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(54) METHOD FOR PREPARING LIGHT-ABSORBING POLYMERIC COMPOSITIONS

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(57) **ABSTRACT**

The present invention recites a method comprising reacting in a solvent in the presence of a base

a) at least one diacidic monomer comprising about 1 to 100 mole % of at least one light-absorbing monomer having a light absorption maximum between about 300 nm and about 1200 nm and 99-0 mole % of a non-light absorbing monomer which does not absorb significant light at wavelengths above 300 nm or has a light absorption maximum below 300 nm, with

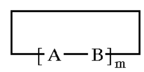
b) an organic compound of Formula II

$$X—B—X_1$$

wherein B is a divalent organic radical to form a light absorbing composition comprising a mixture of a polymer having the formula

$$—[A—B]_n—$$

and a cyclic compound having the general formula



wherein B is as defined above; n is at least 2, m is 1, 2, 3 or 4 and A comprises the residue of a diacidic monomer comprising about 1 to 100 mole % of at least one light-absorbing monomer having a light absorption maximum between about 300 nm and about 1000 nm and wherein the remaining portion of A comprises the residue of a non-light absorbing monomer which does not absorb significant light at wavelengths above 300 nm or has a light absorption maximum below 300 nm.

METHOD FOR PREPARING LIGHT-ABSORBING POLYMERIC COMPOSITIONS

RELATED APPLICATION

[0001] This application is a continuation-in-part of our application Ser. No. 08/976,206 filed Nov. 21, 1997, which is based upon and claims the priority of provisional application 60/031,478 filed Nov. 27, 1996.

BACKGROUND OF THE INVENTION

[0002] This invention relates to an improved method for preparing light-absorbing polymeric compositions, which are useful as powders or pellets for incorporation into a variety of thermoplastic resins such as cellulose esters, polyesters, polyolefins, polycarbonates, polyamides, etc. by conventional melt or solution blending techniques. The colored thermoplastic resins thus produced have good clarity, good color development, excellent fastness to light and are useful for a variety of end uses where nonhazardous, nonmigrating, or nonextractable colorants are needed.

[0003] It is well-known that thermoplastic polymers may be colored by adding pigments or solvent dyes (e.g., see Thomas G. Weber, Editor, *Coloring of Plastics,* John Wiley & Sons, New York, 1979). The use of pigments, however, is accompanied by undesirable properties such as opacity, dullness of color, low tintorial strength, etc. Also, difficulties in uniformly blending the in soluble pigments with the thermoplastic resin are often encountered. Also useful for coloring thermoplastic polymers are the solvent dyes (K. Venkataraman, Editor, *The Chemistry of Synthetic Dyes,* Vol. 8, Academic Press, New York, 1978, pp. 81-131), which provide compositions having improved clarity, brightness in hue and high tinctorial strength, but which may lead to dye migration, extraction, etc. from the colored thermoplastic polymer. These problems are of particular concern when solvent dyes are used to color flexible polymers such as polyvinyl chloride, polyethylene and polypropylene which have low glass transition temperatures.

[0004] Plastics, paints, printing inks, rubber, cosmetics, and similar materials are typically colored by organic pigments when superior brilliance and tinctorial strength are important. Toxicity considerations have presented chronic problems relative to the use of organic pigments since some have been shown to be potential carcinogens and to cause contact dermatitis.

[0005] Plastics are also colored by using color concentrates consisting of physical admixtures of polymers and colorants (usually solvent dyes). However, the use of such physical admixtures to color polymeric materials such as polyester, e.g., poly(ethylene terephthalate) and blends thereof, present a number of problems, including:

[0006] Colorant migration during drying of the colored polyester pellets.

[0007] Colorant migration during extrusion and colorant accumulation on dies which can cause shutdowns for clean-up. Such colorant migration and accumulation result in time consuming and difficult clean-up, particularly when a polymer of another color is subsequently processed on the same equipment.

[0008] Colorants may not mix well, for example, when using two or more color cencentrates to obtain a particular shade.

[0009] Colorants may diffuse or exude during storage and use of the colored polymeric material.

[0010] The colored polymeric compositions which are prepared by the process of this invention eliminate or minimize the aforementioned problems associated with the use of conventional dyes and pigments.

PRIOR ART

[0011] To attempt to overcome some of the problems mentioned above, particularly as relates to coloring polyesters, colored polyester compositions have been prepared by copolymerizing relatively low amounts of monomeric colorants during the polymer preparation (U.S. Pat. Nos. 5,194,571; 5,106,942; 5,102,980; 5,032,670; 4,892,922; 4,740,581; 4,403,092; 4,359,570; 4,267,306 and W092/07913). However, the preparation of these colored polymers require dyes having outstanding thermal stability since the colorants are exposed to very high temperatures for prolonged periods of time necessary for polyester formation, thus severely circumscribing the selection of efficacious colorants. For example, only the nonazo type colorants have been shown to have the adequate thermal stability for copolymerization into polyesters, since azo type compounds do not have the resquite thermal stability for copolymerization.

[0012] Furthermore, it is known to prepare polymeric dyes by reacting dyes containing reactive hydroxy and amino groups with organic di-acid chlorides in solvents (U.S. Pat. Nos. 2,994,693; 3,403,200; 4,619,990; 4,778,742; 5,401,612). Although this method of polymer preparation allows the use of a wide range of chromophoric classes, including azo compounds, as colorant monomers, the polymerization reaction in each case involves the use of very reactive organic di-acid chlorides which are toxic and involve difficult to handle inorganic halogen compounds in their preparation and have accompanying problems of hydrolysis in the presence of water which causes serious handling and storage problems. The hydrolysis product (HCl) is particularly corrosive and makes storage of these compounds difficult. Furthermore, since the di-acid chlorides will react with water, the monomeric dyes must be specially dried to avoid side reactions in the polymer preparation.

[0013] In a similar attempt to prepare polymeric dyes using relatively low temperatures, polyurethanes have been prepared by reacting dyes bearing two hydroxyalkyl group with aliphatic and aromatic isocyanates (U.S. Pat. No. 5,194,463). However, the organic isocyanates themselves are extremely toxic and present difficult handling problems. They also are reactive with water and thus the reaction requires specially dried monomeric dyes. Also, the colored polyurethanes as a class do not have excellent thermal stability.

[0014] It is further known to prepare colored condensation polymers by reacting a polymerizable lactone or a hydroxyalkanoic acid with a dye containing reactive hydroxy group (U.S. Pat. No. 4,933,426). The procedure again requires relatively high reaction temperatures and prolonged times and use a large excess of the lactone reactant. The method is further hindered by the fact that some lactones are suspected carcinogens.

[0015] Light-absorbing polymeric compositions have also been produced by free radical polymerization of vinyl functionalized light-absorbing monomers (U.S. Pat. Nos. 5,310,837; 5,334,710; 5,359,008; 5,434,231 and 5,461,131).

[0016] Finally, it is known that one may color plastics, in particular polyolefins, with low melting, cross-linked colored polyester compositions containing residues of terephthalic acid, isophthalic acid, or both, a low-molecular weight trimethylol alkane, i.e., 1,1,1-trimethylol propane and a copolymerizable colorant, said colorant being present at a level of 0.1-25% by weight (U.S. Pat. No. 4,116,923). Difficulties are encountered, however, in preparing these highly cross-linked colored polymers as extreme care with regard to the temperature, amount of vacuum, the level of colorant present, and the reaction time, is necessary in order to attempt to reproduce the same quality of cross-linked colored polyester composition. Further, these colored polyester compositions are brittle or low melting and may cause deterioration in physical properties of themoplastic polymers when added in quantities sufficient to produce a high level of coloration.

[0017] Practice of the Invention

[0018] This invention relates to a method for preparing a light absorbing linear polymeric having Formula I

$$-\!\!\left[A-B\right]_n\!\!- \qquad \text{I}$$

[0019] wherein A comprises the residue of a diacidic monomer comprising about 1 to 100 mole % of at least one light-absorbing monomer having a light absorption maximum between about 300 nm and about 1200 nm and wherein the remaining portion of A comprises the residue of a non-light absorbing monomer which does not absorb significantly at wavelengths above 300 nm or has a light absorption maximum below 300 nm and wherein B is a divalent organic radical selected from C_2-C_{12} alkylene, C_3-C_8 cycloalkylene, C_1-C_4 alkylene- C_3-C_8-cycloalkylene-C_1-C_4 alkylene, C_1-C_4 alkylene-arylene- C_1-C_4 alkylene, C_2-C_4 alkylene-O— C_2-C_4 alkylene, and C_2-C_4-alkylene-L-arylene- C_2-C_4 alkylene and C_2-C_4 alkylene- (L-C_2-C_4 alkylene)$_{1-4}$, wherein L is a linking group selected from-O—, —S—, —SO_2—, —NH—, —N(C_1-C_6alkyl)-, —N(aryl)-, —N(SO_2 C_1-C_6 alkyl)-, —N(SO_2aryl)-, —SO_2N(C_1-C_6 alkyl)- and combinations thereof; wherein n is at least 2.

[0020] The process comprises reacting said diacidic monomer with an organic compound of Formula II

$$X-B-X_1 \qquad \text{II}$$

[0021] wherein B is as defined above and X and X_1 reactive groups and are independently selected from bromine, iodine and R—SO_2O; wherein R is selected from C_1-C_6 alkyl; C_1-C_6 alkyl substituted with chlorine, fluorine, C_1-C_6 alkoxy, aryl, aryloxy, arylthio or C_3-C_8 cycloalkyl; C_3-C_8 cycloalkyl or aryl, with said reaction being carried out in a solvent in the presence of a base; wherein the useful diacid light-absorbing monomers have Formula III

$$H-Y-H \qquad \text{III}$$

[0022] wherein H represents an acidic hydrogen atom; Y is a divalent light-absorbing moiety selected from a variety of chromophoric classes including azo, disazo, bis-azo, methine, arylidene, polymethine, azo-methine, azamethine, anthraquinone, anthrapyridone (3H-dibenz[f,ij]isoquinoline- 2,7-dione, nitroarylamines anthrapyridine (7H-dibenz [f,ij]isoquinoline-7-one, phthaloylphenothiazine (14H-naphth[2,3-a] phenothiazine-8,13-dione, benzanthrone(7H (de) anthracene-7-one), anthrapyrimidine(7H-benzo[e] perimidine-7-one), anthrapyrazole, anthraisothiazole, triphenodioxazine, thiaxanthene-9-one, fluorindine (5,12-dihydroquinoxaline[2,3-b]phenazine, quinophthalone, phthalocyanine, metal phthalocyanine, naphthalocyanine, metal naphthalocyanine, nickel dithiolenes, squarylium compounds, croconium compounds, coumarin (2H-1-benzopyran-2-one), coumarin imine (2H-1-benzopyran-2-imine), perinone, benzodifuran, phthaloylacridone, phthaloylphenoxazine (14H-naphtho[2,3-a]phenoxazine-8,13-done, phthaloylacridone (13H-naphtho[2,3-c]acridine-5,8, 14-trione), anthraquinonethioxanthane (8H-naphtho[2,3-c] thioxanthene-5,8,13-trione, anthrapyridazone, pyrrolo[3,4-c]pyrrole, indigo, thioindigo, quinoline, xanthene, acridine, azine, cyanine, oxazine, 1,4 and 1,5-naphthoquinones, 2,5-diarylaminoterephthalic acids and esters, pyromellitic acid dimide, naphthalene-1,4,5,8-tetracarboxylic acid diimide, 3,4,9,10-perylene-tetracarboxylic acid diimide, 3-aryl- 2,5-dioxypyrroline, 3-aryl-5-dicyanomethylene-2-oxopyrroline, arylisoindoline, hydroxybenzophenone, benoztriazole, naphthotriazole, diminoisoindoline, naphthopyran (3H-naphtho[2,1-6]pyran-3-one and 3-imine, phthalimides, 2-arylbenzazoles, carbostyryls, 1,2-diarylethenes, 2,5-diarylthiophenes, 2,5-diaryl-1,3,4-oxadiazoles, triazines, 2,5-diarylfurans, 2,5-diaryl-1,3,4-thiadiazoles, thiophenes, 1,3-diphenyl-2-pyrazolines, 2-arylbenzofurans, 2,6-diphenylbenzofurans, quinolines, quinoxalines, 3,4-diarylfuanones, distyrylarenes, benzanthrones, polyarenes and naphthalimides; wherein the hydrogen atoms of Formula III are independently bonded to an oxygen, sulfur, or nitrogen atom which is a part of the light absorbing moiety Y; wherein the useful non light-absorbing monomers have Formula IV,

$$H-Y_1-H \qquad \text{IV}$$

[0023] wherein H represents an acidic hydrogen atom; Y_1 is a divalent moiety, selected from-O_2C—R_1—CO_2— and-O—R_2—O-and-O_2C—R_3—O—, wherein R_1 is selected from C_2-C_{12} alkylene, 1-4-cyclohexylene, arylene, arylene-O-arylene, arylene-S_2-arylene, arylene-S-arylene, and C_1-C_4 alkylene-O—C_1-C_4 alkylene; wherein R_2 is selected from arylene, arylene-O-arylene, arylene-S-arylene, arylene-SO_2-arylene, phenylene-phenylene, and phenylene-C$(R_4)_2$-phenylene; wherein R_4 is selected from hydrogen and C_1-C_4 alkyl; wherein R_3 is selected from arylene.

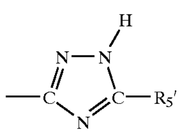
[0024] In diacid light absorbing monomers having Formula III, the hydrogen atoms are preferably attached to an oxygen, a sulfur or a nitrogen atom which in combination provides two acidic functional group which can produce the corresponding anions under basic conditions by removal of the protons. The acidic functional groups usually have an acid dissociation constant of about 10^{-15} to about 10^{-12} (pK_a of from about 1.5 to about 12). In the case of nitrogen, both protons may be attached to a single nitrogen which is attached to a sulfonyl moiety thus providing two acidic hydrogens on a single functional group.

[0025] Typical, acidic groups which provide one acidic hydrogen include-CO_2H, —SH, —OH attached to an aromatic ring, —CONHCO—, —SO_2—NH—CO—, —SO_2—NH—SO_2—, 1(H)-1,2,4-triazol-3-yl-, imidazolyl, benzimidazolyl, pyrazolyl, —SO_2H attached to aromatic ring, —$NHSO_2R_5$ and-SO_2NHR_5, wherein R_5 is selected from C_1-C_6 alkyl; C_1-C_6 alkyl substituted with at least one group selected from C_1-C_6 alkoxy, aryl, aryloxy, arylthio or C_3-C_8 cycloalkyl; C_3-C_8 cycloalkyl; aryl.

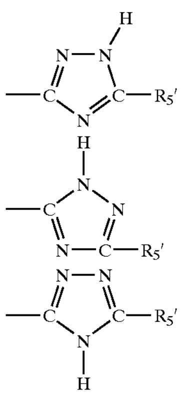
[0026] An example of an acidic functional group providing two acidic hydrogen attached to nitrogen is the sulfamoyl group (—SO_2NH_2).

[0027] The preferred method for producing light absorbing polymeric compositions utilizes the monomers of Formula III, wherein the protons are a part of the-CO_2H, OH attached to aromatic ring, —CO—NH—CO— or 1(H,)-1,2,4-triazol-3-yl functional groups. The carboxy groups are normally attached to an aromatic ring carbon or aliphatic carbon which is a part of Y. The hydroxy groups are normally attached to an unsubstituted or substituted phenyl or naphthyl radical which is a part of Y. The —CO—NHCO— groups are usually attached to an aromatic ring to provide an imide such as phthalimide or naphthalimide which are a part of Y. The 1(H)-1,2,4-triazol-3-yl group has the following Formula V, wherein R_5' is

V



[0028] selected from hydrogen, C_1-C_6 alkyl or aryl. It should be observed that the triazole may exist in isomeric form as follows:



[0029] The 1(H)-1,2,4-triazol-3-yl group is preferably attached to a sulfur atom which is attached to the remainder of Y.

[0030] The method of the invention in the broadest sense involves the preparation of light absorbing polymeric compositions by reacting a diacidic monomer comprising at least 1 mole % of at least one diacidic light absorbing monomer represented by H-A-H with an organic compound containing two reactive groups represented by X—B—X_1, where B, X and X_1 are as defined above. Thus, the method may be summarized as:

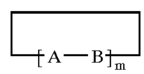
$$\mathrm{H—A—H} + \mathrm{X—B—X_1} \xrightarrow[\text{solvent}]{\text{base}} \mathrm{-[A—B]_n-}$$

[0031] The diacidic monomer H-A-H must be acidic enough to form two nucleophiles in the presence of base under convenient reaction conditions for the most advantageous process. This usually requires that diacidic monomers have pK_a values of about 12 or below.

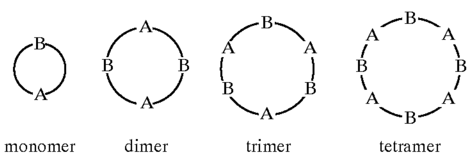
[0032] The dinucleophilic monomer, formed by the removal of the two hydrogen atoms by the base, attacks the electrophilic compound II, thus displacing anions X^- and X_1^-, with head-to-tail combination with covalent bonding to produce a linear polymer $-[A\text{-}B]_n-$, wherein n represents the number of repeating units. The number of repeating units must be at least 2, but usually ranges between about 2 and about 25, with the preferred number being between about 3 and about 15.

[0033] The composition produced by the method of the invention comprises, as stated above, a polymer having the general formula $-[A\text{-}B]_n-$. The composition also comprises one or more cyclic compounds having the general formula

I-A



[0034] wherein m may be 1, 2, 3, or 4, e.g., the cyclic compounds having the general structures:



[0035] The number and concentrations of the cyclic compounds is dependent upon a variety of factors such as the structure of diacid H-A-H, the structure of the organic compound X—B—X_1, and the conditions used to facilitate the reaction to produce the composition. The cyclic compounds may constitute up to about 35 weight percent, typically about 0.5 up to 30 weight percent, of the total weight of the composition produced by the method of the invention.

[0036] Suitable bases include alkali metal carbonates; alkali metal bicarbonates; tertiary amines such as triethylamine, tri-n-butylamine, N-methylpiperidine, N,N'-dimethylpiperazine, N-methylmorpholine, N,N,N',N'-tetramethylenediamine, etc.; aromatic nitrogen bases such as pyridines, picolines, quinolines, isoquinolines, N-alkylpyrroles, N-alkylimidazoles, etc.; bicyclic nitrogen containing bases having non-hindered electron pairs, such as 1,8-diazabicyclo

[4,3,0]undec-7-ene (DBU), 1,5-diazabicylco[4,3,0]non-5-ene (DBN) and 1,4-diazadicyclo[2,2,2]octane (DABCO®).

[0037] Typical solvents useful in the polymerization reaction include aprotic polar solvents such as N,N-dimethylacetamide, N,N-dimethylformamide, N-methyl-2-pyrrolidone, N-methyl-N-phenyl formamide, dimethyl sulfoxide, aliphatic nitriles, sulfolane, hexamethyl phosphoramide, etc. and mixtures thereof. Water, alcohols, ketones pyridine and ether-alcohols, such as the Cellosolves, also are sometimes useful. One requirement is that the solvent not form a stronger nucleophile in the presence of the base than that obtained from the diacidic monomer H-A-H.

[0038] The new improved process of the invention allows the preparation of near ultraviolet (UV-A, UV-B and UV-C), visible and near infrared light absorbing linear polymeric compositions at relatively low temperatures, usually at from about 75° C. to about 125° C., without prolonged heating times. Furthermore, the method is adaptable to batch-process production which is advantageous for expensive products such as colorants, near infrared absorbers and near ultraviolet absorbers. The method is adaptable to a wide range of chromophoric classes since the polymer preparative reaction is carried out at relatively low temperature, which for example, allows colored polymeric compositions to be readily prepared from the very important azo class of colorants.

[0039] The preferred reactants of Formula II

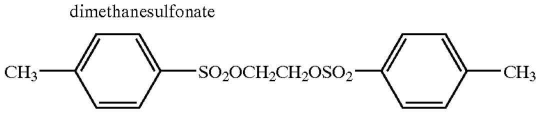
$$X—B—X_1$$

[0040] are the disulfonate compounds where X and X_1 are both a sulfonate ester of the formula-OSO_2R, wherein R is selected from C_1-C_4 alkyl, phenyl or p-methylphenyl and wherein B is selected from C_2-C_6 alkylene, —CH_2-1,4-cyclohexylene-CH_2—, 2,2,4,4-tetramethyl-1,3-cyclobutylene, 1,4-cyclohexylene, —$CH_2CH_2(OCH_2CH_2)_{2-3}$ and —CH_2CH_2O-1,4-phenylene-O—CH_2CH_2—. Particularly, preferred reactants of Formula II are those where B is selected from-CH_2CH_2—, —$CH_2CH(CH_3)CH_2$—, —$CH_2C(CH_3)_2CH_2$—, —$(CH_2)_4$—, —$(CH_2)_6$—, —$CH_2CH_2(OCH_2CH_2)_{1-4}$ and-CH_2-1,4-cyclohexylene-CH_2—.

