V}_{a'-h'})$, % weight loss at °C from TGA

No.	T_0	T_{10}	T_{20}	T_{30}	T_{40}	T_{50}	T_{60}	T_{70}	T_{80}
V	°C	°C	°C	°C	°C	°C	°C	°C	°C
a′	200	282	340	405	525	567	590	615	630
b′	200	230	275	340	410	490	537	565	600
c′	252	285	310	350	440	540	582	610	637
d′	240	280	310	335	370	400	434	479	520
e′	200	230	250	282	325	400	525	565	590
f′	200	230	270	345	425	500	545	575	595
g′	200	282	340	405	525	567	590	615	630
h′	200	270	295	325	390	475	540	565	590

T_0–Temperature (°C) of onset decomposition.
T_{10}–Temperature (°C) for 10% weight loss.
T_{80}–Temperature (°C) for 80% weight loss.

T_0 and T_{10} are the two main criteria for the thermal stability of the polymeric dyes. The higher the values of T_0 and T_{10} the higher will be the thermal stability [12]. The data given in Table V indicate that the dyes have good thermal stability. Dye $\mathbf{V}_{c'}$ has better thermal stability compared to other dyes.

All the dyes were applied as a disperse dyes on nylon and polyester fibres at 2% shade varying from yellowish brown to cream with good levelness, brightness and depth on both the fibres. The variation in the shades of dyed fibres are due to the nature and position of the various substituent present on the maleimide ring.

Table III shows that the light fastness of monomeric dyes $\mathbf{IV}_{a-h}$ ranging from fair to good for nylon and polyester fibres, while its corresponding polymeric dyes $\mathbf{V}_{a'-h'}$ in Table IV shows excellent light, washing, rubbing, perspiration and sublimation fastness properties.

CONCLUSION

It can be concluded from the above studies that the improvement of the fastness properties with increasing the molecular size of the dye molecule by polymerization reaction leads to brilliancy of shade and excellent fastness properties.

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References

[1] Dickey, J. B., Towne, E. B., Bloom, M. S., Moore, W. H., Smith, B. H and Hedberg, D. G. (1958). *J. Soc. Dyers Colour.*, **74**, 123.
[2] Peters, A. T. and Gbadamosi, A. J. (1992). *J. Chem. Tech. Biotechnol.*, **53**, 301.
[3] Hallas, G. and Towns, A. D. (1996). *Dyes Pigm.*, **31**, 273.
[4] Choi, J. H., Hong, S. H. and Towns, A. D. (1999). *J. Soc. Dyers Colour.*, **115**, 32.
[5] Giles, 3rd edn. (1974). A Laboratory Course in Dyeing, Society of Dyers and Colourist, Bradford.
[6] Jan, L. and Frantisek, H. (1978). *Die Angew. Makromol. Chemic.*, **67**, 1.
[7] Katritzky, A. R., Fan, W. Q., Li, Q. L. and Bayyuk, S. (1989). *J. Heterocycl. Chem.*, **26**(4), 885.
[8] Zahn, H. and Altenhoten, U. (1977). *Textilveredlung.*, **12**(1), 9.
[9] Rayn, T. and SangII, H. (1985). *Han'guk Somyu Konghakhoechi*, **22**(1), 36.
[10] Gewald, K. (1962). *Z. Chem.*, **2**, 305.
[11] Searle, N. E. (1948). U.S. 2,44,536; *Chem. Abst.*, **42**, 7340c.
[12] Koton, M. M. and Sazonov, Y. N. (1973). *Polym. Sci. USSR*, **15**(7), 1857.