Res Chem Intermed (2012) 38:2137–2148
DOI 10.1007/s11164-012-0532-y

Polyurethanes as polymerizable dyes for hydrophobic polyester fabric

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Received: 28 June 2011 / Accepted: 6 March 2012 / Published online: 15 March 2012
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Abstract The present invention is to provide a novel benzothiazole-type polymerizable dye containing a urethane bond. A series of monomeric dyes have been prepared by diazotization of various 2-aminobenzothiiazole and coupled with Resorcinol. The polymeric dyes have been prepared by polycondensation of monomeric dyes with hexamethylene diisocyanate (HMDI), and they are characterized by molecular weight, non-aqueous conductometric titration, thermogravimetry analysis, IR, visible spectroscopy, and elemental analysis. The monomeric dyes have also been characterized by elemental analysis and IR spectra. The purity of all the dyes have been checked by thin layer chromatography, and their dyeing performance on nylon and polyester was assessed. The dyeing on polyester fiber had yellow, orange and pink shades with moderate to good light and wash fastness. Polymerizations of monomeric dyes with HMDI on dyed polyester have also been carried out. Color and dyeability of the polymeric dyes have been discussed by comparing them with their corresponding monomeric dyes. The percentage dye bath exhaustion and fixation on fiber have been found to be from good to very good. The dyeing of monomeric dyes showed very good color fastness properties, and their corresponding polymeric dyes showed excellent fastness to light, washing, perspiration, solvent resistance, and sublimation.

Keywords 2-Aminobenzothiazole · Disperse dyes · Hexamethylene diisocyanate (HMDI) · Number average molecular weight · Thermogravimetry · Polyester

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Introduction

There are few reports apart from some patents [1, 2] on the use of azophenol dyes as polymerizable dyes. However, Harbak et al. [3] have carried out much work on polymerizable dyes containing vinylic groups. Kuhn [4] disclosed the first example of polyoxyalkylene polymeric colorants that fulfills acquired performance requirements, such as total removal of fugative tints, and does not influence the final shade of the fabric in 1964. These large, highly water-soluble molecules could not penetrate the surface of fabrics and could readily wash away during normal aqueous dyeing and finishing. 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 such as solubility, absorption, migration, and viscosity that are tunable. They do not sublimate, are nonabrasive, and generally have low toxicity. The range of products possible by combining polymer chemistry and color chemistry is virtually inexhaustible. New examples frequently occur in the chemical literature of research, which are associated with the various applications of polymeric colorants [5–17]. 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 term macromolecular colorants are defined as a group of intermediate or high molar mass compounds that may also be thought of being intrinsically or structurally colored polymers, i.e., possessing inherent properties [18], self-colored polymers [19], polymeric dyes [20], and polymeric pigments [21]. 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. Polymeric dyes are useful polymers or oligomers due to their tinctorial strength [22].

The present communication refers to the synthesis, characterization, and dyeing performance on polyester of various monomeric and polymeric dyes. Polymerization of monomeric dyes on dyed polyester was also carried out, and dyeing properties were compared with those of polymeric dyes.

Experimental

Materials and methods

All the chemicals used were of analytical grade. Various 2-aminobenzothiazoles have been prepared by the methods reported in the literature [23]. The C, H, N, S contents have been estimated by Thermofinigen-1101 Flash elemental analyzer