[0041] Typical reactants of Formula II are as follows:

$CH_3SO_2OCH_2CH_2OSO_2CH_3$

1,2-Ethanediol, dimethanesulfonate



1,2-Ethanediol, bis(4-methylbenzenesulfonate)

$CH_3SO_2O(CH_2)_6OSO_2CH_3$

1,6-Hexanediol, dimethanesulfonate

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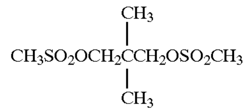
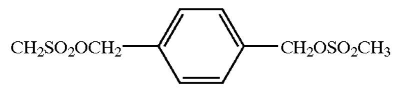


1,3-Propanediol,2-2-dimethyl-, dimethanesulfonate



1,4-Cyclohexanedimethanol, dimethanesulfonate

$CH_3SO_2OCH_2CH_2OCH_2CH_2OSO_2CH_3$

Ethanol,2,2'-oxybis-, dimethanesulfonate

[0042] The invention also relates to a light absorbing linear polymeric composition having Formula Ia:

$$—[A_1—B]_n— \qquad \text{Ia}$$

[0043] wherein A_1 comprises the residue of at least one diacidic monomer having a light absorption maximum between about 300 nm and about 1200 nm, preferably between about 325 nm and 1100 nm and most preferably between about 350 nm and 1000 nm and wherein B is defined above and which has been prepared by reacting a diacid light-absorbing monomer of Formula III (H—Y—H) as defined above with an organic compound having Formula II (X—B—X_1) as defined above, with the polymer producing reaction having been carried out in a solvent in the presence of base. The above-described light absorbing composition of formula Ia also contains or comprises one or more cyclic compounds having the formula

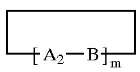
$$\boxed{—[A_1—B]_m—} \qquad \text{I-B}$$

[0044] wherein A_1 and B are defined above and m may be 1, 2, 3, or 4. As stated hereinabove, the number and concentrations of the cyclic compounds is dependent upon a variety of factors such as the structure of diacid H-A-H, the structure of the organic compound X—B—X_1, and the conditions used to facilitate the reaction to produce the composition. The cyclic compounds of formula I-B may constitute up to about 35 weight percent, typically about 1 up 30 weight percent, of the total weight of the above-described light absorbing composition.

[0045] The invention also relates to a light absorbing linear polymeric composition having Formula Ib

$$-\!\!\left[A_2-B\right]_n\!\!- \qquad \text{Ib}$$

[0046] wherein A_2 comprises the residue of at least one diacidic monomer, having a light absorption maximum between about 300 nm and about 1200 nm, preferably between about 325 nm and 1100 nm and most preferably between about 350 nm and 1000 nm and which comprises at least about 50% by weight of the total of the composition of Formula Ib and wherein the remainder of A_2 comprises the residue of at least one non-light absorbing monomer of Formula IV above, and wherein said polymeric composition has been prepared by reacting diacidic monomers of Formula III and Formula IV with an organic compound having Formula II above, with the polymer producing reaction having been carried out in a solvent in the presence of base. The light absorbing composition of formula Ib also contains or comprises one or more cyclic compounds having the formula



I-C

[0047] wherein A_2 and B are defined above and m may be 1, 2, 3, or 4. Again, the number and concentrations of the cyclic compounds is dependent upon a variety of factors such as the structure of diacid H-A-H, the structure of the organic compound X—B—X_1, and the conditions used to facilitate the reaction to produce the composition. The cyclic compounds of formula I-B may constitute up to about 35 weight percent, typically about 1 up 30 weight percent, of the total weight of the above-described light absorbing composition.

[0048] The polymer compositions of Formula I, Ia, and Ib and the cyclic compositions of formulas I-A, I-B and I-C are referred to as "polydyes" herein when they absorb visible light thus rendering them strongly colored.

[0049] The invention further relates to a thermoplastic polymeric composition which comprises a thermoplastic polymer blended with at least one light absorbing linear polymeric composition of Formula I, Ia or Ib above which, as noted above, contain or comprise one or more cyclic compounds having the general formula I-A. The thermoplastic polymeric composition is usually selected from polyesters, polyolefins, polyamides, polyimides, polyvinyl chloride, polyurethanes, polycarbonates, cellulose esters, polyacrylates, polyvinylesters, polyester-amides, polystyrene, polyacrylonitrile- butadiene- styrene and polystyrene-acrylonitrile. The preferred thermoplastic polymeric composition comprises the light-absorbing polymeric compositions of Formula Ia.

[0050] The invention also relates to some of the diacidic light absorbing monomers used to prepare the light absorbing polymeric composition of Formula I, Ia, or Ib.

[0051] Preferred azo compounds useful in the practice of the invention correspond to Formula VI

$$R_6—N{=}N\text{-}Z \qquad \text{VI}$$

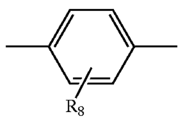
[0052] wherein R_6 is the residue of an aromatic or heteroaromatic amine which has been dizaotized and coupled with a coupling component H-Z and is preferably derived from the aromatic and heteroaromatic amine classes of aniline, 1-aminonaphthalene, 1-aminoanthraquinone, 4-aminoazobenzene, 2-aminothiazole, 2-aminobenzothiazole, 3-amino-2,1-benzisothiazole, 2-aminothieno[2,3-d]thiazole, 5-aminoisothiazole, 5-aminopyrazole, 4-aminopyrazoloisothiazole, 2-amino-1,3,4-thiadiazole, 5-amino-1,2,4-thiadiazole, 5-amino-1,2,3-triazole, 2-amino-1,3,4-triazole, 2(5) aminoimidazole, 3-aminopyridine, 2(3) aminothiophene, 2(3) aminobenzo[b]thiophene, 2-aminothieno[3,2-bithiophene, 3-aminothieno[2,3-c]isothiazole, 3-amino-7-benz- 2,1-isothiazole, 3-aminobenzothienoisothiazole, 3-aminoisothiazole[3,4-d]pyrimidine, 5-amino- 1,2,3-triazole, 3(4) aminophthalimide and 5(6) amino-1,2-benzisothiazolon-1,1-dioxide with said aromatic and heteroaromatic ring systems being unsubstituted or substituted with one or more groups selected from C_1-C_{10} alkyl, C_1-C_6 alkoxy, C_3-C_8 cycloalkyl, carboxy, halogen, C_1-C_6 alkoxycarbonyl, formyl, C_1-C_6 alkanoyl, C_1-C_6 alkanoyloxy, dicyanovinyl, C_3-C_8-cycloalkanoyl, thiocyano, trifluroacetyl, cyano, carbamoyl, —CONH C_1-C_6 alkyl, CONHaryl, CON(C_1-C_6 alkyl)$_2$, sulfamoyl, SO_2NH C_1-C_6 alkyl, SO_2N(C_1-C_6 alkyl)$_2$, SO_2NHaryl, SO_2NH C_3-C_8 cycloalkyl, CONH C_3-C_8 cycloalkyl, aryl, aroyl, —$NHSO_2$ C_1-C_6 alkyl, —N(C_1-C_6 alkyl)SO_2 C_1-C_6 alkyl, —$NHSO_2$ aryl, NHCO C_1-C_6 alkyl, NHCO C_3-C_8 cycloalkyl, NHCOaryl, $NHCO_2$ C_1-C_6 alkyl, NHCONH C_1-C_6 alkyl, NHCONHaryl, N(C_1-C_6 alkyl)aryl, arylazo, heteroaryl, aryloxy, arylthio, C_3-C_8 cycloalkoxy, heteroarylazo, heteroarylthio, arylsulfonyl, tricyanovinyl, aryloxysulfonyl, C_1-C_6 alkylsulfonyl, trifluoromethyl, fluorosulfonyl, trifluoromethylsulfonyl, thiocyano, hydroxy, nitro or CH=D, wherein D is the residue of an active methylene compound as defined below.

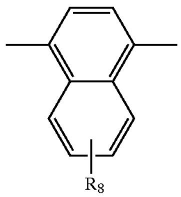
[0053] Z is the residue of an electron rich coupling component selected from the classes of anilines, 1-aminonaphthalenes, 1,2-dihydroquinolines,1,2,3,4-teterahydroquinolines, benzmorpholines (3,4-dihydro-2H-1,4-benzoxazine), pyrazolones, pyrazoles, 3-cyano-6-hydroxy-2-pyridones, 2,3-dihydroindoles, indoles, 4-hydroxycoumarins, 4-hydroxy-2-quinolones, imidazo[2,1-bithiazoles, julolidines (2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizines), 1-oxajulolidines, 1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinolines, 2,6-diamino-3 cyanopyridines, 2-aminothiazoles, 2-aminothiophenes, 5,5-dimethyl-1,3-cyclohexanedione (dimedone), phenols, naphthols, 2,4-pentanediones or acetoacetarylides; with the proviso that the compounds of Formula VI contain two acidic functional groups containing one acidic hydrogen each or contain one sulfamoyl group (—SO_2NH_2) which contains two acidic hydrogens.

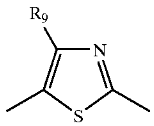
[0054] Preferred disazo compounds correspond to Formula VII

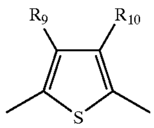
$$R_6—N{=}N—R_7N{=}N\text{-}Z \qquad \text{VII}$$

[0055] wherein R_6 and Z are as defined above and R_7 is a divalent aromatic or heteroaromatic radical selected from the classes 1,4-phenylene, naphthalene-1,4-diyl, thiazol-2, 5-diyl and thiophene-2,5-diyl:









[0056] wherein R_8 is selected from hydrogen or 1-2 groups selected from C_1-C_6 alkyl, C_1-C_6 alkoxy, cyano, halogen, —NHCO C_1-C_6 alkyl, —$NHCO_2$ C_1-C_6 alkyl, —NHCO aryl, —NHCONH aryl or NHCONH C_1-C_6 alkyl; R_9 is selected from hydrogen, C_1-C_6 alkyl, halogen, aryl, heteroaryl; R_{10} is selected from hydrogen, C_1-C_6 alkoxycarbonyl, cyano, carbamoyl, aryl, arylsulfonyl, aroyl, —CONH C_1-C_6 alkyl, or C_1-C_6 alkylsulfonyl; with the provision that two acidic functional groups containing one acidic hydrogen each or one functional group containing two acidic hydrogens are present on compounds of Formula VII.

[0057] The preferred methine, arylidene, polymethine, azamethine, 3-aryl-2,5-dioxypyrroline, 3-aryl-5-dicyanomethylene-2-oxopyrroline and aryl isoindoline compounds correspond to Formula VIII, VIIIa, VIIIb, IX, X, XI and XII, respectively:

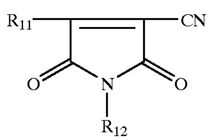
$$R_{11}—CH═D \quad \text{VIII}$$

$$R_{11}—\underset{}{\overset{CN}{\overset{|}{C}}}H═D \quad \text{VIII a}$$

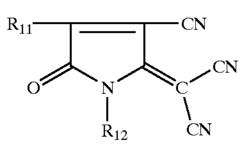
$$R_{11}—CH═CH—CH═D \quad \text{VIII b}$$

$$R_{11}—N═D \quad \text{IX}$$

X



XI



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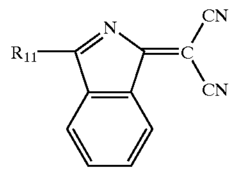
XII



[0058] wherein R_{11} is the residue of an aniline, 1-naphthylamine, 1,2-dihydroquinoline, 1,2,3,4-tetrahydroquinoline, 1,3,3-trimethyl-2-methyleneindole, 1,3-dihydro-2-methylene-1,1,3-trimethyl-2H-benz[e]indole, imidazo [2,1-b] thiazole, benzomorpholine (3,4-dihydro-2H-1,4,benzoxazine), indole, 2,3-dihydroindole, 2-aminothiazole, julolidine (2,3,6,7-tetrahydro-1H, 5H-benz [ij] quinolizine, 1-oxajulolidine, 4H-pyrrolo [3,2,1-ij]-quinoline, phenol, naphthol, thiophenol, pyrrole, pyrazole, furan, thiophene, carbazole, phenothiazine or phenoxazine compound; R_{12} is selected from hydrogen, C_1-C_{10} alkyl, C_3-C_8 alkenyl, C_3-C_8-alkynyl, C_3-C_8 cycloalkyl, aryl, $-(CH_2CH_2O)_{1-3}$ R_{13} and C_1-C_4 alkylene- C_3-C_8 cycloalkylene, wherein the C_1-C_6 alkyl groups may be substituted by at least one group selected from carboxy, C_1-C_6 carbalkoxy, C_1-C_6 alkanoyloxy, cyano, hydroxy, chlorine, fluorine, C_1-C_6 alkoxy, C_3-C_8 cycloalkyl or aryl; R_{13} is selected from hydrogen, C_1-C_6 alkoxy or C_1-C_6 alkanoyloxy; wherein D is the residue of an active methylene compound selected from malononitrile, -cyanoacetic acid esters, malonic acid esters, -cyanacetic acid amides, —C_1-C_6 alkylsulfonylacetonitriles, -arylsulfonylacetonitriles, —C_1-C_6 alkanoylacetonitriles, -aroylacetonitriles, -heteroarylacetonitriles, bis(heteroaryl-)methanes, 1,3-indanediones, 2-furanones, benzo-2-furanones, naphtho-2-furanones, 2-indolones. 3-cyano-1,6-dihydro-4-methyl-2,6-dioxy (2H)-pyridines, benzo (b) thieno-3-ylidene propane dinitrile-5,5-dioxides, 1,3-bis (dicyanomethylene) indanes, barbituric acid, 5-pyrazolones, dimedone, 3-oxo-2,3-dihydro-1-benzothiophene-1,1-dioxides or aryl-$C(CH_3)C{=}C(CN)_2$, with the proviso that two acidic functional groups containing one acidic hydrogen each, or a functional group containing two acidic hydrogens are present in compounds of Formula VIII, VIIIa, VIIIb, IX, X, XI, and XII.

[0059] Preferred azo-methine compounds corresond to Formula XIII

$$D{=}HC—R_7—N{=}N\text{-}Z \quad \text{XIII}$$

[0060] wherein D, R_7 and Z are as defined previously.

[0061] The bis-azo compound corresponds to Formula VIIa

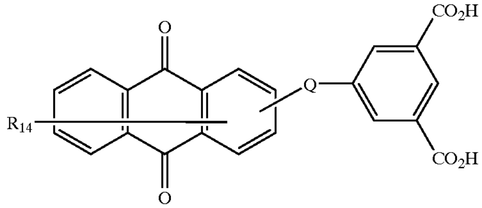
$$R_6—N{=}N—Y_1N{=}N—R_6 \quad \text{VIIa}$$

[0062] wherein R_6 is as defined above and Y_1 is the residue of a bis coupling component selected from the classes of anilines, 1,2-dihydroquinolines, 1,2,3,4-tetrahydroquinolines, benzomorpholines (3,4-dihydro-2H-1,4-benzoxazines), 3-cyano-6-hydroxy-2-pyridones, 2,6-diaminopyridines, 2,3-dihydroindoles, naphthylamines, 2-aminothiazoles, or a combination of these; with the provision the compounds of Formula VIIa contain two acidic functional groups containing one acidic hydrogen each or contain one sulfamoyl group (—SO_2NH_2) which contains two acidic hydrogens.

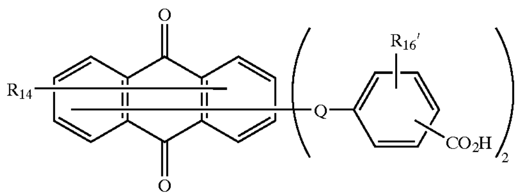
[0063] Several diacid monomers which are described in U.S. Pat. Nos. 4,804,719 and 3,689,501 are useful in the practice of the invention, including various anthraquinones, anthrapyridones, anthraisothiazoles, anthrapyrimidines, anthrapyrimidones, phthaloylacridones, etc.

[0064] Some of the preferred anthraquinone, anthrapyridone and anthrapyrimidine compounds correspond to the light absorbing compounds of Formulae XIV-XIXf

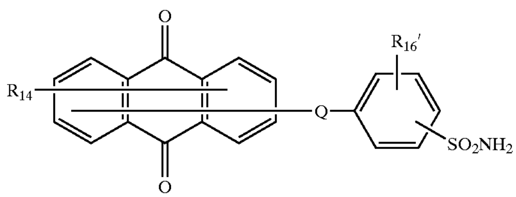
XIV



XV



XVI



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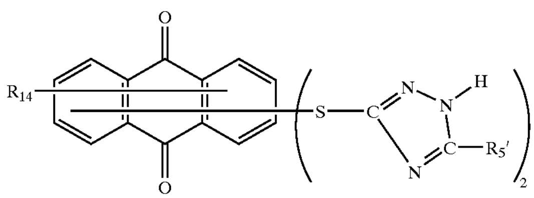
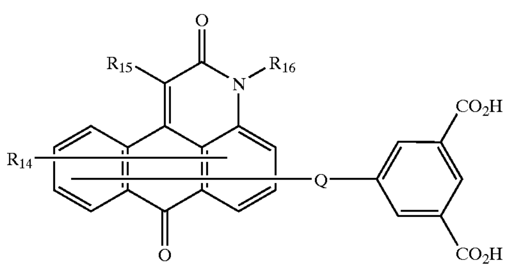


XVIII



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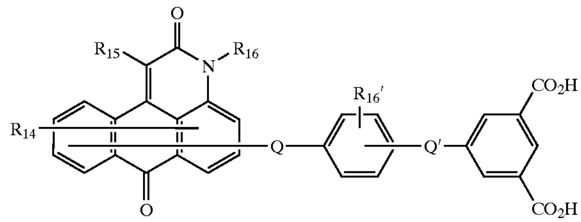
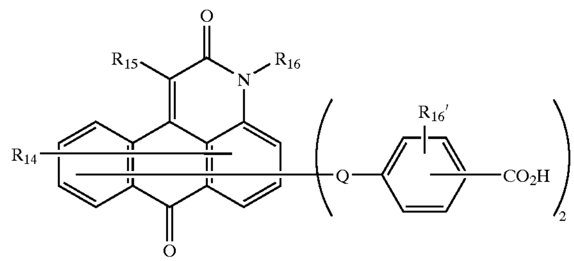
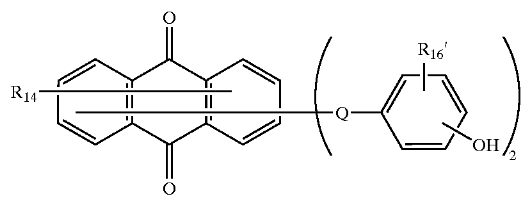
XVIIIa



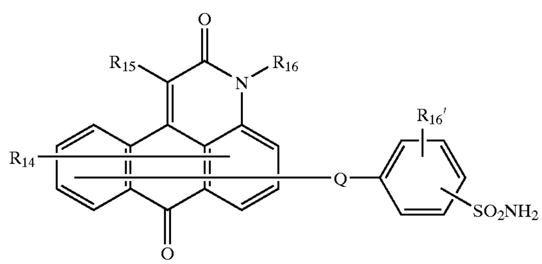
XVIIIb



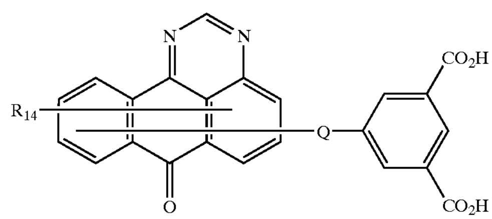
XIX



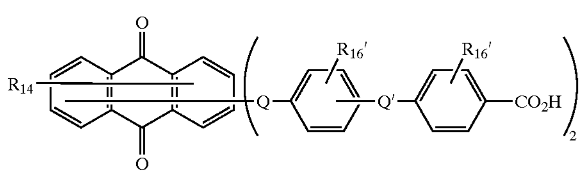
XIXa



XIXb



XIXc



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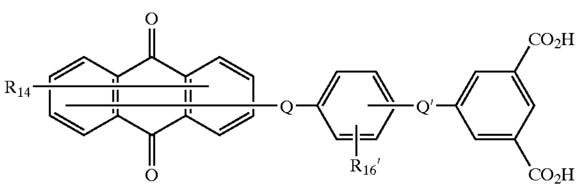
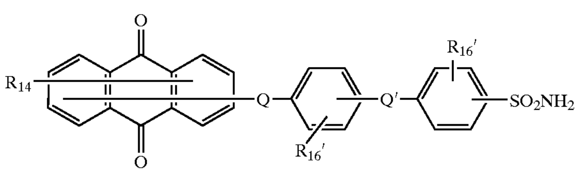
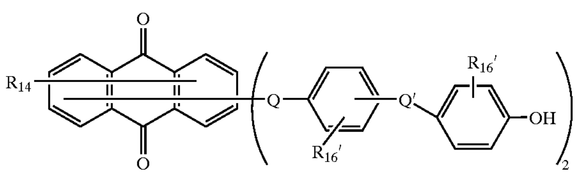
XIXd



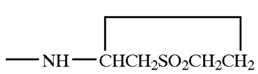
XIXe



XIXf

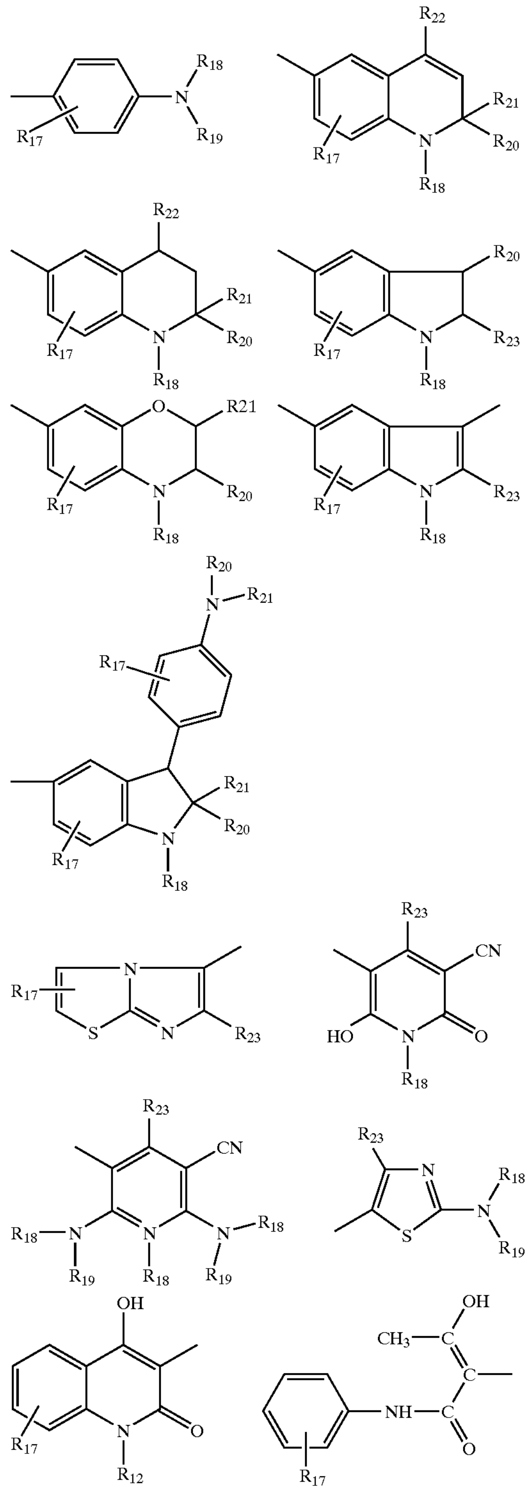


[0065] wherein R_{14} is selected from the group consisting of hydrogen, 1-4 groups selected from amino, C_1-C_{10} alkylamino, C_3-C_8 alkenylamino, C_3-C_8 alkynylamino, C_3-C_8 cycloalkylamino, arylamino, halogen, C_1-C_6 alkoxy, C_1-C_6 alkylthio, aryl, aroyl, C_1-C_6 alkanoyl, C_1-C_6 alkanoyloxy, NHCO C_1-C_6 alkyl, NHCOaryl, $NHCO_2$ C_1-C_6 alkyl, $NHSO_2$ C_1-C_6 alkyl, $NHSO_2$ aryl, C_1-C_6 alkoxycarbonyl, aryloxy, arylthio, heteroarylthio, cyano, nitro, trifluoromethyl, thiocyano, SO_2C_1-C_6 alkyl, SO_2 aryl, —SO_2NH C_1-C_6 alkyl, —$SO_2N(C_1$-C_6 alkyl$)_2$, —$SO_2N(C_1$-C_6 alkyl) aryl, CONH C_1-C_6 alkyl, CON(C_1-C_6 alkyl$)_2$, CON(C_1-C_6 alkyl) aryl, C_1-C_6 alkyl, furfurylamino, tetrahydrofurfurylamino, 4-(hydroxymethyl) cyclohexanemethylamino,



[0066] or hydroxy; Q and Q' are independently selected from-O—, —N(COR_{10})—, —N(SO_2R_{10})—, —N(R_{10})—, —S—, —SO_2—, —CO_2—, —CON(R_{10})—, SO_2N (R_{10})—, wherein R_{10} is selected from hydrogen, aryl, C_3-C_8 cycloalkyl, or C_1-C_{10} alkyl; R_{15} is selected from hydrogen, cyano, C_1-C_6 alkylamino, C_1-C_6 alkoxy, halogen, arylthio, aryl, heteroaryl, heteroarylthio, C_1-C_6 alkoxycarbonyl, aroyl or arylsulfonyl; R_{16} is selected from hydrogen, C_1-C_{10} alkyl, C_3-C_8 cycloalkyl and aryl; R_{16}' is selected from the group consisting of hydrogen, one or two groups selected from C_1-C_6 alkyl, halogen and C_1-C_6 alkoxy; wherein each C_1-C_6 alkyl group and C_1-C_6 alkyl group which is a portion of another group may contain at least one substituent selected from hydroxy, cyano, chlorine, fluorine, C_1-C_6 alkoxy, C_3-C_8 cycloalkoxy, C_1-C_6 alkylcyclohexyl, hydroxmethyl cyclohexyl, aryl and heteroaryl; with the provision that two acidic groups containing one acidic proton each or one acidic group containing two acidic hydrogens be present in the compounds of Formula XIV-XIXf.

[0067] Typical coupler residues which are represented by Z above in Formulae VI, VII, XIII for the classes of azo, disazo and azo-methine compounds, respectively include:



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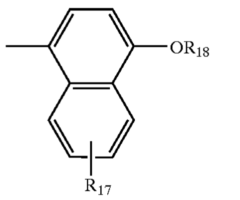
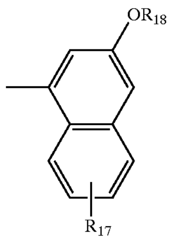
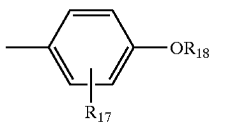
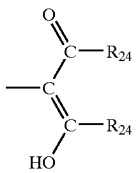

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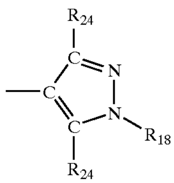
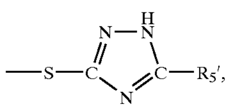
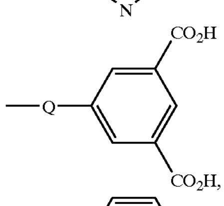
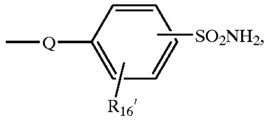
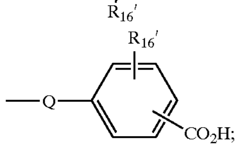
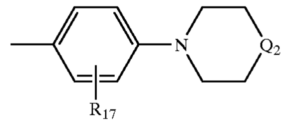


[0068] wherein R_{17} is selected f rom the group consisting of hydrogen, 1-2 groups selected from C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 alkylthio, —O—C_2-C_6 alkylene-OH, O—C_2-C_6 alkylene-C_1-C_6 alkanoyloxy, C_1-C_6 alkylene-OH, C_1-C_6 alkylene-C_1-C_6 alkanoyloxy, halogen, carboxy, C_1-C_6 alkoxycarbonyl, trifluoromethyl, $NHCOR_{24}$, $NHCO_2R_{24}$, $NHCON(R_{24})R_{25}$, and $NHSO_2R_{25}$, wherein R_{24} is selected from hydrogen, C_1-C_{10} alkyl, C_3-C_8 cycloalkyl or aryl, R_{25} is selected from C_1-C_{10} alkyl, C_3-C_8 cycloalkyl or aryl wherein each C_1-C_{10} alkyl group in R_{24} and R_{25} may be further substituted with one or more groups selected from C_3-C_8 cycloalkyl, aryl, aryloxy, arylthio, CO_2H, CO_2 C_1-C_6 alkyl, cyano, hydroxy, succinimido, C_1-C_6 alkoxy,

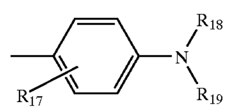
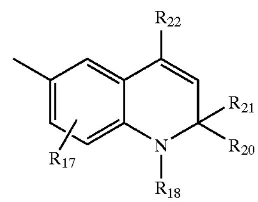
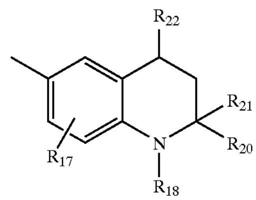
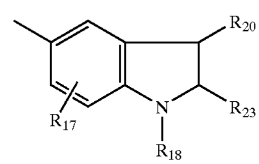
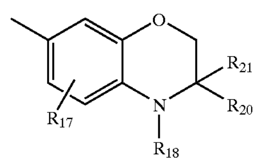
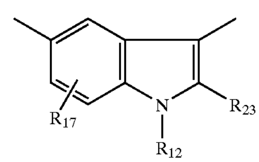
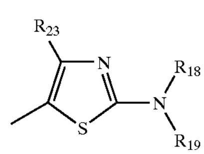
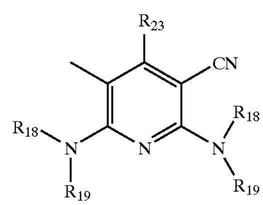
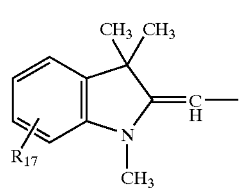
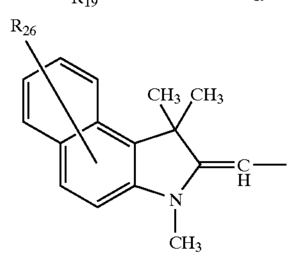





[0069] wherein R_5', R_{16}' and Q are as defined above; R_{18} and R_{19} are independently selected from hydrogen, unsubstituted C_1-C_{10} alkyl, substituted C_1-C_{10} alkyl, C_3-C_8 cycloalkyl, C_3-C_8 alkenyl, C_3-C_8 alkynyl and aryl or R_{18} and R_{19} may be combined with another element to which they are attached to form a radical Z having the formula



[0070] wherein Q_2 is selected from a covalent bond, —O—, —S—, —SO_2—, —CO—, —CO_2—, —N—(C_1-C_6 alkyl)-, —N(CO C_1-C_6 alkyl)-, —N(SO_2 C_1-C_6 alkyl)-, —N(CO aryl)-, or-N(SO_2 aryl); R_{20}, R_{21} and R_{22} are independently selected from the group consisting of or C_1-C_6 alkyl; R_{23} is selected from hydrogen, C_1-C_6 alkyl, C_3-C_8 cycloalkyl, heteroaryl or aryl.

[0071] Typical electron, rich aromatic residues which are represented by R_{11} in Formulae VIII-XII include:

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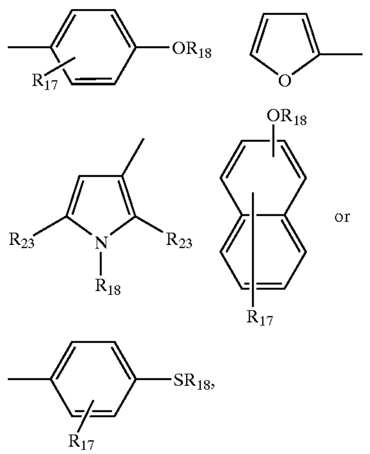
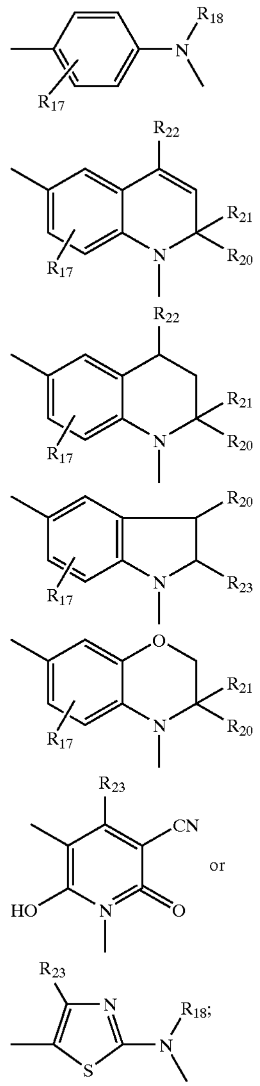
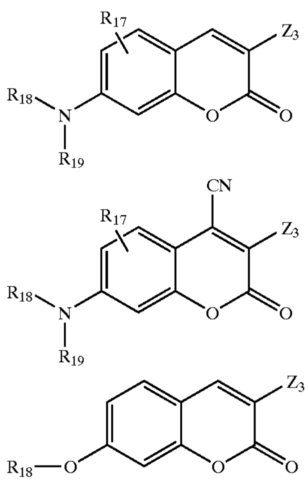




[0072] wherein R_{26} is selected from the group consisting of hydrogen, a group selected from C_1-C_6 alkoxycarbonyl, CO_2H, C_1-C_6 alkyl or C_1-C_6 alkoxy; wherein R_{17}-R_{23} are as defined previously.

[0073] Preferred coumarin compounds useful in the practice of the invention correspond to the following formulae:



[0074] wherein Z_3 is selected from cyano, C_1-C_6 alkoxycarbonyl, C_1-C_6 alkylsulfonyl, arylsulfonyl, aryl, heteroaryl, formyl, aroyl, C_1-C_6 alkanoyl or-CH=D, wherein D, R_{17}, R_{18} and R_{19} are as defined previously with the provision that the coumarin compounds contain two acidic functional groups containing one acidic hydrogen each or contain one sulfamoyl (—SO_2NH_2) group which contains two acidic hydrogens.

[0075] Typical coupler residues which are represented by Y_1 in Formula VIIa above include those of the formula (Z_1-L_1-Z_2) wherein Z_1 and Z_2 are independently selected from

[0076] wherein L_1 is bonded to the nitrogen atom of Z_1 and Z_2; wherein L_1 is selected from C_2-C_{12} alkylene, C_3-C_8 cycloalkylene, arylene, C_1-C_4 alkylene-C_3-C_8 cycloalkylene-C_1-C_4 alkylene, C_1-C_4 alkylene-arylene-C_1-C_4 alkylene, C_2-C_4 alkylene-O-arylene-O—C_2-C_4 alkylene, —C_2-C_4 alkylene O_{1-3}—C_2-C_4 alkylene, C_2-C_4 alkylene-S—C_2-C_4 alkylene, C_2-C_4 alkylene-SO_2—C_2-C_4 alkylene, C_2-C_4 alkylene-N(SO_2 C_1-C_6 alkyl) —C_2-C_4 alkylene, C_2-C_4 alkylene-N(SO_2 aryl) —C_2-C_4 alkylene, C_2-C_4 alkylene-OCO_2—C_2-C_4 alkylene, C_2-C_4 alkylene-O_2C-arylene-CO_2—C_2-C_4 alkylene, C_2-C_4 alkylene-O_2C—C_1-C_{12} alkylene-CO_2—C_2-C_4 alkylene, C_2-C_4 alkylene-O_2C—C_3-C_8 cycloalkylene-CO_2—C_2-C_4 alkylene, C_2-C_4 alkylene-NHCO—C_2-C_4 alkylene and C_2-C_4 alkylene-$NHSO_2$—C_2-C_4 alkylene; wherein R_{17}, R_{18}, R_{20}, R_{21}, R_{22}, and R_{23} are as defined previously.

[0077] In the above definitions it is intended that in the terms C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 alkoxycarbonyl, C_1-C_6 alkylthio, C_1-C_6 alkylsulfonyl, C_1-C_6 alkanoyl,

—CONH C_1-C_6 alkyl, —SO_2NH C_1-C_6 alkyl, —CON(C_1-C_6 alkyl)$_2$, —SO_2N(C_1-C_6 alkyl)$_2$, —$NHSO_2$ C_1-C_6 alkyl, —N(C_1-C_6 alkyl) SO_2 C_1-C_6 alkyl, etc. unless otherwise stated that the C_1-C_6 alkyl portion of the group refers to a straight or branched chain alkyl group containing one to six carbon atoms and these substituted with one or more groups selected from carboxy, cyano, —SO_2NH_2, SO_2NH C_1-C_6 alkyl, cyano, fluorine, chlorine, C_1-C_6 alkoxy, aryloxy, aryl, heteroaryl, arylthio, heteroarylthio, C_3- C_8-cycloalkyl, —O_2C C_1-C_6 alkyl or-CO_2 C_1-C_6 alkyl.

[0078] The terms C_1-C_4 alkylene, C_2-C_4 alkylene, C_1-C_6 alkylene, C_2-C_6 alkylene, and C_2-C_{12} alkylene are used to refer to divalent aliphatic hydrocarbon radicals containing one to four carbon atoms, two to four carbon atoms one to six carbon atoms, two to six carbon atoms, or two to twelve carbon atoms, respectively, and these optionally substituted with one or more groups selected from C_1-C_6 alkoxy, hydroxy, —O_2C C_1-C_6 alkyl, carboxy, CO_2 C_1-C_6 alkyl, chlorine, fluorine, aryl or aryloxy.

[0079] The terms C_3-C_8 cycloalkyl and C_3-C_8 cycloalkylene are used to refer to fully saturated monovalent and divalent cycloaliphatic radicals, respectively, and these substituted by one or more C_1-C_6 alkyl groups.

[0080] The terms C_3-C_8 alkenyl and C_3-C_8 alkynyl are used to refer to straight or branced hydrocarbon radicals containing at least one double bond or at least one triple bond, respectively.

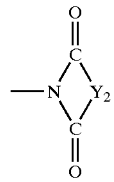
[0081] In the terms aryl, NH aryl, aryloxy, aroyl, arylthio, arylsulfonyl, aryloxysulfonyl, —N(SO_2 aryl)-, —N(CO aryl)-, NHCO aryl, —NH CONH aryl, $NHSO_2$, aryl, etc., the aryl portion of the group represents phenyl and naphthyl and these substituted with one or more groups selected from-CO_2H, C_1-C_6 alkyl, CO_2 C_1-C_6 alkyl, SO_2NH_2, SO_2NH C_1-C_6 alkyl, hydroxy, O C_1-C_6 alkyl, S C_1-C_6 alkyl, phenyl, O-arylene-CO_2H, —S-arylene-CO_2H, SO_2 arylene-CO_2H, halogen, $NHSO_2$ C_1-C_6 alkyl, trifluoromethyl, NH CO C_1-C_6 alkyl, cyano, or 1(H)-1,2,4-triazol-3-ylthio.

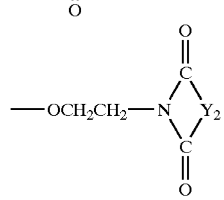
[0082] The term arylene is used to represent 1,2-, 1,3-, and 1,4-phenylene and these optionally substituted with one or more groups mentioned above as possible substituents on the aryl radical.

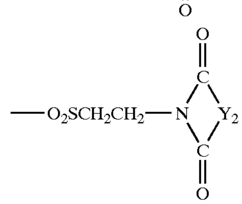
[0083] The term "heteroaryl" is used to describe a 5 or 6 membered heterocyclic aromatic ring containing one oxygen atom, and/or one sulfur atom, and/or up to three nitrogen atoms, said heterocyclic aryl ring optionally fused to one or two phenyl rings or another 5 or 6-membered heteroaryl ring. Examples of such ring systems include thienyl, furyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, triazolyl, thiadiazolyl, oxadiazolyl, tetrazolyl, thiatriazolyl, oxatriazolyl, pyridyl, pyrimidyl, pyrazinyl, pyridazinyl, thiazinyl, oxazinyl, triazinyl, thiadiazinyl, oxadiazinyl, dithiazinyl, dioxazinyl, oxathiazinyl, tetrazynyl, thiatriazinyl, oxatriazinyl, dithiadiazinyl, imidazolinyl, dihydropyrimidyl, tetrahydropyrimidyl, tetrazolo [1,5-b]-pyridazinyl and purinyl, benzoxazolyl, benzothiazolyl, benzimidazolyl, indolyl, and the like and those rings substituted with one or more substituents listed above in the definition of the term "aryl".

[0084] The term halogen is used to refer to fluorine, chlorine, bromine and iodine.