(Italy). The sulfur content has been determined by the Carius method [24]. IR spectra of all the polymers have been scanned in KBr pellets on a Perkin Elemer 257 spectrophotometer. The visible spectra were recorded on a Carl Zeiss UV/Vis Specord spectrophotometer. Number average molecular weights (Mn) of PUs have been estimated by non-aqueous conductometric titration. The titration has been carried out in formic acid against perchloric acid as titrant. A digital conductometer (Toshniwal, India) was used for this purpose. Values of the number average molecular weight (Mn) of all polymer samples have been calculated by the method reported in the literature [25]. Thermogravimetric analysis for polymers was carried out on a DuPont thermobalance in air at a heating rate of 10 K min^{-1}. The fastness to light, sublimation, perspiration, and organic solvents was assessed in accordance with BS: 1,006–1,978. The rubbing fastness test was carried out using a crock meter (Atlas) in accordance with AATCC-1961. The wash fastness test was carried out in accordance with IS: 765–1,979. The details of various fastness tests are mentioned in the literature [26]. The percentage dyebath exhaustion and fixation of the dyes on fabric were also calculated according to the standard method described in the literature [27].

Synthesis of monomeric dyes **4a**–**h**

The synthesis of the monomeric dye **4a**–**h** comprises of two steps.

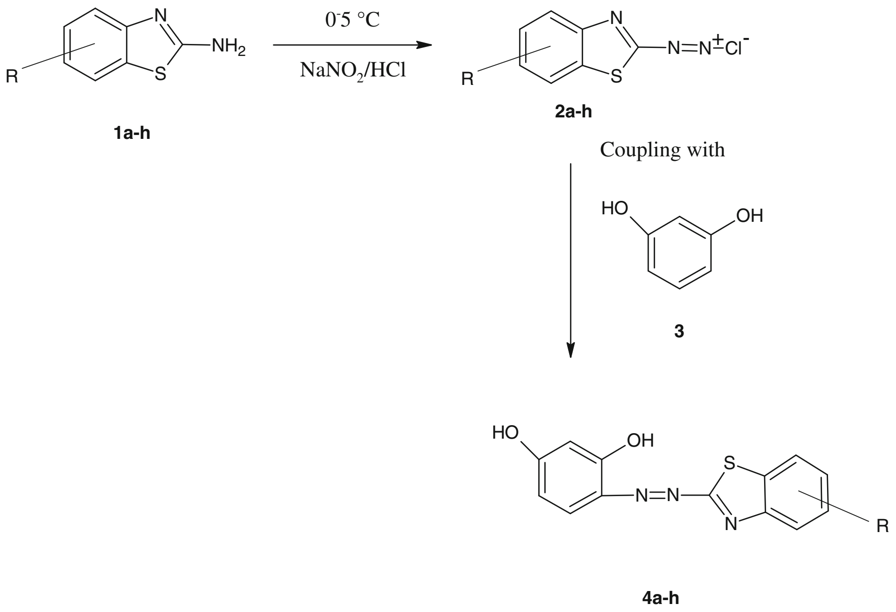
(a) Diazotization of 2-aminobenzothiazole derivatives **1a**–**h**.

Dry sodium nitrite (0.02 mol) was added by stirring to cold concentrated sulfuric acid (1.2 mL) at such a rate that brown fumes were not produed. After addition, the mixture was warmed gradually on a water bath to between 60 and 65 °C, when all the sodium nitrite went into the solution. The solution was then cooled to 3 °C and a mixture (20 mL) of acetic acid–propionic acid (17:3) was added dropwise. The resulting nitrosylsulfuric was then cooled to 0 °C and the finely ground compound **1a**–**h** (0.02 mol) was added portionwise and vigorous stirring was continued at 0–3 °C for 2 h. The excess nitrous acid (giving a positive test on starch-iodide paper) was decomposed with urea. The clear diazonium salt solution **2a**–**h** thus obtained was used immediately in the coupling reaction (Scheme. 1).

(b) Coupling of diazonium salt solution **2a**–**h** with Resorcinol **3**.