[0085] In the above definitions the unsubstituted and substituted C_1-C_{10} alkyl groups or portion of groups mentioned refer to fully saturated hydrocarbon radicals containing one to ten carbon atoms, either straight or branched chain, and such alkyl radicals substituted with one or more of the following: C_3-C_8 cycloalkyl, aryl, hydroxy, cyano, —O—C_2-C_4 alkylene OH, —O—C_2-C_4 alkylene O_2 C—C_1-C_6 alkyl, —S—C_2-C_4 alkylene-OH, chlorine, fluorine, —O—C_1-C_6 alkyl, —O-aryl, —SO_2 aryl, —SO_2—C_1-C_6 alkyl, 2-pyrrolidino, phthalimidino, phthalimido, succinimido, glutarimido, o-benzoic sulfimide, vinyl sulfonyl, —NHCO C_1-C_6 alkyl, NHCOH, —$NHSO_2$-C_1-C_6 alkyl, $NHSO_2$ aryl, —NHCO aryl, —NH—CO_2—C_1-C_6 alkyl, —SO_2NH_2, —SO_2—NH—C_1-C_6 alkyl, —SO_2N—(C_1-C_6 alkyl)$_2$, —CO_2—C_1-C_6 alkyl, $CONH_2$, —CONH—C_1-C_6 alkyl, —CO_2-aryl, —CON(C_1-C_6 alkyl)$_2$, —CCONH aryl, —CONH(C_1-C_6 alkyl) aryl, —SO_2N(C_1-C_6 alkyl) aryl, —SO_2—NH—C_3-C_8 cycloalkyl, —CONH—C_3-C_8 cycloalkyl, —OCO_2—C_1-C_6 alkyl, —O C_2-C_4 alkylene CN; groups of the formulae:

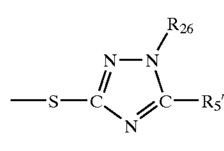






[0086] wherein Y_2 is selected from 1,2-phenylene; 1,2 pheylene substituted with C_1-C_6 alkyl, C_1-C_6 alkoxy, halogen, —CO_2H, —CO_2 C_1-C_5 alkyl or nitro; C_2-C_4 alkylene, vinylene, —O CH_2—, —SCH_2—, —CH_2OCH_2—, —OCH_2CH_2—, —CH_2SCH_2—, —$NHCH_2$—, —$NHCH_2CH_2$, —N(C_1-C_6 alkyl)CH_2—, NHC(C_1-C_6 alkyl)$_2$, —N(C_1-C_6 alkyl) CH_2CH_2 or-NHC (aryl)$_2$-; groups of the formulae:

—SR_{25}, —$SO_2CH_2CH_2SR_{25}$, —$OCH_2CH_2SR_{25}$,



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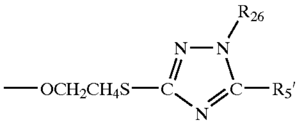

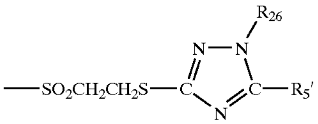

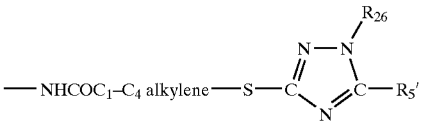

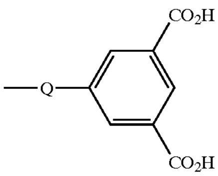

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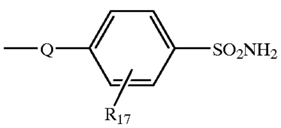
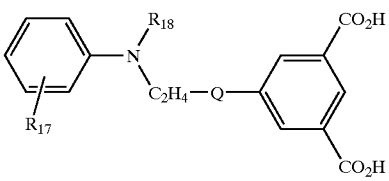
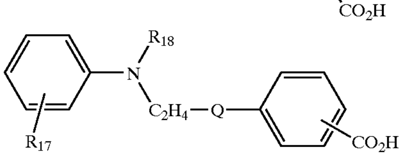


[0087] wherein R_{26} is selected from hydrogen, C_1-C_{10} alkyl, C_2-C_4 alkylene-OH, C_2-C_4 alkylene-CO_2H, C_2-C_4 alkylene-CO_2 C_1-C_6 alkyl, chloro, C_1-C_6 alkoxy, C_1-C_4 alkylene-arylene-CO_2H, C_2-C_4 alkylene-O-arylene-CO_2H or C_2-C_4 alkylene-S-arylene-CO_2H and R_5' R_{17}, R_{25} and Q are as defined previously:

[0088] The term "light absorbing" is used to indicate the property of absorbing near ultra violet, visible or near infrared light, more particularly absorbing light between the wavelengths of 300-1200 nm, preferably between about 325 nm and 1100 nm, and most preferably between about 325 nm and 1000 nm.

[0089] Typical aromatic amines which are useful as the coupling components to prepare compounds of Formulae VI, VII and VIII and as intermediates for preparing the compounds of Formula VIII, VIIIa, IX, X, XI and XII are as follows:





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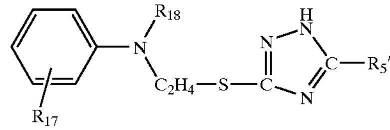

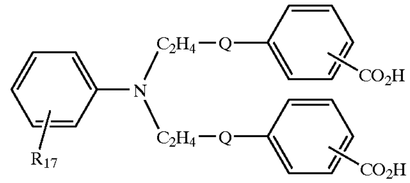

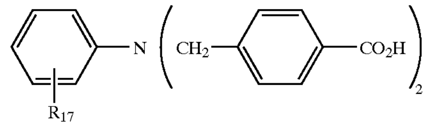

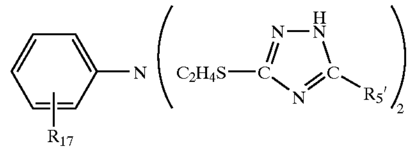

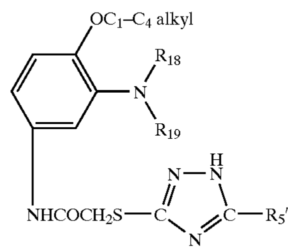

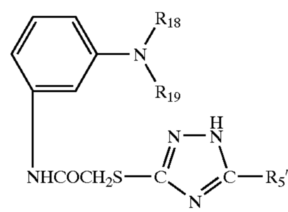

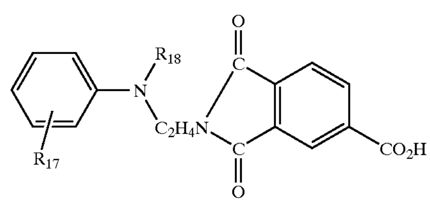

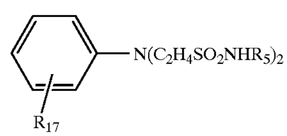

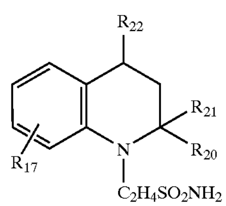

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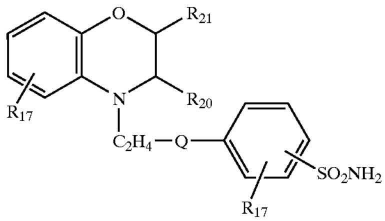

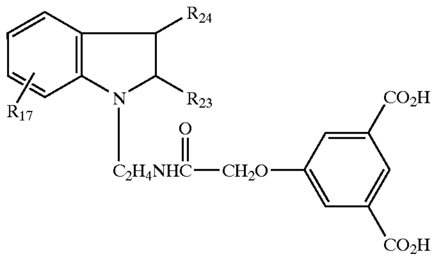

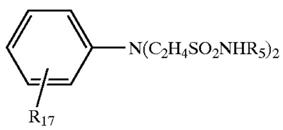

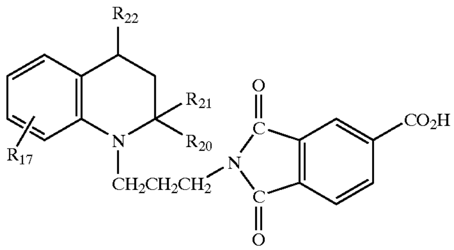

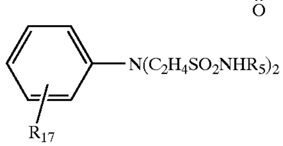

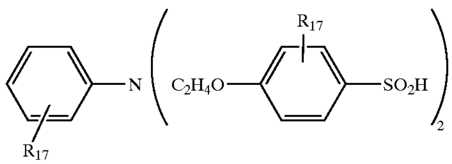

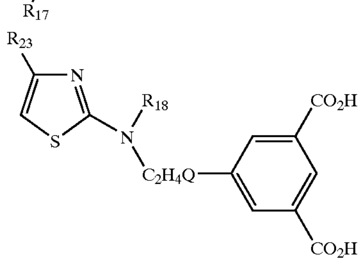

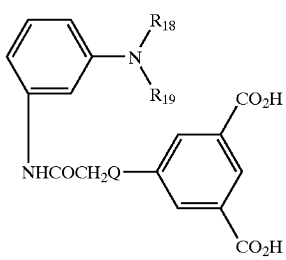

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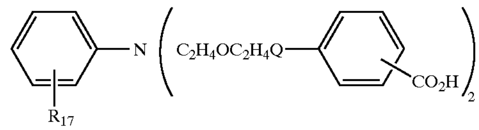

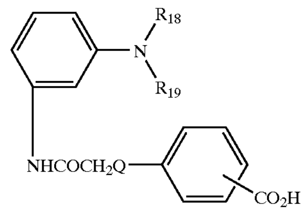

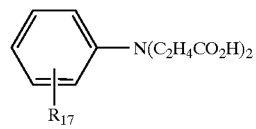

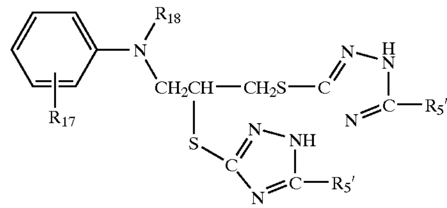

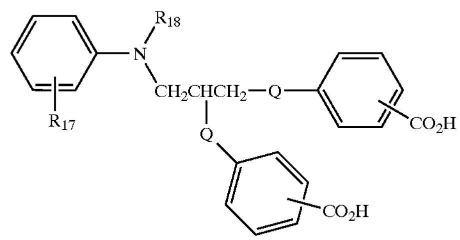

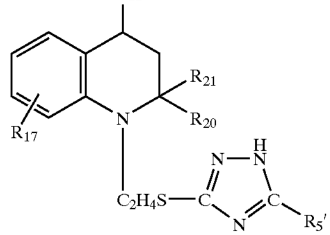

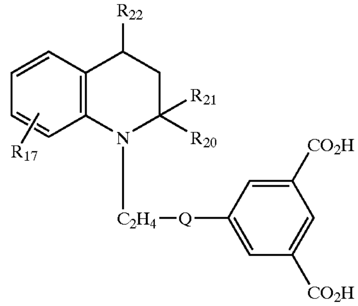

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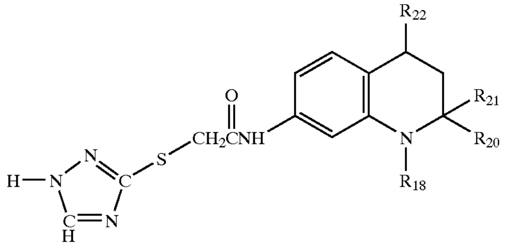
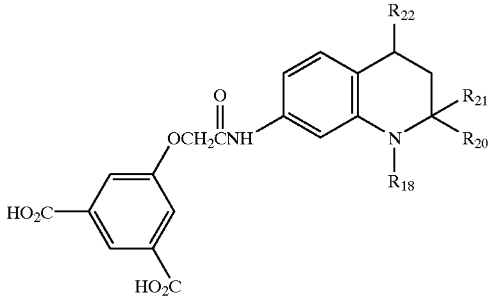
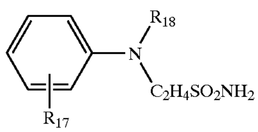
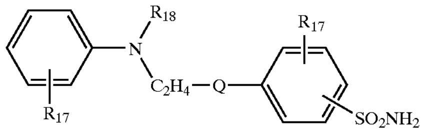
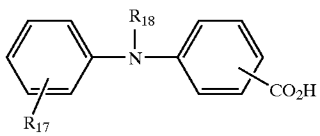










[0090] wherein Q, R_5', R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22} and R_{23} are as defined previously.

[0091] Typical diazotizable amines (R_6 NH_2) useful in the preparation of azo, disazo and bis-azo compounds of Formulae VI, VII, and VIIa, respectively, are adequately disclosed in the literature, e.g.:

[0092] M. Weaver and L. Shuttleworth, Dyes and Pigments, 3 (1982) 81-121;

[0093] L. Shuttleworth and M. Weaver, Chem. Appl. Dyes, 1990, 107-63, edited by D. Waring and G. Hallas, Plenum, New York, N.Y.;

[0094] U.S. Pat. Nos. 3,438,961; 3,573,273; 3,639,384; 3,707,532; 3,790,557; 3,816,388; 3,816,392; 3,878,189; 3,980,634; 4,012,372; 4,039,522; 4,049,643; 4,083,684; 4,083,844; 4,097,475; 4,105,655; 4,119,621; 4,140,683; 4,180,503; 4,189,428; 4,207,233; 4,211,696; 4,264,495; 4,283,332; 4,400,318; 4,431,585; 4,456,551; 4,487,719; 4,542,207; 4,564,673; 4,619,991; 4,621,136; 4,650,861; 4,668,775; 4,734,490; 4,751,288; 4,760,133; 4,764,600; 4,837,269; 4,841,036; 4,843,153; 4,888,432; 4,960,874; 5,037,966; 5,132,411; 5,144,015; 5,283,326; 5,296,325; 5,352,774.

[0095] Typical coupling components H-Z useful in preparing azo compounds, disazo and azo-methine compounds of Formula VI, VII and XIII, respectively, are disclosed in the literature, e.g: H. R. Schwander, Dyes and Pigments, 3(1982) 133-160; L. Shuttleworth and M. Weaver, Chem. Appl. Dyes, 1990, 107-63, edited by D. Waring and G. Hallas, Plenum, New York, N.Y.; U.S. Pat. Nos. 3,639,384; 3,639,385; 3,657,215; 3,673,169; 3,816,388; 3,829,410; 3,919,188; 3,950,130; 3,980,634; 4,041,025; 4,097,475; 4,119,621; 4,179,435; 4,234,482; 4,283,332; 4,341,700; 4,400,318; 4,431,585; 4,396,547; 4,619,992; 4,642,339; 4,650,861; 4,668,775; 4,764,600; 4,837,269; 4,843,153; 5,235,047; 5,283,326; 5,352,774.

[0096] Typical active methylene compounds useful in the preparation of methine, arylidene, polymethine, azamethine and azo-methine compounds corresponding to Formulae VIII, VIIIa, VIIIb, IX and XIII, respectively, are disclosed in the literature, e.g. U.S. Pat. Nos. 4,338,247; 4,617,373; 4,617,374; 4,707,537; 4,749,774; 4,826,903; 4,845,187; 4,950,732; 4,981,516 and 5,283,326.

[0097] According to the present invention the light-absorbing polymeric and cyclic compositions are incorporated into a wide variety of thermoplastic polymers using conventional techniques, e.g. solution or melt blending, such as those employed to incorporate other additives in such polymers (see R. Gächter and H. Müeller, Editors: Plastics Additives Handbook, Hansu Publishers, New York, 1985, pp. 507-533; 729-741). For example, the light absorbing polymeric and cyclic compositions may be dry blended in the form of pellets or powders with or without adhesion promoters or dispersing agents. This premix can be subsequently processed on extruders or injection molding machines. Other conventional additives such as plasticizers, nucleating agents, flame retardants, lubricants, etc. may also be present in the final thermoplastic composition.

[0098] A wide range of thermoplastic polymers useful for blending with the light absorbing polymeric and cyclic compositions are known in the art and includes the homopolymers, copolymers and blends of polyesters, e.g., poly(ethylene terephthalate); polyolefins, e.g., polypropylene, polyethylene, linear low density polyethylene, polybutylene, and copolymers made from ethylene, propylene and/or butylene; copolymers from acrylonitrile, butadiene, and styrene; copolymers from styrene and acrylonitrile; polyamides, e.g., Nylon 6 and Nylon 66; polyvinyl chloride; polyurethanes; polyvinylidene chloride; polycarbonates; cellulose esters, e.g., cellulose acetate, propionate, butyrate, or mixed esters; polyacrylates, e.g., poly(methyl methacrylate); polyimides; polyester-amides; polystyrene; and mixtures or blends thereof etc.

[0099] It should also be appreciated that a multiplicity of colors may be obtained by combining individual colors, e.g., subtractive colors such as yellow, magenta and cyan according to known color technology (see N. Ohta, *Photographic Science and Engineering*. Volume 15, No. 5, September-October 1971, pp. 395-415).

[0100] The particular chromophore groups present will, of course, determine the color (hue+value+chroma) of the colored polymer composition and finally the color (hue+value+chroma) of the thermoplastic polymer blends of the present invention. A large gamut of colors may be obtained, as noted above.

[0101] The actual amount of the light absorbing polymers used in combination with thermoplastic polymer will depend upon the inherent tinctorial strength of the chromophore used to prepare the light absorbing polymer, the mole % of the light absorbing monomer used to prepare the light absorbing polymer and the required level of light absorption necessary to achieve a certain property. Typically, the amount of light-absorbing polymer added to the thermoplastic polymer is such that the total amount of light-absorbing polymer in the final thermoplastic blend is from about 0.001% by weight to about 20% by weight, preferably from about 0.01% by weight to about 10% by weight. The final thermoplastic polymer blends thus provided are useful as a variety of molded and extruded articles, including thick and thin plastic films, plastic sheeting, molded plastic articles, containers and fibers, and the like.

[0102] When the light-absorbing polymeric compositions absorb visible light they may be used to impart light or heavy shades of a variety of colors to thermoplastics. Certain compounds which possess unique visible light-absorbing properties are useful also as toners in imparting a desirable neutral to slightly blue hue to polyesters having a yellow appearance as described in U.S. Pat. No. 5,384,377, which discloses the copolymerization of certain thermally stable colorants for this purpose during polyester manufacture. Some of the infra-red absorbing polymeric and cyclic compositions are useful in imparting invisible markings to thermoplastics as described in U.S. Pat. No. 5,461,136, wherein the infrared absorbing compounds are fluorescent in the near infrared and are copolymerized into the thermoplastic condensation polymer during manufacture. The ultra violet absorbing polymeric and cyclic compositions may be used to impart ultra violet (UV) light screening properties to the thermoplastics; to serve as optical brighteners for the thermoplastics or to serve as UV stabilizers for the polymers themselves or for other light absorbers such as colorants.

[0103] The weight average molecular weights (Mw) and the number average molecular weights (Mn) of the polymeric compositions were determined using gel permeation chromatography (GPC) analysis.

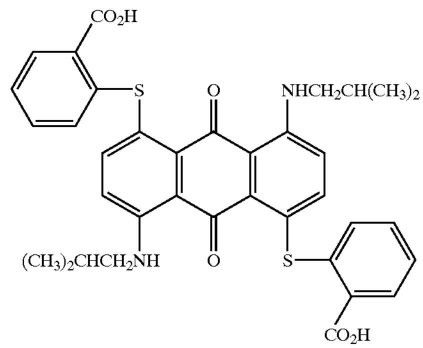
[0104] The following examples illustrate further the practice of the invention.

EXAMPLE 1

[0105] A mixture of 1,5-bis(2-carboxyphenylthio) anthraquinone (25.60 g, 0.05 mole), 1,2-ethanediol, dimethanesulfonate (10.90 g, 0.05 mole), potassium carbonate (13.82 g, 0.10 mole) and N-methyl-2-pyrrolidinone (NMP) (400 mL) was heated with stirring at 125° C. for 1.0 hr. The reaction mixture was poured into methanol (600 mL) with stirring. The yellow polymeric product was collected by filtration and washed with methanol until filtrate was essentially clear. The methanol-wet filter cake was slurried in 1.0 L of water, the mixture acidified by the addition of acetic acid and the yellow product was collected by filtration, washed with hot water and dried in air (yield- 21.16 g). By gel permeation chromatography (GPC) the polymeric product has a weight average molecular weight of 6,083, and number average molecular weight of 3,000 and a polydispersity value of 2.03.

EXAMPLE 2

[0106] A mixture of a blue anthraquinone compound (19.65 g 0.03 mole) containing two carboxy groups and having the following structure:



[0107] 1,2-ethanediol, dimethanesulfonate (6.54 g, 0.03 m),potassium carbonate (8.28 g, 0.06 mole) and N,N-dimethylformamide (DMF) (100 mL) was heated with stirring at about 95° C. for 1.5 hr. The reaction mixture became too thick to stir effectively and additional DMF (50 mL) was added to facilitate stirring. Stirred about 15 min. longer at about 95° C., and then added methanol (100 mL) with good stirring to the slightly cooled reaction mixture. The blue polymeric product was collected by filtration and washed with methanol. The methanol-wet filter cake was added to water (600 mL) and the mixture was acidified with acetic acid, and then the polymeric product was collected by filtration, washed with water and dried in air (yield 18.18 g). By GPC analysis the blue polymer had a molecular weight average of 3,038, a number average molecular weight of 1,814 and a polydispersity of 1.67.