The Resorcinol **3** (0.02 mol) was dissolved in 10 mL acetic acid and cooled at 0 °C. Freshly prepared diazonium salt solution **2a**–**h** 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 by the help of 10 % sodium acetate solution. The reaction mass was then diluted with 100 mL water, filtered, washed, and dried in an oven at 50 °C. The dye **4a**–**h** thus obtained was recrystallized from a minimum amount of DMF. The same procedure was repeated for the preparation of the dyes **4b**–**h** using Resorcinol **3**. The synthetic

Synthesis of Monomeric Dyes 4a-h



Where,

R = 6- Cl, 6- OCH_3, 4- CH_3, 6- NO_2, 6-F, H, 6- OC_2H_5, 6-Br

Scheme 1 Synthetic scheme of monomeric dyes **4a**–**h**

scheme is shown in Scheme. 1. The characterization data for dyes **4a**–**h** are given in Table 1.

Synthesis of polymeric dyes **5a**–**h**

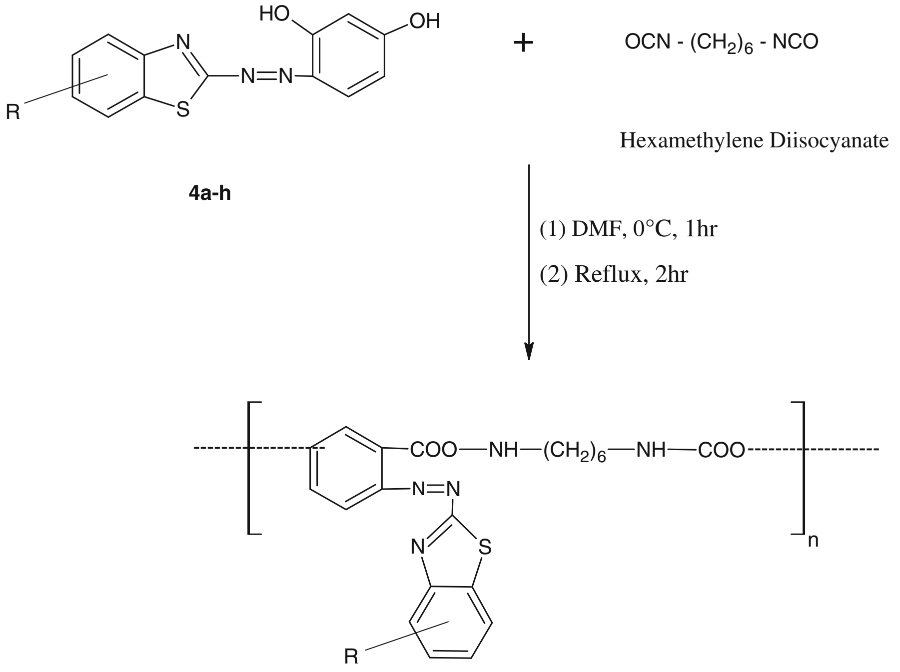
The synthesis of the polymeric dyes **5a**–**h** was carried out by polycondensation reaction of the monomeric dyes **4a**–**h** with the Hexamethylene diisocyanate (HMDI). A typical synthesis was described below. The synthetic scheme is shown in Scheme 2. The characterization data for polymeric dye **5a**–**h** are given in Table 2.

To an ice-cooled solution of monomeric dye **4a**–**h** (0.01 mol) in dry tetrahydrofuran (50 mL), a solution of HMDI (0.01 mol) in 50 mL dry tetrahydrofuran was added gradually with constant stirring. The colloidal suspension that formed immediately was then stirred at room temperature for an hour. The resultant suspension was refluxed for 2 h. The resulting solid product was then filtered off and air-dried (95 % yields).

Table 1 Characteristic parameters of monomeric dyes **4a–h**

Dye no.	Yield (%)	MP (°C)	Absorption maxima (λmax) (nm)		Log ε	Molecular formula (mol. wt)	Rf value	Exhaustion (%)	Fixation (%)
			λmax in DMF	λmax in conc. H_2SO_4					
4a	81	236–237	480	400	3.29	$C_{13}H_8ClN_3O_2S$ (305.7)	0.87	75	71
4b	84	217–218	440	415	4.10	$C_{14}H_{11}N_3O_3S$ (301.3)	0.84	70	75
4c	72	225–227	450	395	4.60	$C_{14}H_{11}N_3O_2S$ (285.3)	0.88	79	70
4d	78	195–196	430	415	3.36	$C_{13}H_8N_4O_4S$ (316.2)	0.82	72	62
4e	70	208–209	450	485	4.70	$C_{13}H_8FN_3O_2S$ (289.2)	0.92	74	68
4f	68	200–201	410	390	4.47	$C_{13}H_9N_3O_2S$ (271.2)	0.90	65	70
4g	69	186–188	450	400	3.11	$C_{15}H_{13}N_3O_3S$ (315.3)	0.87	71	71
4h	71	192–193	440	485	3.29	$C_{13}H_8BrN_3O_2S$ (350.1)	0.81	72	75

Synthesis of Polymeric Dyes 5a-h



4a-h

5a-h

Where,

R = 6- Cl, 6- OCH_3, 4- CH_3, 6- NO_2, 6-F, H, 6- OC_2H_5, 6-Br

Scheme 2 Synthetic scheme of polymeric dyes **5a–h**

Dyeing method

Dyeing method for monomeric dyes

Dyeing at 130–135 °C temperature and high pressure (24–30 psi) is a convenient method for dyeing polyester fabric in the laboratory. A laboratory model glycerin-bath high-temperature beaker dyeing machine was used. A paste of finely powder dye (40 mg) was prepared with dispersing agent Dodamol (80 mg); wetting agent Tween-80 (5 mg) and water (1 mL) in a ball mill for 10 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 polyester fabric was rolled into the beaker. The beaker was then placed vertically on the rotatory carrier inside the tank and the clamp plate was

Table 2 Characteristic parameters of polymeric dyes **5a–h**

Dye no.	Yield (%)	Mol. wt	Absorption maxima (λmax) (nm)		Log ε	C	H	N	S	Rf value	Exhaustion (%)	Fixation (%)
			λmax in DMF	λmax in conc. H_2SO_4								
5a	78	4,762	475	391	3.18	51.89 (55.02)	4.72 (4.80)	18.20 (18.34)	6.86 (6.99)	0.82	62	58
5b	76	4,348	436	380	3.06	57.97 (58.15)	5.43 (5.51)	18.43 (18.50)	7.00 (7.05)	0.80	68	60
5c	77	4,348	442	386	3.19	60.11 (60.27)	5.64 (5.71)	19.00 (19.18)	7.26 (7.31)	0.86	68	62
5d	81	4,348	426	392	4.02	53.63 (53.73)	4.56 (4.69)	20.84 (20.90)	6.77 (6.82)	0.85	71	62
5e	75	4,348	442	385	4.50	56.87 (57.01)	4.86 (4.98)	18.93 (19.00)	7.14 (7.24)	0.81	68	66
5f	80	4,348	432	405	3.20	59.35 (59.43)	5.37 (5.42)	19.73 (19.81)	7.46 (7.55)	0.80	75	67
5g	74	4,348	403	470	4.60	58.86 (58.97)	5.64 (5.77)	17.82 (17.95)	6.76 (6.84)	0.76	68	61
5h	70	4,348	445	408	4.20	50.12 (50.20)	4.27 (4.38)	16.66 (16.73)	6.28 (6.37)	0.79	70	65

firmly tightened. The rotatory carrier was then allowed to rotate in the glycerin bath, the temperature of which was raised to 135 °C (for polyester fabric) 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 pattern was thoroughly washed with hot water at 50 °C and then with cold water, and finally dried at room temperature.

Dyeing method for polymeric dyes

Polycondensation of monomeric dyes on dyed polyester After dyeing, the dyed fabrics were rinsed with water, squeezed and introduced into *n*-hexane (100 mL) containing diisocyanate (0.5 mL 37–40 % w\v) and stirred at room temperature for half an hour. The fabrics were washed with water and treated with detergent (0.2 % v\v) in water at 80 °C for 30 min. After washing with water, the fabrics were dried.