EXAMPLE 2a

[0108] A mixture of 1,5-bis (isobutylamino)-4,8-dibromoanthraquinone (25.3 g, 0.05 mole), thiosalicylic acid (23.1 g, 0.15 mole), anhydrous K_2CO_3 (20.7 g, 0.15 mole), cupric chloride dihydrate (1.2 g) and DMF (250 mL) was heated at 90-95° C. with stirring for 2.0 hours. Thin layer chromatography (TLC) using 1:1 tetrahydrofuran (THF):cyclohexane showed complete conversion of the red starting material to the desired blue polar product. The reaction mixture was allowed to cool and then was drowned into water (800 mL). The blue solid was precipitated by acidification with acetic acid with stirring. The mixture was heated to about 60° C. with occasional stirring and the solid was collected by filtration, washed with hot water and dried in air. Further purification was accomplished by reslurrying the product in hot methanol (300 mL), allowing to cool to room temperature, collecting by filtration, washing with methanol and air drying to yield the starting material (31.5 g) for Example 2.

EXAMPLE 2b

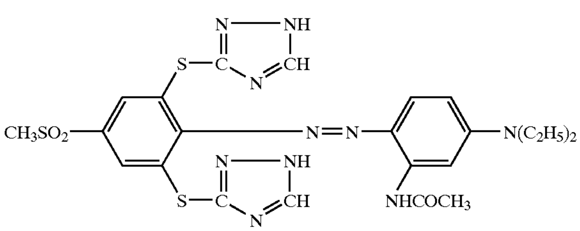
[0109] 1,5-Bis(isobutylamino)anthraquinone (28.0 g, 0.08 mole) was added to DMF (300 mL) and the mixture stirred at room temperature. A solution of 1,3-dibromo-5,5-dimethylhydantoin (23.0 g, 0.08 m) dissolved in DMF (75.0 mL) was added dropwise to the reaction mixture while warming to about 50° C. After complete addition of the brominating agent, the reaction mixture was heated at 50-60° C. for 1.5 hours, allowed to cool and then drowned by gradual addition to water (500 mL) with stirring. The red product was collected by filtration, washed with water and dried in air. The yield of product was 39.6 g and field desorption mass spectrum analysis (FDMS) showed the product to be 1,5-bis(isobutylamino)-4,8-dibromoanthraquinone used as the intermediate in Example 2a.

EXAMPLE 2c

[0110] A mixture of 1,5-dichloroanthraquinone (69.5 g, 0.25 mole), isobutylamine (100 g, 1.4 mole) and 2-ethoxyethanol (400 mL) was heated at reflux for 36.0 hours and allowed to cool. Methanol (400 mL) was added to make the mixture containing the crystallized product more stirrable. The dark red product was collected by filtration, washed with methanol, reslurried in hot methanol and allowed to cool, collected by filtration, washed with methanol and dried in air (yield—67.7 g). FDMS showed the product to be the 1,5-bis(isobutylamino)anthraquinone in high purity which was used as the starting material for Example 2b.

EXAMPLE 3

[0111] A mixture of an azo compound (2.93 g, 0.005 m) containing two 1(H)-1,2,4-triazol-3-thio groups and having the following structure:



[0112] 1,2-ethanediol, dimethanesulfonate (1.08 g, 0.005 mole), potassium carbonate (1.50 g) and DMF (25.0 mL) was heated at about 95° C. with stirring for 2.5 hrs. The reaction mixture was drowned into methanol (150 mL) and the red polymeric product was collected by filtration, washed with. water containing a little acetic acid and then washed with hot water and dried in air (yield—2.35 g). The polymer by GPC analysis had a weight average molecular weight of 5,396, a number average molecular weight of 3,044 and a polydispersity value of 1.77.

EXAMPLE 4

[0113] Eastar® PETG copolyester 6763, a poly(ethylene-1,4-cyclohexanedimethylene) terephthalate, (Eastman Chemical Co.) (400 g. of previously dried pellets) was dry blended with the yellow anthraquinone polymeric composition (0.12 g) of Example 1. The blend was extruded with a C. W. Brabender ¾ in. extruder, equipped with a mixing screw, at 250° C. into a water bath and the extrudate pelletized.

[0114] The pellets were redried at 70° C. for about 17 hrs. at a pressure of about 1-5 torr. A portion of the dried pellets (1.40 g) was pressed into a 18-20 mil film at 250° C. using a 2-inch diameter circular mold in a Pasadena Hydraulic, Inc. press using 12,000 pounds ram force (4 inch ram). A transparent yellow film was produced with excellent color development, which contained about 300 ppm by weight of the yellow polymeric composition.

EXAMPLE 5

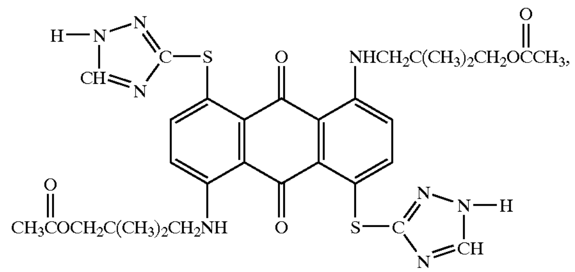
[0115] Example 4 was repeated using 0.12 g of the blue anthraquinone polymeric composition of Example 2 to give a bright blue transparent copolyester film with good color development.

EXAMPLE 6

[0116] Example 4 was repeated using 0.12 g of the red azo polymeric composition of Example 3 to produce a bright red transparent film having good color development.

EXAMPLE 7

[0117] A mixture of a blue anthraquinone compound (3.46 g, 0.005 mole) containing two acidic 1(H)-1,2,4-triazol-3-ylthio groups and having the following structure



[0118] 1,2-ethanediol, dimethanesulfonate (1.09 g, 0.005 mole) DMF (30 mL) and potassium carbonate (1.5 g) was heated with stirring at about 95° C. for 2.0 hours and then drowned into methanol (100 mL). The blue polydye was collected by filtration and washed with methanol. The methanol-wet cake was reslurried in water (400 mL) and the stirred mixture was acidified by addition of acetic acid and heated to about 60° C. The final polymeric product was collected by filtration, washed with water and dried in air (yield—1.5 g). Absorption maxima were observed at 594, 636 nm in a solution of DMF in the visible light absorption spectrum. By GPC, the polydye has a weight average molecular weight (Mw) of 3,769, a number average molecular weight (Mn) of 2,119 and a polydispersity of 1.78.

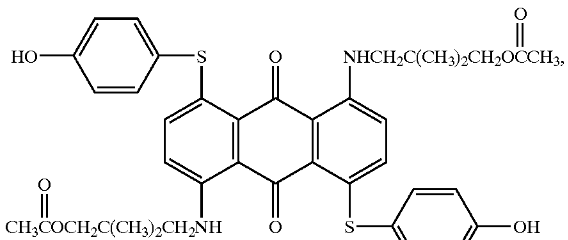
EXAMPLE 7a

[0119] A mixture of 1,5-bis[(3-acetoxy-2,2-dimethylpropyl)amino-4,8-dibromoanthraquinone (6.50 g, 0.01 mole) (product of Example 2—Invention Report Docket No. 70524), 3-mercapto-1(H)-1,2,4-triazole (3.03 g, 0.03 mole), potassium carbonate (4.15 g, 0.03 mole), cupric chloride dihydrate (0.65 g) and DMF (100 mL) was heated 14 hours at about 100-105° C. The reaction mixture was drowned into a mixture of water (400 mL) and 10% aqueous solution of hydrochloric acid (200 mL). The blue product was collected by filtration, washed with hot water and dried in air (yield—

6.58 g). FDMS supported the desired structure of the starting anthraquinone compound for Example 7.

EXAMPLE 8

[0120] A mixture of blue anthraquinone compound (2.48.g, 0.0033 mole) having the following structure



[0121] 1,2-ethanediol, dimethanesulfonate (0.73 g, 0.0033 mole), potassium carbonate (0.5 g) and DMF (30.0 mL) was heated at about 95° C. for 3.0 hours. The reaction mixture was drowned into methanol (150 mL) with stirring and the blue polydye product was collected by filtration and washed with methanol. The. methanol-wet cake was reslurried in water (200 mL) and the mixture acidified with acetic acid. Collecting the blue solid by filtration, washing with hot water and air drying gave 1.21 g of polydye product, which has absorption maxima at 606,652 nm in DMF in the visible absorption spectrum, a weight average molecular weight of 4,453, a number average molecular weight of 2,721 and a polydispersity of 1.6.

EXAMPLE 8a

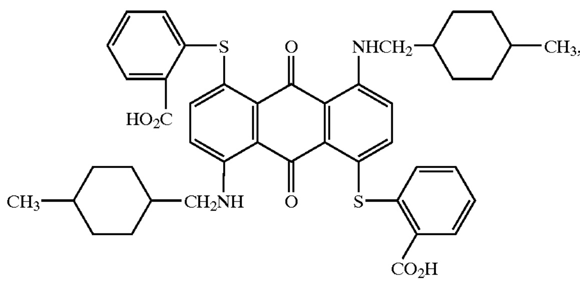
[0122] A mixture of 1,5-bis[(3-acetoxy-2,2-dimethylpropyl)amino]-4,8-dibromoanthraquinone (19.56 g, 0.03 mole), p-hydroxybenzenethiol (17.64 g, 0.14 mole), potassium carbonate (19.32 g, 0.14 mole), cupric chloride dihydrate (1.0 g) and DMF (150 mL) was heated and stirred at 90-95° C. for 7.0 hours and then at 120° C. for about 2.0 additional hours. TLC (50:50 THF:cyclohexane) showed mostly the desired blue product, but still a small amount of violet half-reacted product was present. The reaction mixture was drowned into methanol (500 mL) and the mixture allowed to cool. After crystallization, the blue solid was collected by filtration, washed with methanol, washed with hot water and then dried in air (yield—17.6 g). FDMS supported the desired structure of the starting anthraquinone compound for Example 8. In the visible light absorption spectrum in DMF, a maximum absorbance (λmax) was observed at 652 nm (extinction coefficient ϵ of 24,638).

EXAMPLE 9

[0123] A mixture of 1,4-bis-(2,6-dimethyl-4-hydroxyanilino)anthraquinone (4.78 g, 0.01 mole) (Synthesis Example 1 of U.S. Pat. No. 3,918,976), 1,2-ethanediol, dimethanesulfonate (2.18 g, 0.01 mole), potassium carbonate. (3.0 g) and DMF (60 mL) was heated at 90-95° C. with stirring for 4.0 hours. After drowning the reaction mixture into methanol (300 mL), the product was collected by filtration and washed with methanol until filtrate was essentially colorless. The methanol-wet cake was reslurried in 100 mL water and acidified by adding acetic acid with stirring. After heating to about 50° C., the product was collected by filtration, washed with hot water and dried in air (yield—1.2 g). By GPC, the blue polydye had a weight average molecular weight (Mw) of 2,764, a number average molecular weight (Mn) of 1,607 and a polydispersity of 1.72. In DMF, the visible light absorption maxima were at 586,630 nm.

EXAMPLE 10

[0124] A mixture of an anthraquinone diacidic compound (1.52 g, 0.002 mole) having the following structure



[0125] 1,2-ethanediol, dimethanesulfonate (0.44 g, 0.002 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated at about 95° C. with occasional stirring for 20 hours. The reaction mixture was downed into methanol (50 mL) and the product was collected by filtration, washed with methanol, water plus acetic acid, hot water and then dried in air (yield—1.05 g). The blue polydye had a weight average molecular weight (Mw) of 3,586, a number average molecular weight (Mn) of 1,867 and a polydispersity value of 1.92. In the visible light absorption spectrum, maxima of absorbance occurred at wavelengths of 605 and 647 nm in DMF.

EXAMPLE 10a

[0126] A mixture of 1,5-bis-(4-methylcyclohexanemethylamino)-4,8-dibromoanthraquinone (20.0 g, 0.0324 mole), thiosalicyclic acid (11.55 g, 0.075 mole), potassium carbonate (10.35 g, 0.075 m), cupric chloride dihydrate (1.0 g) and DMF (175 mL) was heated at about 95° C. for 4.0 hours and then drowned into acetone (400 mL). The solid which crystallized was collected by filtration, washed with acetone until the filtrate was no longer red. The dipotassium salt of the diacidic anthraquinone compound was dissolved by adding to water (500 mL) and stirring. The blue product which was precipitated by acidification with acetic acid was collected by filtration, washed with hot water and then dried in air (yield—21.5 g). FDMS indicated the structure to be consistent with that given above in Example 10 for the starting diacidic anthraquinone compound.

EXAMPLE 10b

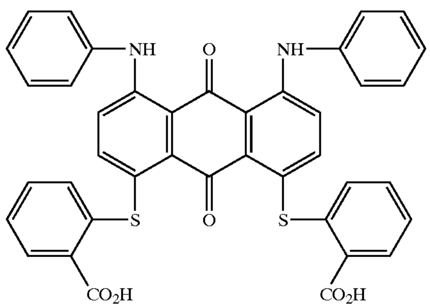
[0127] A solution of 1,5-bis-(4-methylcyclohexanemethylamino)anthraquinone (65.0 g, 0.142 mole) dissolved in DMF (1.0 L) by stirring at about 55° C. was treated with a solution of N-bromosuccinimide (50.5 g, 0.284 mole) in DMF (200 mL). After addition was completed, the bromination reaction was completed by heating at 55-60° C. for 2.0 hours. Water (1.0 L) was added. to precipitate the red product which was collected by filtration, washed with water and dried in air. After being reslurried in hot methanol and cooling, the product was collected by filtration, washed with a little methanol and air dried (yield—84.0 g). FDMS indicated the structure to be that of the starting, dibrominated anthraquinone compound of Example 10a.

EXAMPLE 10c

[0128] A mixture of 1,5-dichloroanthraquinone (48.0 g, 0.17 mole), 4-methyl-1-aminomethylcyclohexane (88.9 g, 0.70 mole), 2-ethoxyethanol (400 mL) was stirred and heated at reflux for 35.0 hours and the reaction mixture allowed to cool. The red product was precipitated by the addition of methanol and was the collected by filtration, washed with methanol and dried in air (yield—66.0 g). FDMS indicated the product to be the starting anthraquinone compound for Example 10b.

EXAMPLE 11

[0129] A mixture of diacidic anthraquinone compound (0.69 g, 0.001 m) having the following structure



,

[0130] 1,6-hexanediol, dimethanesulfonate (0.27 g, 0.001 mole), potassium carbonate (0.3 g) and DMF (5.0 mL), was heated with occasional stirring for 2.5 hours at about 95° C. The reaction mixture was drowned into methanol (100 mL) and the product collected by filtration, washed with methanol, water containing a little acetic acid and then finally with hot water and air dried (yield—0.45 g). The blue polydye had an absorption maximum at 610 nm in DMF, a weight average molecular weight of 3,311 a number average molecular weight of 1,272 and a polydispersity value of 2.63.

EXAMPLE 11a

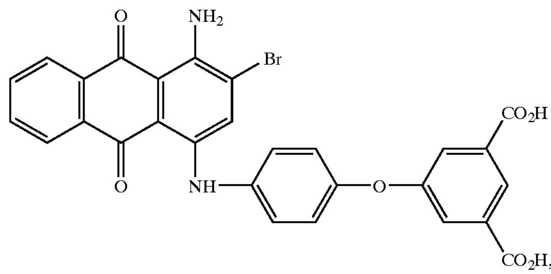
[0131] A mixture of 1,8-di-(2-carboxyphenylthio)-4,5,-dinitroanthraquinone (4.00 g, 0.0066 mole), aniline (2.5 g) and nitrobenzene (30.0 mL) was heated at reflux with stirring for 5.0 hours. The reaction mixture was drowned into hexane and the hexane decanted. The product was washed again by adding hexane, stirring and decanting. The crude product was slurried in acetone and heated to reflux and the blue product collected by filtration, washed with water and air dried (yield—0.75 g). FDMS indicated the product to be mostly 1,8-dianilino-4,5-di-(2-carboxyphenylthio)anthraquinone, the starting diacidic, anthraquinone compound for Example 11.

EXAMPLE 11b

[0132] The potassium salt of thiosalicyclic acid (4.75 g, 0.03 mole) was made by addition to DMF (75 mL) and heating in the presence of potassium carbonate (8.70 g, 0.06 mole) for 2.0 hours at about 95° C. The cooled mixture was added to a solution of 1,8-dichloro-4,5-dinitroanthraquinone (5.51 g, 0.015 mole) dissolved in DMF (150 mL) at about 0-5° C. with stirring. The reaction mixture was allowed to warm to about 25° C. with stirring continued for 2.0 hours and then poured into water. The product was obtained in essentially quantitatively yield by slowly acidifying with 10% hydrochloric acid and was then collected by filtration, washed with water and dried in air. FDMS indicated the product to be mostly the starting anthraquinone compound used in Example 11a.

EXAMPLE 12

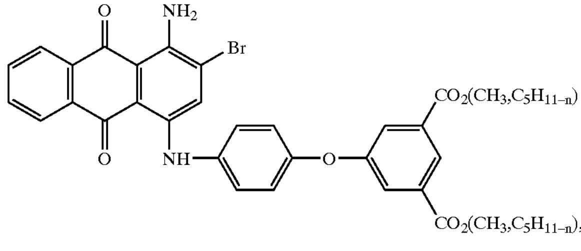
[0133] A mixture of the diacidic anthraquinone compound (0.85 g. 0.0015 m) having the following structure



[0134] 1,6-hexanediol, dimethanesulfonate (0.41 g, 0.0015 m), potassium carbonate (0.5 g) and DMF (5.0 mL) was heated at about 95° C. for 2.0 hours with occasional stirring. The reaction mixture was drowned into methanol (100 mL) and the blue polydye was collected by filtration, washed with methanol, water containing a little acetic acid and finally hot water and then dried in air (yield—0.62 g). GPC analysis indicated a weight average molecular weight of 20,020, a number average molecular weight of 2,313 and a polydispersity of 8.66. An absorption maximum was observed at 591 nm in the visible light absorption spectrum in DMF.

EXAMPLE 12a

[0135] The anthraquinone diester compound (4.00 g) having the following structure



[0136] 50% aqueous sodium hydroxide (2.40 g) and 2-ethoxyethanol (60 mL) were combined and heated with stirring at about 95° C. for 0.5 hour. Hydrolysis of ester groups appeared to be complete by TLC (50:50 THF:cyclohexane). The reaction mixture was drowned into water (600 mL) and the blue solution acidified using acetic acid. The blue solid was collected by filtration washed with water and dried in air (yield—3.80 g). FDMS indicated the structure to be mostly that of the starting diacidic anthraquinone compound in Example 12 plus a small amount of a violet compound probably produced by displacement of the bromine atom with the 2-(ethoxy)ethoxy group.

EXAMPLE 12b

[0137] A mixture of 1-amino-2,4-dibromoanthrquinone (7.62 g, 0.02 mole), dimethyl 5(4-aminophenoxy)isophthalate (9.03 g, 0.03 mole), 1-pentanol (100 mL), potassium acetate 4.0 g), and cupric acetate (0.2 g) was heated at reflux for 4.0 hours and until all of the starting material had been used up as indicated by TLC analysis (20:80 THF:cyclohexane). Several blue components presumed to be a mixture of ester products produced by transesterification were observed. The reaction mixture was drowned into methanol (100 mL) and the product was collected by filtration, washed thoroughly with methanol to remove a red by-product and then washed with water and dried in air (yield—7.81 g). FDMS indicated ions corresponding to the dimethylester, monopentyl ester and dipentylester of the product—the structure of the starting material for Example 12a.

EXAMPLE 12c

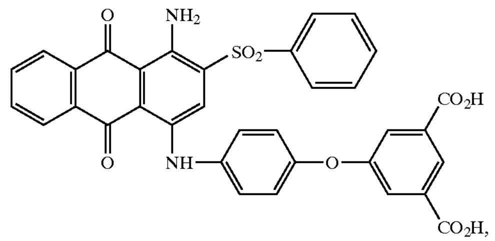
[0138] A mixture of dimethyl 5-(4-nitrophenoxy)isophthalate (30.0 g, 0.09 mole), isopropanol alcohol (350 mL) and ethanol wet Raney nickel catalyst (5.0 g) was hydrogenated at 90° C. for 4.0 hours at 1500 psi hydrogen pressure in an autoclave. Isopropanol (100 mL) was added to the reaction mixture from the autoclave and the solid product dissolved by heating. The Raney nickel was removed by hot filtration and the filtrate allowed to cool. The off-white solid was collected by filtration and dried in air (yield—17.8 g). FDMS indicated the product to be dimethyl 5-(4-aminophenoxy)isophthalate used in Example 12b.