Result and discussion

A weak amine, such as compound **1a**–**h**, required the use of nitrosylsulfuric acid, and it was diazotized satisfactorily at 0 °C by adding to nitrosylsulfuric acid in an acetic acid–propionic acid mixture. The resulting diazonium salt solution **2a**–**h** was generally used within a few hours since this decomposed on standing, even when cold. Coupling was usually accompanied by some evidence of decomposition; however, by careful addition of the diazonium salt solution **2a**–**h** 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 nitrosylsulfuric 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. 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 the coupling components used. The purity of the dyes was checked by thin layer chromatography (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.

The IR spectra of the dyes reveal that the band appearing at 1,573 cm^{-1} is due to the stretching vibration of the C=C, which is conjugated with C=O. The unsaturation is also indicated by the C–H stretching vibrations, which appear at 3,320–3,330 and 720–740 cm^{-1} (out-of-plane deformation vibrations). The band at 623 cm^{-1} is an out-of-plane-deformation vibration characteristic of CH=CH. The band appearing at 625–675 cm^{-1} can be attributed to an in-plane deformation vibration of the C=O. The bands at 1,336 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 1,573 cm^{-1}, and the band at 1,620 cm^{-1} is due to –N=N– stretching vibration. The strong characteristics band at 620–630 cm^{-1} is due to –S–H stretching vibration and that at 1,123 cm^{-1} is due to –C–N stretching. The band around 1,450–1,480 cm^{-1} is due to an ester group.

Thermogravimetric investigations were carried out for the polymeric dyes in the range 25–650 °C, at a heating rate of 10 °C min^{-1} in air atmosphere. Typical TGA curves for the selected polymeric dyes **5b**, **5f**, **5g**, and **5h** are shown in Fig. 1. All the polymeric dyes have good thermal stability and degrade in a single step.

All the dyes were applied at 2 % depth on polyester fabric. No problem was encountered in preparing satisfactory dispersions when the monomeric dyes were milling with the dispersing agent. Then, the polymerization was carried out on these polyester fabrics dyed with monomeric dyes with the HMDI. All the fastness properties shown in Tables 3 and 4 are interrelated, since all depend, among other things, on the rate of diffusion of dye in the fabric. This rate is a function of the geometry of the dye molecule and depends on both the slimness of the molecule, i.e., the magnitude of its smallest cross-section, and the molecular weight. Rate of dyeing and wash fastness are the most important of this type of diffusion-related properties and may be considered to be directly related. The concentration of the dye in the fabric appeared to be the most influential factor in the fastness of the dyes. For example, the variation of light fastness of dye with their concentration in the substrate is partly a function of their particle size. In any system where particles are formed from a liquid phase, they appear in a random range of sizes. Moreover, their average size increases with concentration. This concept will be met only in dye systems that are molecularly dispersed, but it is also likely to occur with polymer dyes are dispersed in a medium. The polymeric dyes have larger molecular size and they were slightly less soluble in polyester fabric compared to the monomeric dyes, slightly restricting the depth of dyeing. The wash fastness rating of the polyester dyeing was primarily influenced by the depth of the shade. The lighter shade of the polyester dyeing means that staining was low, which did not lose color. Thus, the lighter shade restricted the occurrence of any staining. Monomeric dyes were much more soluble in polyester, which suggests that the higher solubility of these dyes allows greater depths to be achieved.