EXAMPLE 12d

[0139] A mixture of 1-chloro-4-nitrobenzene (47.1 g, 0.30 mole), dimethyl 5-hydroxyisophthalate (63.0 g, 0.30 mole), anhydrous potassium carbonate (41.4 g), potassium iodide (0.2 g) and DMF (200 mL) was heated at 120-125° C. for 1.5 hours, under a slow nitrogen sweep allowing some distillate to be removed (about 75 mL) via a Dean-Stark trap. Additional DMF (50 mL) was added back to the reaction mixture and heating continued for an additional 1.5 hours while an additional amount of distillate (25 mL) was allowed to collect in the Dean-Stark trap. The reaction mixture was allowed to cool to about 45° C. A heavy slurry of pale yellow product resulted which was diluted further by the addition of an ice-water mixture (350 g) with good stirring. Filtration followed by washing with water and drying in air gave the pale yellow dimethyl 5-(4-nitrophenoxy)isophthalate (90.7 g) (structure supported by FDMS) which was used in Example 12c.

EXAMPLE 13

[0140] A mixture of the diacidic anthraquinone compound (1.26 g, 0.002 mole) having the following structure



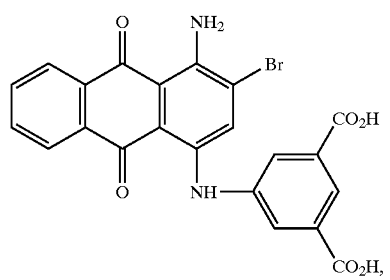
[0141] 1,6-hexandiol, dimethanesulfonate (0.58 g, 0.002 mole), potassium carbonate (0.5 g) and DMF (6.0 mL) was heated at 90-95° C. for 2.0 hours with occasional stirring. The reaction mixture was drowned into methanol (100 mL) and the dark blue-green polydye was collected by filtration, washed with methanol, water containing a little acetic acid and finally with water and then dried in air (yield 1.13 g). GPC analysis indicated a weight average, molecular weight of 14,776, a number average molecular. weight of 2,514 and a polydispersity of 5.88. An absorption maximum was observed at 620 nm in the visible light absorption spectrum in DMF.

EXAMPLE 13a

[0142] A portion (1.72 g, 0.003 mole) of the bromoanthraquinone product of Example 12a, benzenesulfinic acid, Na salt (0.98 g, 0.006 mole), potassium carbonate (1.38 g) and DMF (25 mL) were mixed and the reaction mixture heated with stirring at 90-95° C. for 1.0 hour. A bathochromic shift in color was observed as the 2-bromo substituent was replaced by the 2-phenylsulfonyl group on the anthraquinone nucleus. The greenish-blue solution was drowned into acetone (100 mL) and the solid material was collected by filtration and washed with acetone until the filtrate was pale blue. The acetone-wet solid was added with stirring to water (200 mL) and the mixture acidified with acetic acid. After being heated to about 75° C., the reaction mixture was filtered and the dark blue solid was washed with hot water and dried in air (yield—1.50 g). FDMS indicated the structure to be that of the starting diacidic anthraquinone compound used in Example 13.

EXAMPLE 14

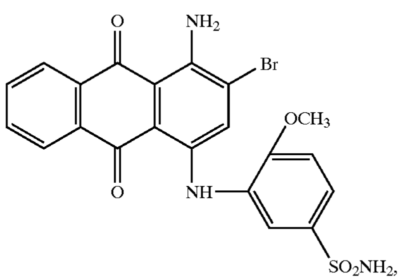
[0143] A mixture of the diacidic anthraquinone compound (1.45 g, 0.003 mole) having the structure



[0144] 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated at about 95° C. for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the blue polydye was collected by filtration and washed with methanol, water containing a little acetic acid and finally hot water and dried in air (yield—1.10 g). GPC analysis indicated a weight average molecular weight of 3,727, a number average weight of 1,031 and a polydispersity of 3.61. Absorption maxima were observed at 623 nm and 585 nm in the visible light absorption spectrum in DMF.

EXAMPLE 15

[0145] A mixture of the diacidic anthraquinone compound (1.50 g, 0.003 mole) having the following structure



[0146] 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated with occasional stirring at about 95° C. for 2.0 hours. The reaction mixture was then drowned into methanol (100 mL) and the blue polydye was collected by filtration, washed with methanol, water containing a little acetic acid, and hot water and then dried in air (yield—0.90 g). An absorption maximum at 591 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 15a

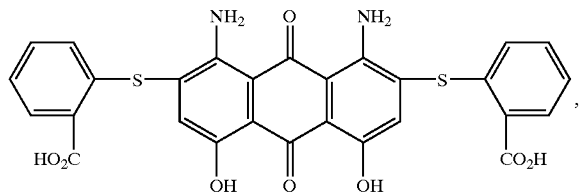
[0147] To DMF (40 mL) was added 1-amino-2-Br-4-(5-chlorosulfonyl-2-methoxyanilino) anthraquinone (4.0 g) with stirring. When solution appeared to be complete, conc. ammonium hydroxide (4.0 g) was added and stirring was continued at ambient temperature for 30 minutes. TLC using 50:50 THF:cyclohexane indicated complete reaction of the sulfonyl chloride compound to produce the desired sulfonamide. The reaction mixture was drowned into water and the blue product was collected by filtration, washed with water and air dried (yield—3.8 g). FDMS indicated the structure to be that of the starting compound for Example 15.

EXAMPLE 15b

[0148] To chlorosulfonic acid (100 mL) was added 1-amino-4-o-anisidino-2-bromoanthraquinone (10.0 g, 0.0236 mole) portionwise with good stirring at 25-30° C. After addition was completed, the reaction mixture was stirred at room temperature for 1.0 hour. The reaction mixture was added in a fine stream to cold isopropanol (800 mL) with stirring. The blue product was collected by vacuum filtration on a sintered glass funnel, washed with isopropanol and dried in air (yield—10.3 g) and used without further purification in Example 15a.

EXAMPLE 16

[0149] A mixture of the diacidic anthraquinone compound (0.58 g, 0.001 m) having the following structure



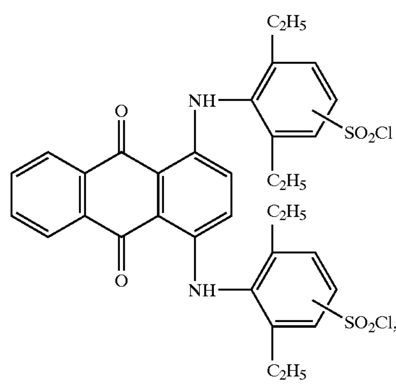
[0150] 1,2-ethanediol, dimethanesulfonate (0.22 g, 0.001 m), potassium carbonate (0.3 g) and DMF (5.0 mL) was heated at 95° C. for 2.5 hours. The reaction mixture was drowned into methanol (100 mL) and the greenish-blue polydye was collected by filtration, washed with methanol, water containing a little acetic acid and water and then air dried (yield—0.33 g). GPC analysis indicated a weight average molecular weight of 4,144 a number average molecular weight of 1,643 and a polydispersity of 2.52. An absorption maximum at 629 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 16a

[0151] A mixture of 1,8-diamino-2,7-dibromo-4,5-dihydroxyanthraquinone (2.19 g, 0.005 mole), thiosalicyclic acid (1.60 g, 0.104 mole), potassium carbonate (1.5 g) and DMF (25.0 mL) was heated at 95-100° C. for 6.0 hours. A bathochromic shift in color occurred as the two bromine atoms were replaced by the 2-carboxyphenylthio groups. The reaction mixture was drowned into methanol and the solid product was collected by filtration and washed with methanol. The product was dissolved in water (100 mL) and the diacidic anthraquinone which precipitated by addition of acetic acid was collected by filtration, washed with water and dried in air (yield—0.86 g). FDMS indicated the product to be that used as starting material for Example 16.

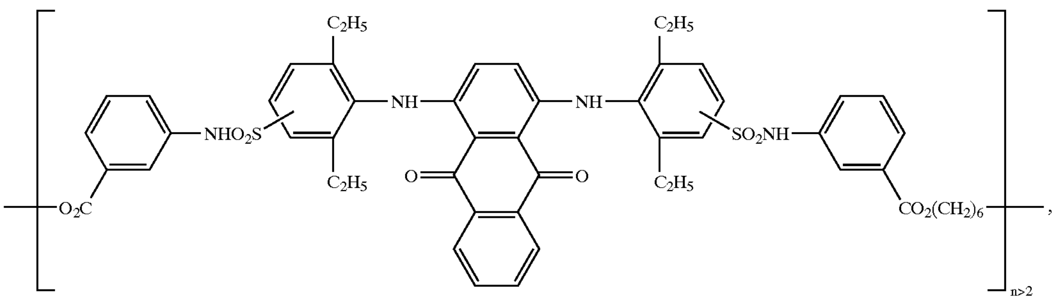
EXAMPLE 17

[0152] The anthraquinone disulfonyl chloride compound (3.50 g, 0.005 mole) having the following structure



[0153] (prepared according to the procedure of U.S. Pat. No. 5,453,482, Example 2), m-aminobenzoic acid (1.37 g, 0.10 mole), potassium carbonate (2.80 g) and DMF (30 mL) were mixed and the reaction mixture heated at 90-95° C. for

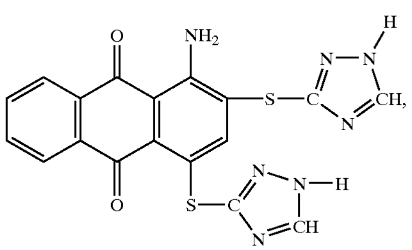
30 minutes. TLC (50:50 THF:cyclohexane) indicated complete reaction of the disulfonyl chloride to produce the disulfonamide derivative. To the reaction mixture were added 1,6-hexanediol, dimethanesulfonate (1.38 g, 0.005 m), potassium carbonate (1.38 g) and heating and stirring were continued for 2.0 hours at 90-95° C. The reaction mixture was drowned into water and acidified with acetic acid. The bright blue polydye was collected by filtration, washed with water and then air dried (yield—2.07 g) and is believed to have the following repeat unit:



[0154] GPC analysis indicated a weight average molecular weight of 5,252, a number average molecular weight of 2,179 and a polydispersity of 2.41. Absorption maxima at 583 nm and 628 nm were observed in the visible light absorption spectrum in DMF.

EXAMPLE 18

[0155] A mixture of the diacidic anthraquinone compound (4.21 g, 0.01 mole) having the following structure



[0156] 1,2-ethanediol, dimethanesulfonate (2.18 g, 0.01 mole), potassium carbonate (2.68 g, 0.02 mole) and DMF (50 mL) was heated and stirred at 90-95° C. for 1.5 hours. The reaction mixture was drowned into water (400 mL) and acidified with stirring and by adding acetic acid. After being heated to about 50° C., the mixture was filtered and the red polydye washed well with water and dried in air (yield—4.47 g). GPC analysis showed the polydye to have a weight average molecular weight of 1,603, a number average molecular weight of 922 and a polydispersity of 1.74. An absorption maximum at 524 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 18a

[0157] A mixture of 1-amino-2,4-dibromoanthraquinone (11.43 g, 0.03 mole), 3-mercapto-1(H)-1,2,4-triazole (9.09 g, 0.09. mole), potassium carbonate (11.52 g, 0.09 mole) and DMF (150 mL) was heated at about 95° C. with stirring for 1.0 hour. The reaction mixture was drowned into water (500 mL) with stirring and acidified with acetic acid and the red product collected by filtration, washed with water and dried in air (yield—12.64 g). FDMS indicated the product to be the diacidic anthraquinone compound used in Example 18.

EXAMPLE 19

[0158] A mixture of 1,5-bis-(4-hydroxyphenylthio)anthraquinone (4.56 g, 0.01 mole), 1,2-ethanediol, dimethanesulfonate (2.18 g, 0.01 mole), potassium carbonate (3.0 g) and DMF (50 mL) was heated and stirred at about 95° C. for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the yellow polydye was collected by filtration and washed with methanol. The methanol-wet cake was reslurried in water (500 mL) and acidified and the polydye then collected by filtration, washed with water and dried in air (yield—4.25 g). GPC analysis indicated the polydye to have a weight average molecular weight of 1,901, a number average molecular weight of 1,588 and a polydispersity of 1.20. An absorption maximum at 461 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 19a

[0159] A mixture of 1,5-dichloroanthraquinone (5.54 g, 0.02 mole), 4-hydroxybenzenethiol (6.30 g, 0.05 mole), potassium carbonate. (6.90 g, 0.05 mole) and DMF (100 mL) was heated at about 95° C. for 5.0 hours. The reaction mixture was drowned into water (400 mL) and the yellow product was collected by filtration, washed with water and dried in air (yield—9.0 g). The solid was added to acetic acid (150 mL) and the mixture heated to boiling. After being allowed to cool, the yellow solid was collected by filtration, washed with acetic acid and dried in air (yield—6.75 g). FDMS confirmed that the product was the 1,5-bis(4-hydroxyphenylthio)anthraquinone used in Example 19.

EXAMPLE 20

[0160] A mixture of 1,4-bis-(2-carboxyphenylthio)anthraquinone (1.53 g, 0.003 m), 1,2-ethanediol, dimethanesulfonate (0.66 g, 0.003 mole), potassium carbonate (0.75 g) and DMF (8.0 mL) was heated at about 95° C. with occasional stirring for 2.0 hours. The reaction mixture was then drowned into methanol (100 mL) and the dark orange polydye was collected by filtration, washed with water containing some acetic acid then with hot water and dried in air (yield—0.50 g). GPC analysis indicated a weight average molecular weight of 8,686, a number average molecular weight of 1,356 and a polydispersity of 6.41.

EXAMPLE 20a

[0161] A mixture of 1,4-dichloroanthraquinone (2.77 g, 0.01 mole), thiosalicylic acid (3.85 g, 0.025 m), potassium carbonate (3.45 g, 0.025 m), cupric chloride dihydrate (0.1 g) and DMF (50 mL) was heated at 95-100° C. with stirring for 4.0 hours. The reaction mixture was drowned into acetone and the solid was collected by filtration and washed with acetone. The resulting potassium salt of the product was dissolved by stirring in water (200 mL). The red solution was neutralized to give the orange product which was collect by filtration, washed with water and dried in air (yield—4.58 g). FDMS indicated the structure to be that of the starting material for Example 20. An absorption maximum at 501 nm was observed in the visible light absorption spectrum.

EXAMPLE 21

[0162] A mixture of 1,8-bis- (2-carboxyphenylthio)-4,5-bis-(p-tolylthio)anthraquinone (1.51 g, 0.002 mole), 1,4-butanediol, dimethanesulfonate (0.49 g, 0.002 mole), potassium carbonate (0.60 g and DMF (8.0 mL) was heated at 90-95° C. with occasional stirring for 2.5 hours. The reaction mixture was drowned into methanol (106 mL) and the red polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and then dried in air (yield—1.1 g). GPC analysis indicated a weight average molecular weight of 2,157, a number average molecular weight of 1,111 and a polydispersity of 1.94. An absorption maximum was observed at 529 nm in the visible light absorption spectrum in DMF.

EXAMPLE 21a

[0163] A mixture of thiosalicyclic acid (4.75 g, 0.03 mole), potassium carbonate (8.70 g, 0.06 mole) and DMF (75 mL), was heated at about 100° C. for 1.0 hour and the reaction mixture, which was allowed to cool, was added at 0-5° C. to a solution of 1,8-dichloro-4,5-dinitroanthraquinone (5.51 g. 0.015 mole) dissolved in DMF (150 mL) with good, stirring. Cooling was removed and the temperature of the reaction mixture allowed to come to ambient temperature and the mixture was stirred for about 3.0 hours. A solution of p-thiocresol (3.73 g, 0.03 mole) dissolved in DMF (80 mL) was added to the reaction mixture with stirring and the temperature raised to about 100° C. and held for 2.0 hours. After allowing to cool, the reacting mixture was drowned into water (300 mL) and the mixture gradually acidified by the addition of 10% aqueous hydrochloric acid. The red solid product was collected by filtration, washed with water and dried in air (yield—11.28 g). FDMS analysis indicated that the product consisted mostly of the starting material for Example 21.

EXAMPLE 22

[0164] A mixture of 1,5-bis(2-carboxyphenylthio)anthraquinone (1.54 g, 0.003 mole), 1,5-bis(2-carboxyhenylthio)-4,8-bis(isobutylamino)anthraquinone (1.31 g, 0.002 mole) (product of Example 2a), 1,2-ethandiol, dimethanesulfonate (1.09 g, 0.005 mole), potassium carbonate (1.0 g) and DMF (10 mL) was heated at 90-95° C. with occasional stirring for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the green polydye was washed with methanol, water containing acetic acid, hot water and then dried in air (yield—1.30 g). GPC analysis indicated a weight average molecular weight of 1,839, a number average molecular weight of 1,040 and a polydispersity of 1.77. Absorption maxima were observed in the visible light absorption spectrum in DMF at 448, 603, and 645 nm.

EXAMPLE 23

[0165] A mixture of 1,5-bis(2-carboxyphenylthio)anthraquinone (1.28 g, 0.0025 mole), 1,4- cyclohexanedimethanol, dimethanesulfonate (1.75 g, 0.0025 mole), potassium carbonate (0.82 g) and DMF (7.5 mL) was heated at about 95° C. with occasional stirring for 3.0 hours. The reaction mixture was drowned into methanol (100 mL) and the yellow polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and then dried in air (yield—0.31 g). GPC analysis indicated a weight average molecular weight of 1,158, a number average molecular weight of 1,008 and a polydispersity of 1.15.

EXAMPLE 24

[0166] Example 23 was repeated except that the disulfonate used was 1,3-propanediol, 2,2-dimethyl, dimethanesulfonate (0.65 g, 0.0025 mole) to give the yellow polydye (yield—0.76 g) which had a weight average molecular weight-of 1,056, a number average molecular weight of 979 and a polydispersity of 1.08 by GPC analysis.

EXAMPLE 25

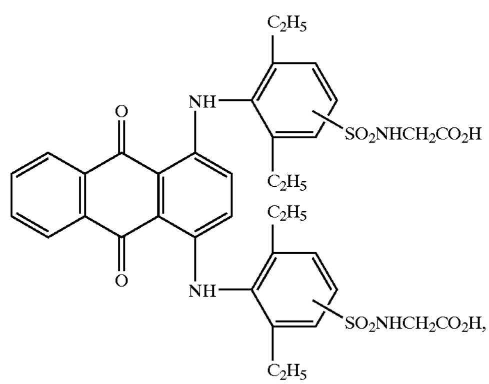
[0167] Example 23 was repeated except that 1,6-hexanediol, dimethanesulfonate (0.68 g, 0.0025 mole) was used as the disulfonate to give the yellow polydye (yield—1.16 g) which had a weight average molecular weight of 1,827, a number average molecular weight of 961 and a polydispersity of 1.90 by GPC analysis.

EXAMPLE 26

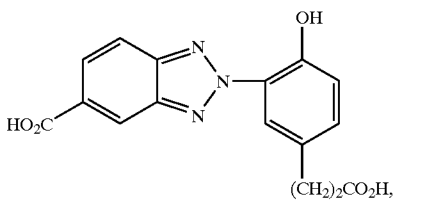
[0168] Example 23 was repeated except that 1,2-ethanediol, bis(4-methylbenzenesulfonate (0.82 g, 0.0025 mole) was used as the disulfonate to yield the yellow polydye (yield—0.41 g) which had a weight average molecular weight of 2,442, a number average molecular weight of 1,885 and a polydispersity of 1.29 by GPC analysis.

EXAMPLE 27

[0169] A mixture of the acidic anthraquinone compound (2.02 g, 0.0027 mole) having the structure



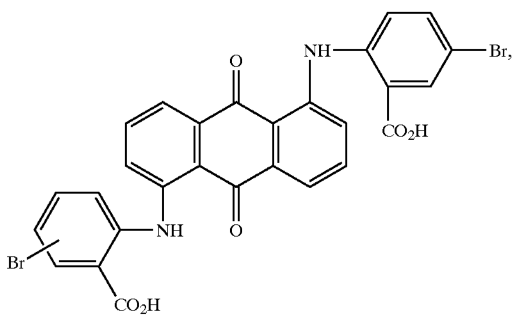
[0170] the acidic UV light absorbing compound (0.29 g, 9×10^{-4} mole) having the structure



[0171] 1,2-ethanediol, dimethanesulfonate (0.78 g, 0.0036 mole), potassium carbonate (1.0 g) and DMF (25 mL) was heated and stirred at 90-95° C. for 2.0 hours. The cooled reaction mixture was drowned into water (200 mL) and made slightly acidic by the addition of acetic acid with stirring. The polymeric product was collected by filtration, washed well with water and dried in air (yield—2.00 g). GPC analysis indicated a weight average molecular average of 5,642, a number average molecular weight of 1,720 and a polydispersity of 3.28.

EXAMPLE 28

[0172] A mixture of the diacidic anthraquinone compound (1.27 g, 0.002 mole) having the structure



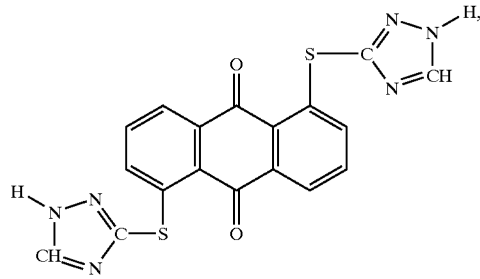
[0173] 1,2-ethanediol, dimethanesulfonate (0.44 g, 0.002 mole), potassium carbonate (0.75 g) and DMF (8.0 mL) was heated at 90-95° C. with occasional stirring for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the dark red polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and then dried in air (yield—1.23 g). GPC analysis indicated a weight average-molecular weight of 1,545, a number average molecular weight of 1,213 and a polydispersity of 1.27.

EXAMPLE 28a

[0174] To a mixture of 1,5-bis(2-carboxyanilino)anthraquinone (9.57 g, 0.02 mole) in DMF (250 mL) was added portionwise N-bromosuccinimide (7.12 g, 0.04 mole) with stirring at room temperature. The reaction mixture was then heated at about 60° C. for 1.5 hours and allowed to cool. Water was added dropwise to precipitate the product, which was collected by filtration, washed with water and dried in air (yield—11.17 g). FDMS indicated the structure of the product to be that of the starting anthraquinone compound in Example 28.

EXAMPLE 29

[0175] A mixture of the diacidic anthraquinone compound (4.06 g, 0.01 mole) having the structure



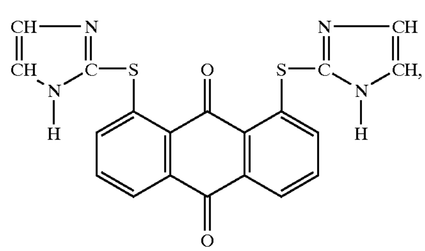
[0176] 1,2-ethanediol, dimethanesulfonate (2.18 g, 0.01 mole), potassium carbonate (2.76 g) and DMF (150 mL) was heated at about 100° C. for 3.0 hours. The reaction mixture was drowned into water, acidified with acetic acid and the yellow polydye was collected by filtration, washed with water and dried in air. GPC analysis indicated a weight average molecular weight of 5,333, a number average molecular weight of 2,441, and a polydispersity of 2.18.

EXAMPLE 29a

[0177] A mixture of 1,5-dichloroanthraquinone (6.93 g, 0.025 mole), 3-mercapto-1(H)-1,2,4-triazole (5.56 g, 0.055 mole), potassium carbonate (6.91 g, 0.05 mole) and DMF (100 mL) was heated and stirred at about 95° C. for 5.0 hours. The mixture was drowned into water and the yellow product was collected by filtration, washed with water and air dried. The cake was reslurried in hot isopropanol and the product collected by filtration, washed with isopropanol and dried in air (yield 8.62 g). FDMS indicated the product to be 1,5-bis[1(H)-1,2,4-triazol-3-ylthio]anthraquinone used as the diacidic anthraquinone starting material in Example 29.

EXAMPLE 30

[0178] A mixture of diacidic anthraquinone compound (1.01 g, 0.0025 mole) having the structure



[0179] 1,2-ethanediol, dimethanesulfonate (0.55 g, 0.0025 mole), potassium carbonate (0.75 g) and DMF (10 mL) was heated at about 95° C. for 3.0 hours. The reaction mixture was then drowned into methanol (100 mL) and the yellow polydye was collected by filtration, water containing acetic acid, hot water and then air dried (yield—0.35 g). GPC analysis indicated a weight average molecular weight of 2,478, a number average molecular weight of 742 and a polydispersity of 3.34. An absorption maximum was observed in the visible light absorption spectrum at 425 nm in DMF.

EXAMPLE 30a

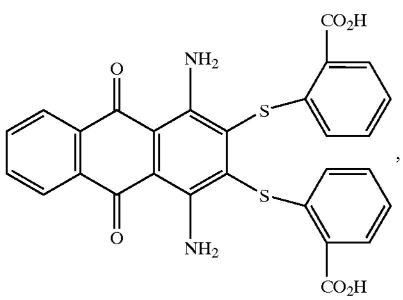
[0180] A mixture of 1,8-dichloroanthraquinone (6.93 g, 0.025 mole), 2-mercaptoimidazole (5.01 g, 0.05 mole), potassium carbonate (6.91 g) and DMF (60 mL) was heated and stirred at about 95° C. for 8.0 hours. The reaction mixture was drowned into water and acidified using acetic acid. The yellow product was collected by filtration, washed with water and dried in air. FDMS indicated the product to be the 1,8-bis(imidazol-2ylthio) anthraquinone diacidic compound used as the starting material in Example 30.

EXAMPLE 31

[0181] A mixture of 1,5-bis[1(H)-1,2,4-triazol-3ylthio] anthraquinone (1.80 g, 0.00443 mole) (product of Example 29a); 1,4-dibromobutane (0.96 g, 0.00444 mole), tributylamine (1.64 g, 0.00885 mole), and N-methyl-2-pyrrolidinone (30 mL) was heated at 8.0 hours at about 130° C. with stirring. The reaction mixture was drowned into acetone (150 mL) and the yellow polydye was collected by filtration, washed with acetone until filtrate was essentially clear and dried in air. GPC analysis indicated a weight average molecular weight of 5,022, a number average molecular weight of 3,220 and a polydispersity of 1.56.

EXAMPLE 32

[0182] A mixture of the diacidic anthraquinone compound (1.63 g, 0.003 mole) having the structure



[0183] 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated at about 95° C. with occasional stirring for 2.0 hours. The mixture was drowned into methanol (100 mL) and the dark blue polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—0.92 g). Absorption maxima at 602 and 644 nm were observed in the visible light absorption spectrum in DMF. GPC analysis indicated a number average molecular weight of 1,860.

EXAMPLE 32a

[0184] A mixture of 1,4-diamino-2,3-dichloroanthraquinone (12.24 g, 0.04 mole), thiosalicylic acid (15.4 g, 0.10 mole), potassium carbonate (13.8 g, 0.10 mole) and DMF (150 mL) was heated at about 95° C. with stirring for 2.0 hours. A bathochromic shift in color from violet to blue was observed as the reaction progressed. The reaction mixture was drowned into acetone (500 mL) and the solid product was collected by filtration and washed well with acetone. The acetone-wet cake was added to water (600 mL) and the mixture acidified with acetic acid to precipitate the free acid compound, which was collected by filtration, washed with water and dried in air (yield—21.4 g). FDMS indicated the product to be the 1,4-diamino-2,3-bis(2-carboxyphenylthio) anthraquinone used in Example 32.

EXAMPLE 33

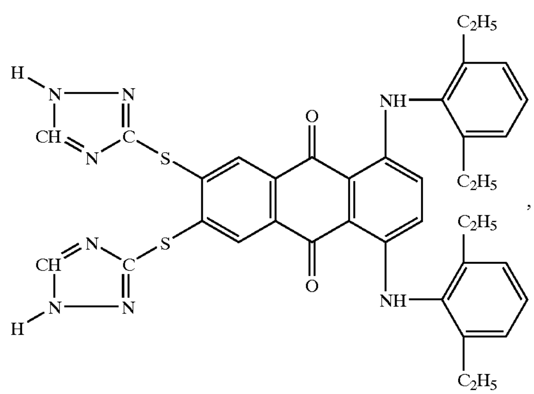
[0185] A mixture of 1,5-bis(2-carboxyphenylthio) anthraquinone (1.02 g, 0.002 mole), terephthalic acid (1.00 g, 0.006 mole), potassium carbonate (1.38 g) 1,2-ethanediol, dimethanesulfonate (1.74 g, 0.008 mole) and DMF (10 mL) was heated at about 95° C. with occasional stirring for 2.0 hours. The mixture was then drowned into methanol (100 mL) and the yellow polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—1.88 g). GPC analysis indicated a weight average molecular weight of 794, a number average molecular weight of 713 and a polydispersity of 1.11.

EXAMPLE 34

[0186] Example 33 was repeated using 1,5-bis(2-carboxyphenylthio) anthraquinone (1.02 g, 0.002 mole) and terephthalic acid (0.33 g, 0.002 mole), 1,2-ethanediol, dimethanesulfonate (0.87 g, 0.004 mole) and potassium carbonate (0.87 g) to yield the yellow polydye (0.90 g). GPC analysis indicated a weight average molecular weight of 875, a number average molecular weight of 811, and a polydispersity of 1.08.

EXAMPLE 35

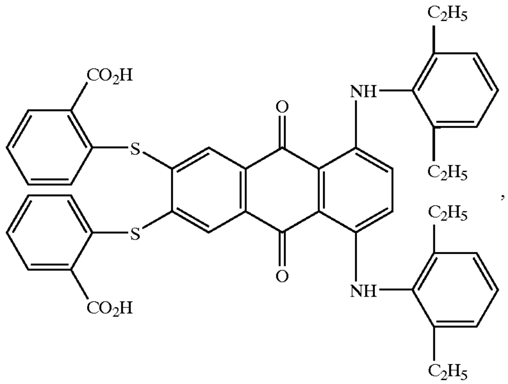
[0187] A mixture of the diacidic anthraquinone compound (2.00 g, 0.00285 mole) having the following structure (Preparation 5 of IR Docket 70351):



[0188] 1,2-ethanediol, dimethanesulfonate (0.63 g, 0.00289 mole), potassium carbonate (0.80 g) and DMF (25 mL) was heated at 95° C. for 4.0 hours with stirring. The reaction mixture was drowned into methanol (100 mL) and the greenish-blue polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—1.01 g). GPC indicated a weight average molecular weight of 6,720, a number average molecular weight of 2,211 and a polydispersity of 3.04. Absorption maxima were observed at 599 and 647 nm in the visible absorption spectrum in DMF.

EXAMPLE 36

[0189] A mixture of the diacidic anthraquinone compound (0.41 g, 0.508 mmole) having the following structure (Preparation 4 in IR Docket 70351):



[0190] 1,2-ethanediol, dimethanesulfonate (0.11 g, 0.504 mmole), potassium carbonate (0.14 g) and DMF (5.0 mL) was heated with occasional stirring or about 95° C. for 3.0 hours. The reaction mixture was drowned into methanol (50 mL) and the greenish-blue polydye was collected by filtration; washed with methanol, water containing acetic acid, hot water and dried in air (yield 0.15 g). Absorption maxima were observed at 599 and 645 nm in the visible light absorption spectrum in DMF.

EXAMPLE 37-66

[0191] Colored EASTAR® copolyester 6763 film was produced by melt blending the polydyes of Examples 7-36 and extruding according to the following procedure to produce Examples 37-66 (Table 1).

[0192] EASTAR® PETG polyester 6763, a poly(ethylene-1,4-cyclohexanedimethylene) terephthalate (Eastman Chemical Company) (300 g of previously dried pellets) was dry blended with the anthraquinone polydye composition (0.12 g). The blend was extruded with a C. W. Brabender ¾ in extruder, equipped with a mixing screw, at 250° C. into a water bath and the extrudate pelletized.

[0193] The pellets were redried at 70° C. for 17 hrs. at a pressure of about 1-5 torr. A portion (1.40 g) of the dried pellets was pressed into a 18-20 mil film at 250° C. using a 2-inch diameter circular mold in a Pasadena Hydraulic, Inc. press using 12,000 pounds ram force (4 inch ram). The transparent films contained about 300 ppm of the polydyes and each showed excellent color development to produce the colors indicated in Table 1.

EXAMPLE 67

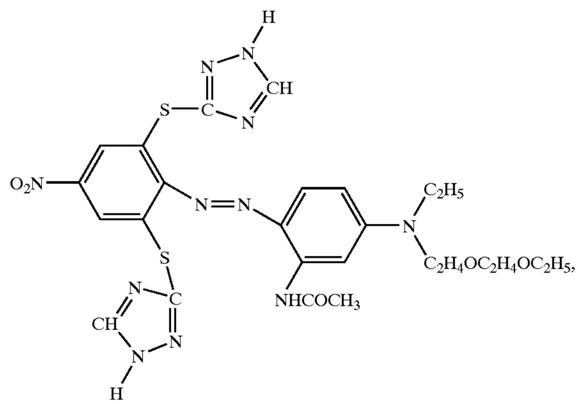
[0194] A mixture of 1,4-bis(2-carboxyphenythio) anthraquinone (15.4 g, 0.03 mole) (prepared as in Example 20a), 1,5-bis(2-carboxyphenylthio)-4,8-bis(isobutylamino)anthraquinone (6.55 g, 0.01 mole) (Example 2a), 1,2-ethanediol, dimethanesulfonate (8.72 g, 0.04 mole), potassium carbonate (8.0 g) and DMF (100 mL) was stirred and heated at about 95° C. for 2.0 hours with occasional stirring. The reaction mixture was drowned into methanol (500 mL) and the black polydye was collected by filtration, washed with water containing acetic acid, hot water and dried in air (yield—9.5 g). GPC analysis indicated a weight average molecular weight of 7,512, a number average molecular weight of 1,700 and a polydispersity of 4.42.

EXAMPLE 68

[0195] EASTAR® PETG copolyester 6763 (291 g of previously dried pellets) was dry blended with the black polydye of Example 67 (9.0 g) and the blend extruded and a portion of the resulting pellets was pressed into a black film containing approximately 3.0% by weight of polydye by using the procedure described in Example 4.

EXAMPLE 69

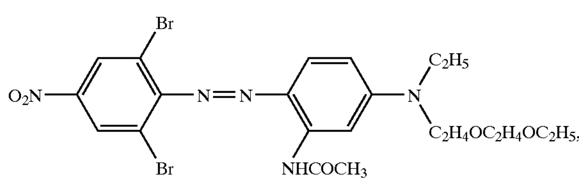
[0196] A mixture of the diacidic azo compound (3.20 g, 0.005 mole) having the structure



[0197] 1,2-ethanediol, dimethanesulfonate (1.09 g, 0.005 mole), potassium carbonate (1.5 g) and DMF (25 mL) was heated and stirred at about 95° C. for 3.0 hours. The reaction mixture was drowned into methanol and the violet polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—1.60 g). GPC analysis indicated a weight average molecular weight (Mw) of 6,403, a number average molecular weight (Mn) of 3,700 and a polydispersity (Mw/Mn) of 1.73. In the visible light absorption spectrum in DMF an absorption maximum was observed at 556 nm.

EXAMPLE 69a

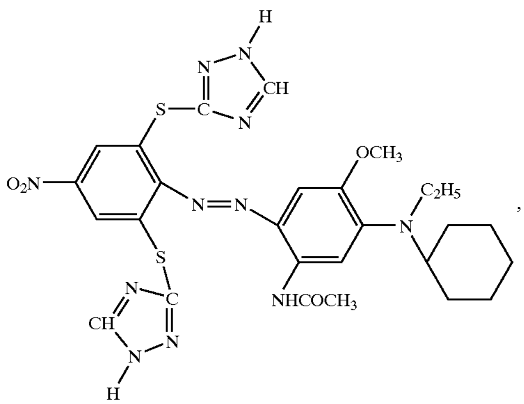
[0198] A mixture of the dibromoazobenzene dye (6.01 g, 0.010 mole) having the structure



[0199] 3-mercapto-1(H)1,2,4-triazole (2.2 g, 0.022 mole), potassium carbonate (3.45 g, 0.025 mole) and DMF (100 mL) was stirred and heated at about 95° C. for 2.0 hours. TLC (75 parts THF: 25 parts cyclohexane) showed incomplete reaction. An additional quantity (1.01 g, 0.01 m) 3-mercapto-1(H)-1,2,4-triazole was added and heating and stirring were continued for 2.0 additional hours. TLC indicated essentially complete reaction to produce the violet product. The reaction mixture was drowned into water (400 mL) and the mixture was acidified by addition of acetic acid, heated to about 40° C. and filtered. The product was washed with warm water and dried in air (yield—5.60 g). FDMS indicated the product to have the structure of the diacidic azobenzene compound used in Example 69.

EXAMPLE 70

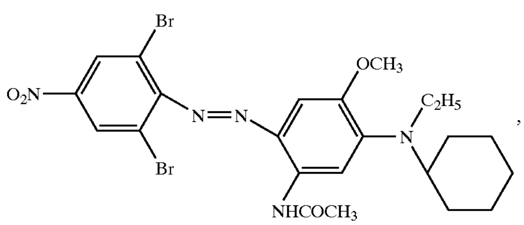
[0200] A mixture of the diacidic azo compound (1.59 g, 0.0025 mole) having the structure



[0201] 1,2-ethanediol, dimethanesulfonate (0.55 g, 0.0025 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated at 95° C. with occasional stirring for 3.0 hours. The reaction mixture was drowned into methanol (100 mL) and the blue polydye product was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—1.06 g). GPC analysis indicated a Mw of 5,497, a Mn of 2,648 and a Mw/Mn of 2.08. An absorption maximum was observed at 605 nm in DMF in the visible light absorption spectrum.

EXAMPLE 70a

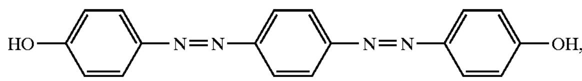
[0202] A mixture of the dibromo azobenzene dye (2.38 g, 0.004 mole) having the structure



[0203] 3-mercapto-1(H)-1,2,4-triazole (1.21 g, 0.012 mole), potassium carbonate (1.65 g, 0.012 mole) and DMF (25 mL) was heated and stirred for 1.0 hour. TLC (50 parts THF:50 parts cyclohexane) showed complete reaction to produce the product. The reaction mixture was drowned into water (100 mL) and the mixture acidified with acetic acid. The dark blue product was collected by filtration, washed with water and dried in air (yield—2.55g). FDMS indicated the product to have the structure of the diacidic azobenzene compound used in Example 70.

EXAMPLE 71

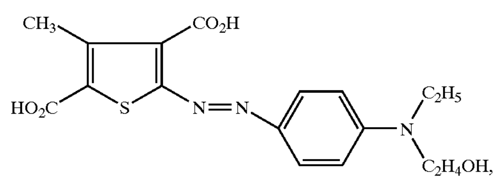
[0204] A mixture of the diacidic disazo compound (1.59 g, 0.005 mole) having the structure



[0205] 1,2-ethanediol, dimethanesulfonate (1.09 g. 0.005 mole), potassium carbonate (1.5 g), DMF (10 mL) was heated and stirred at about 95° C. for 3.0 hours. The reaction mixture was drowned into methanol (100 mL) and the dark brown polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and then dried in air (yield—0.66 g). GPC analysis indicated a Mw of 4,926, a Mw of 1,574 and a Mw/Mn of 3.13.

EXAMPLE 72

[0206] A mixture of the diacidic azo compound (1.88 g, 0.005 mole) having the structure



[0207] 1,2-ethanediol, dimethanesulfonate (1.09 g, 0.005 mole), potassium carbonate (1.5 g) and DMF (20 mL) was heated at about 95° C. with stirring for 3.0 hours. The reaction mixture was drowned in methanol (100 mL) and the red polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—1.35 g). GPC analysis indicated a Mw of 6,888, a Mn of 2,127 and a Mw/Mn of 3.24. An absorption maximum was observed at 527 nm in the visible light absorption spectrum in DMF.

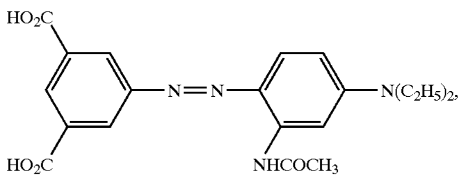
EXAMPLE 72a

[0208] To a stirred mixture of the azo compound (4.05 g, 0.01 mole) [4-(3',5'-dicarbomethoxy-4'-methylthiophene-2-ylazo)-N-ethyl-N(2-hydroxyethyl)aniline) and 2-ethoxyethanol (50 mL) at room temperature was added aqueous

50% NaOH solution(3.75 g). After being heated at about 95° C. for 1.0 hour, the reaction product was drowned into acetone (300 mL). The disodium salt of the diacidic azo dye was collected by filtration washed with acetone and then quickly dissolved in water (200 mL). Acidification with acetic acid precipitated the free diacid dye, which was collected by filtration, washed with water and dried in air (yield—2.35 g). FDMS indicated the product to have the structure of the diacidic azo compound used in Example 72.