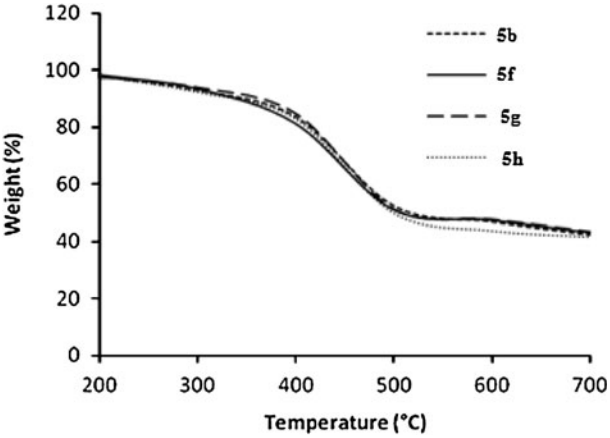


Fig. 1 Thermogravimetric analysis curves of polymeric dyes

Table 3 Dyeing and fastness properties of monomeric dyes on polyester

Dyes no.	Shade on polyester	Light fastness	Wash fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
4a	Pink	4	4–5	4–5	4–5	5	4–5	4–5
4b	Yellow	4–5	5	4–5	5–4	5	4	4–5
4c	Light yellow	4–5	4–5	5–4	4–5	4–5	4	4–5
4d	Light pink	3–4	5–6	4–5	4–5	5	4	4
4e	Orange	4–5	5–6	4–5	5–4	4–5	4–5	4–5
4f	Light orange	4	4–5	4–5	4–5	5	4–5	4–5
4g	Bright pink	5	6	5	5–4	5	5	5
4h	Light yellow	4–5	5–6	5	5–4	5	4–5	5

Table 4 Dyeing and fastness properties of polymeric dyes on polyester

Dyes no.	Shade on polyester	Light fastness	Wash fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
5a	Dark pink	4–5	5	5	5	5	5–4	5
5b	Dark yellow	5–6	5–6	5	4	5	5	5
5c	Dark yellow	5–6	5	5	5	5	5	5–4
5d	Dark pink	4–5	5–6	5	5	5	5–4	5
5e	Dark orange	5–6	5–6	5	5–4	5	5	5
5f	Dark orange	5–6	5	5	5–4	5	5	5
5g	Pink	6	5	5	5	5	5	5
5h	Yellow	5	5	5	5	5	5	5

All the fastness properties of fabric containing the monomeric dyes (Table 3) range from good to excellent, while dyed fabric with corresponding polymeric dyes (Table 4) shows excellent fastness properties. Table 5 indicates the results of the bleeding test. The dyed fabric 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 can be suggested that the polymeric dyes may react with polyester fabric and are easily soluble under the dyeing condition. Thus, polymeric dyes applied to polyester fabric are more resistant to removal by solvent extraction.

Absorption maxima of dyes recorded in DMF solution and concentrated sulfuric acid are shown in Tables 1 and 2. The logarithm of molar extinction coefficient (log e) 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 1 shows that the exhaustion and fixation of the monomeric dyes on polyester fabric are higher than those of their corresponding polymeric dyes (Table 2). The polymeric

Table 5 Bleeding properties of polymeric dyes **5a**–**h**

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

dyes have larger molecular size and tend to have more interactions with the fabric. Polyester fabric is crystalline and hydrophobic in structure. Consequently, diffusion of the polymeric dye within the fabric proceeds slowly under the given dyeing conditions, thereby affecting the exhaustion value. The polymeric dyes exhaust smoothly onto the fabric when applied from a stable dispersion under dyeing conditions and provide satisfactory color shade with slightly lower depths. The substantivity of the dye, which determines its tendency to partition in favor of the fabric, depends on factors such as molecular size, geometry, and (in particular) the polarity of the molecule. During the dyeing process, the fabric is in the glasslike state below about 80 °C and inaccessible to aqueous solutions of dye. When the glass-to-rubber transition temperature is reached, the fabric immediately becomes readily dyeable.

Conclusion

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 utilization of these dyes was possible because of certain essential dye properties, such as fast leveling on fabric, 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 has led to improvements of the fastness properties. The polymeric dyes on polyester fabric have a relatively low depth shade with excellent fastness and staining ratings.

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