EXAMPLE 73

[0209] A mixture of the diacidic azobenzene compound (1.19 g, 0.003 mole) having the structure



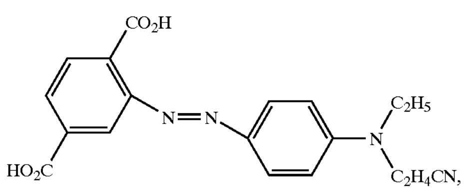
[0210] 1,2-ethanediol, dimethanesulfonate (0.66 g., 0.003 mole), potassium carbonate (0.75 g), and DMF (8.0 mL) was stirred occasionally and heated at about 95° C. for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the orange polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—0.65 g). GPC analysis showed a Mw of 3,015, a Mn of 2,128 and a Mw/Mn of 1.42. An absorption maximum was observed in the visible light absorption at 479 nm in DMF.

EXAMPLE 73a

[0211] To a mixture of 3-acetamido-4-(3',5'-dicarbomethoxyphenylazo)-N,N-diethylaniline (1.7 g, 0.004 mole) in 2-ethoxyethanol (20 mL) was added aqueous 50% NaOH (1.6 g). The reaction mixture was heated with stirring of 95° C. for 10 minutes and then drowned into water (100 mL). The solution was acidified with acetic acid to precipitate the diacid dye which was collected by I filtration, washed with water and dried in air (yield—1.6 g). FDMS indicated the structure to be that of the starting diacid azobenzene compound in Example 73.

EXAMPLE 74

[0212] A mixture of the diacidic azobenzene compound (1.10 g, 0.003 mole) having the structure



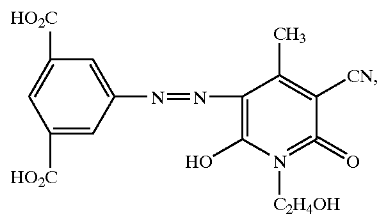
[0213] 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.45 g) and DMF (8.0 mL) was heated at 95° C. with-occasional stirring for 2.0 hours. The reaction mixture was drowned into methanol (100 mL). A slightly sticky yellow product resulted. The methanol was removed by decantation and the product dissolved in DMF (10 mL) by heating and stirring. Water (100 mL) was added and the mixture acidified by addition of acetic acid. The solid yellow polydye was collected by filtration, washed with water and dried in air (yield—0.47 g). GPC analysis indicated a Mw of 9,314, a Mn of 3,208 and a Mw/Mn of 2.90. An absorption maximum at 428 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 74a

[0214] To a mixture of 4-(2',5'-dicarbomethoxyphenylazo)-N-(2-cyanoethyl)-N-ethylaniline (1.97 g, 0.005 mole) in 2-ethoxyethanol (20 mL) was added aqueous 50% NaOH (1.90 g). The reaction solution was heated at 95° C. for 15 minutes and then drowned into water (200 mL). The solution was acidified and the yellow dye which precipitated was collected by filtration, washed with water and dried in air (yield—1.75 g). FDMS indicated the structure to be that of the starting diacid azobenzene dye of Example 74.

EXAMPLE 75

[0215] A mixture of diacidic azo compound (38.6 g, 0.10 mole) having the structure



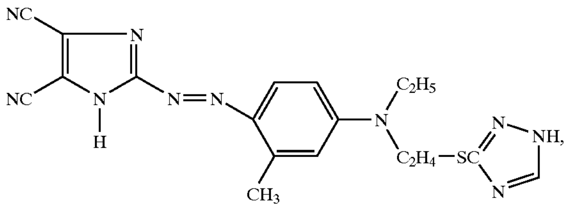
[0216] 1,6-hexanediol, dimethanesulfonate (27.4 g, 0.10 mole), potassium carbonate (27.6 g, 0.20 mole), and DMF (350 mL) was heated at 95-100° C. for 2.0 hours. The reaction mixture was drowned into a solution of acetic acid (70.0 mL) in water (1700 mL) with good stirring. After stirring for about 15 minutes, the yellow polydye was collected by filtration, washed with hot water and dried in air (yield—42.6 g). An absorption maximum at 422 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 75a

[0217] To a mixture of the diester dye (41.4 g, 0.10 mole) [3-cyano-5-(3',5'-dicarbomethoxyphenylazo)-6-hydroxy-N-(2-hydroxyethyl)-4-methyl-2-pyridone] in 2-ethoxyethanol (400 mL) was added aqueous 50% NaOH (40.0 g) and the reaction mixture was heated at 75-80° C. for about 30 minutes. Acetone (200 mL) was added to the slightly cooled reaction mixture. The yellow solid was collected by filtration, washed with acetone and then reslurried in warm water (750 mL). After acidification using conc. HCl (20 mL), the yellow diacid dye was collected by filtration, washed with hot water and dried in air (yield—36.0 g). FDMS indicated the structure to be that of the starting diacid azo compound of Example 75.

EXAMPLE 76

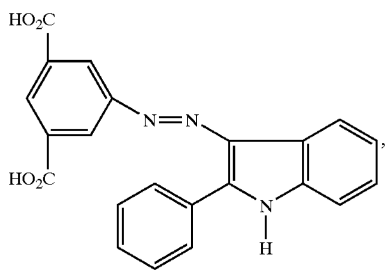
[0218] A mixture of the diacidic azo compound (2.03 g, 0.005 mole) having the structure



[0219] 1,2-ethanedioli dimethanesulfonate (1.09 g, 0.005 mole), potassium carbonate (1.5 g) and DMF (20 mL) was heated at about 95° C. with occasional stirring for 5.0 hours. The reaction mixture was drowned into methanol. Acetic acid (1.0 mL) was added and the polydye was collected by filtration and washed with water and dried in air. GPC analysis indicated a Mw of 9,876, a Mn of 3,917 and a polydispersity of 2.52. An absorption maximum at 506. nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 77

[0220] A mixture of the diacidic azo compound (0.60 g, 0.00155 mole) having the structure



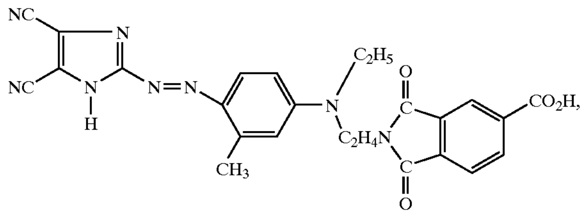
[0221] 1,2-ethanediol, dimethanesulfonate (0.34 g, 0.00155 mole), potassium carbonate (0.3 g) and DMF (4.0 mL) was heated at about 95° C. for 4.0 hours. The reaction mixture was drowned into methanol (20 mL) and the yellow polydye was collected by filtration, washed with methanol, water containing acetic acid, water and then air dried (yield—0.5 g). GPC analysis showed a Mw of 4,566, a Mn of 2,474 and a Mw/Mn of 1.84. In the visible light absorption spectrum in DMF an absorption maximum was observed at 420 nm.

EXAMPLE 77a

[0222] To a mixture of 3-(3',5'-dicarboxymethoxyphenylazo)-2-phenylindole (1.0 g, 0.00242 mole) in 2-ethoxyethanol (10 mL) was added aqueous 50% NaOH (0.75 g) and the hydrolysis reaction carried out by heating at about 95° C. for 30 minutes. The reaction mixture was drowned into water (100 mL) and the solution treated with acetic acid to precipitate the product which was collected by filtration, washed with water and dried in air (yield—0.85 g). FDMS indicated the structure to be that of the starting diacidic azo compound in Example 77.

EXAMPLE 78

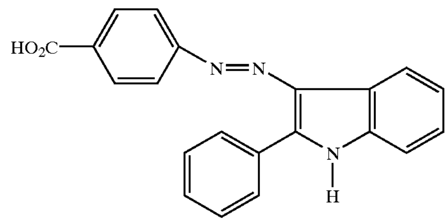
[0223] A mixture of the diacidic azo compound (0.99 g, 0.002 mole) having the structure



[0224] 1,2-ethanediol, dimethanesulfonate (0.42 g, 0.002 mole), potassium carbonate (0.5 g) and DMF (7.0 mL) was heated at about 95° C. for 3.0 hours. The reaction mixture was drowned into methanol (50 mL) and the scarlet polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and then dried in air (yield—0.18 g). GPC analysis indicated a Mw of 8,246, a Mn of 2,619 and a polydispersity of 3.15.

EXAMPLE 79

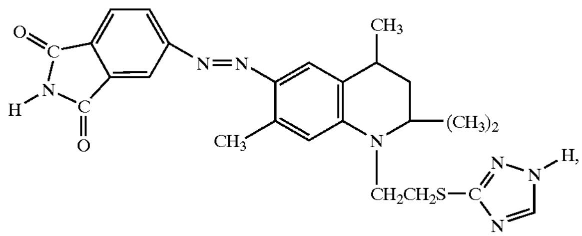
[0225] A mixture of the diacidic azo dye (2.50 g, 0.00733 mole) having the following structure



[0226] 1,2-ethanediol, dimethanesulfonate (1.60 g, 0.00733 mole), potassium carbonate (2.07 g) and DMF (25 mL) was heated at 95° C. for 3.0 hours. The reaction mixture was drowned into methanol and a small amount of acetic acid added. The yellow polydye was collected by filtration, washed with a little methanol, water containing acetic acid, hot water and dried in air. GPC analysis indicated a Mw of 1,949, a Mn of 1,569 and a Mw/Mn of 1.24. An absorption maximum was observed at 411 nm the visible light absorption spectrum.

EXAMPLE 80

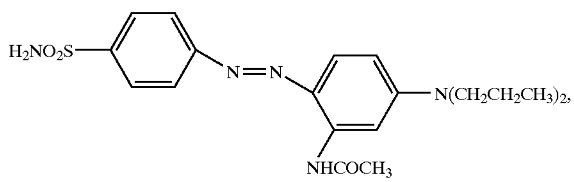
[0227] A mixture of the diacidic azo compound (1.22 g, 0.0025 mole) having the structure



[0228] 1,2-ethanediol, dimethanesulfonate (0.55 g, 0.0025 mole), potassium carbonate (0.75 g) and DMF (8.0 mL) was heated and stirred at about 95° C. for 3 hours with occasional stirring. The reaction mixture was drowned into methanol (50 mL) and the polydye was collected by filtration washed with methanol, water containing acetic acid, hot water and then dried in air (yield—0.68 g). GPC analysis indicated a Mw of 2,259, a Mn of 1,571 and a Mw/Mn of 1.44. An absorption maximum was observed at 503 nm in DMF in the visible light absorption spectrum.

EXAMPLE 81

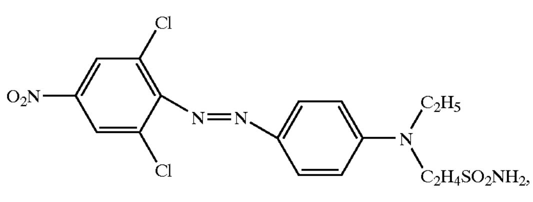
[0229] A mixture of the diacidic azo compound (1.25 g, 0.003 mole) having the structure



[0230] 1,2-ethanediol, dimethanesulfonate (0.65 g, 0.003 mole), potassium carbonate (1.0 g) and DMF (10 mL) was heated at about 95° C. for 3.0 hours with occasional stirring. The reaction mixture was drowned into methanol (25 mL) and the orange polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—0.75 g). GPC analysis indicated a Mw of 2,014, a Mn of 1,520 and a Mw/Mn of 1.32. An absorption maximum was observed at 493 nm in the visible light absorption spectrum in DMF.

EXAMPLE 82

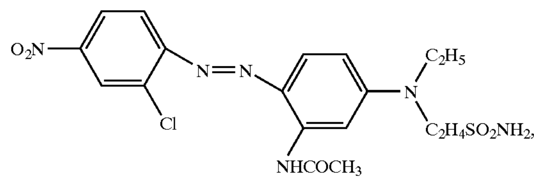
[0231] A mixture of the diacidic azo compound (1.11 g, 0.0025 mole) having the structure



[0232] 1,2-ethanediol, dimethanesulfonate (0.55 g, 0.0025 mole), potassium carbonate (0.80 g and DMF (8.0 mL) was heated at about 95° C. for 2.5 hours. The reaction mixture was drowned into methanol (100 mL) and the brown polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—0.30 g). GPC analysis indicated a Mw of 2,301, a Mn of 1,345 a Mw/Mn of 1.71. In the visible light absorption spectrum in DMF a maximum absorption was observed at 434 nm.

EXAMPLE 83

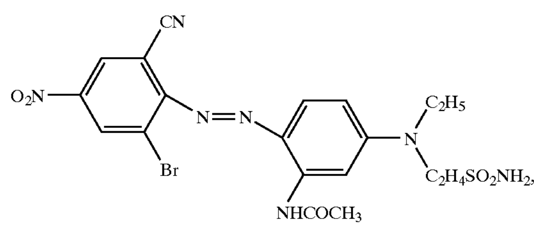
[0233] A mixture of the diacidic azo compound (2.40 g, 0.005 mole) having the structure



[0234] 1,2-ethanediol, dimethanesulfonate (1.09 g, 0.005 mole), potassium carbonate (1.5 g) and DMF (25 mL) was heated at about 95° C. for 3.0 hours with occasional stirring. The reaction mixture was drowned into methanol (200 mL) and the dark red polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and then dried in air (yield—1.80 g). GPC analysis indicated Mw of 2,914, a Mn of 809 and a Mw/Mn of 3.60. An absorption maximum at 528 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 84

[0235] A mixture of the diacidic azo compound (1.07 g, 0.002. mole) having the structure



[0236] 1,2-ethanediol, dimethanesulfonate (0.44 g, 0.002 mole), potassium carbonate (0.5 g) and DMF (10 mL) was heated at 95° C. with occasional stirring for 5 hours. The reaction mixture was drowned into methanol (50 mL) and the reddish-blue polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—0.83 g). GPC analysis indicated a Mw of 7,038, a Mn of 832 and a Mw/Mn at 8.44. An absorption maximum was observed at 574 nm in the visible light absorption spectrum in DMF.

EXAMPLE 85

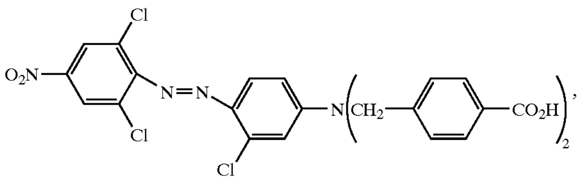
Displacement of Bromine in Polydye of Example 84 with Cyano Group

[0237] A mixture of a portion (0.5 g) of the polydye of Example 84, sodium dicyanocuprate (0.2 g) and DMF (8.0 mL) was heated at about 95° C. with occasional stirring for 3.0 hours. The reaction mixture, the color of which changed from reddish-blue to neutral-blue as the displacement reaction occurred, was then drowned into methanol and the polydye was collected by filtration, washed with methanol and dried in air. GPC analysis indicated a Mw of 9,427, a

Mw of 1,117 and a Mw/Mn of 8.44. An absorption maximum at 590 nm was observed in DMF in the visible light absorption spectrum.

EXAMPLE 86

[0238] A mixture of diacidic azo compound (1.53 g, 0.0025 mole) having the structure



[0239] 1,6-hexanediol, dimethanesulfonate (0.69 g, 0.0025 mole), K_2CO_3 (0.8 g) and DMF (8.0 mL) was heated at about 95° C. with occasional stirring for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the brown polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and then dried in air (yield—0.62 g). GPC analysis indicated a Mw of 4,795, a Mn of 2,051 and a Mw/Mn of 2.33. An absorption maximum at 434 nm in DMF was observed in the visible light absorption spectrum.

EXAMPLE 86a

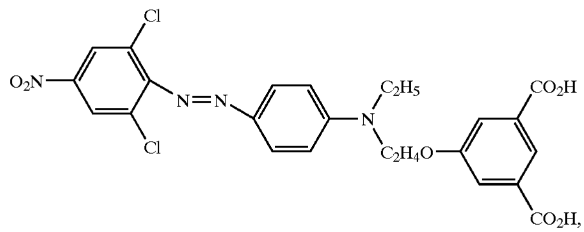
[0240] To conc. H_2SO_4 (33.0 mL) was added 2,6-dichloro-4-nitroaniline (6.21 g, 0.03 mole) with stirring. The solution was cooled to 0-5° C. and stirred while a nitrosyl sulfuric acid mixture, prepared by adding sodium nitrite (2.19 g) to conc. H_2SO_4 (15 mL) portionwise with stirring and allowing the temperature to rise, was added below SOC with stirring. The diazotization reaction mixture was stirred at 0-5° C. for 2.0 hours. An aliquot of the diazonium salt solution (0.01 mole) was added to a chilled solution of the diacid coupler (3.95 g, 0.01 mole) (N,N-bis(4-carboxyphenylmethyl)-3-chloroaniline) dissolved in 1:5 (1 part propionic acid:5 parts acetic acid) (120 mL) containing some conc. HCl (5.0 mL) with stirring at 0-5° C. The coupling reaction mixture was neutralized by the addition of ammonium acetate with stirring and allowed to stand with occasional stirring at below 5° C. for about 1.0 hour. Water was added to precipitate the solid dye, which was collected by filtration, washed with water and dried in air (yield—4.0 g). The crude dye was reslurried in hot methanol and the mixture allowed to cool. The final dye was collected by filtration, washed with methanol and dried in air. An absorption maximum was observed at 431 nm in DMF. The diacid dye was used as the starting material in Example 86.

EXAMPLE 86b

[0241] A mixture of m-chloroaniline (2.56 g, 0.02 mole), methyl 4-(bromomethyl)benzoate (10.08 g, 0.044 mole), sodium carbonate (4.66 g) and sodium iodide (0.2 g) and 2-ethoxyethanol (50 mL) was heated under nitrogen at about 90° C. for 3.0 hours with stirring. The reaction mixture was drowned into water and the product was extracted into methylene chloride. Methylene chloride was removed to leave an oily product (11.0 g), which was added to 2-ethoxyethanol (100 mL). To the solution was added aqueous 50% NaOH solution (7.50 g) and the reaction mixture was warmed. At about 30° C., white solids began to precipitate and at about 50° C. the reaction mixture become very thick. When the temperature had reached 70° C., water (20 mL) was added to dissolve the salts of the diacidic product. After stirring at 70° C. for 1.5 hours the reaction mixture was clarified by filtering through Celite filter aid and the filtrate acidified by the addition of 10% aqueous HCl to pH of about 4.0. The white solid was collected by filtration, washed with water and dried in air (yield—7.20 g). FDMS indicated the product to have the structure of the coupler used in Example 86a.

EXAMPLE 87

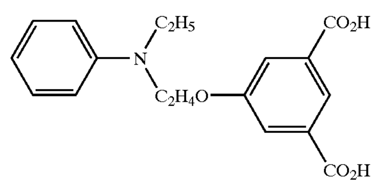
[0242] A mixture of the diacidic azo compound (1.64 g, 0.003 mole) having the structure



[0243] 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.5 g) and DMF (8.0 mL) was heated at about 95° C. for 25 hours with occasional stirring. The reaction mixture was drowned into methanol (150 mL) and the polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—1.5 g). GPC analysis indicated a Mw of 2,741, a Mn of 1,367 and a Mw/Mn of 2.00. An absorption maximum at 441 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 87a

[0244] An aliquot (0.01 mole) of the diazonium salt from 2,6-dichloro-4-nitroaniline prepared in Example 86a was added to a chilled solution of the coupler (3.29 g, 0.01 mole) having the formula



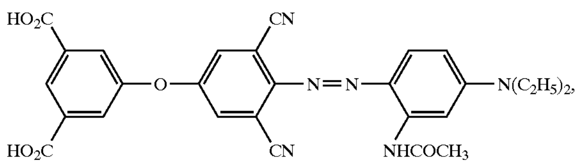
[0245] dissolved in 1:5 acid (100 mL) with stirring at 0-5° C. Ammonium acetate was added with stirring until the coupling mixture was neutral to Congo Red Test paper. After allowing to stand for 1.0 hour, water was added to the coupling mixture to precipitate the dye, which was collected by filtration, washed with-water and dried in air (yield—4.27 g). An absorption maximum was observed at 460 nm in the visible light absorption spectrum in DMF.

EXAMPLE 87b

[0246] A mixture of N-(2-chloroethyl)-N-ethylaniline (46.0 g, 0.25 mole), dimethyl 5-hydroxyisophthalate (52.5 g, 0.25 mole), potassium carbonate (69.08), a trace of pulverized potassium iodide and DMF (350 mL) was heated at 125-30° C. for 3.5 hours with stirring. The reaction mixture was allowed to cool and drowned in water/ice mixture (1.0 L). The product separated as a brown oil and the aqueous layer was removed by decantation. To the oily product was added 2-ethoxyethanol (175 mL) and aqueous 50% NaOH (50.0 g) and the hydrolysis reaction mixture was heated at 60-65° C. for about 20 minutes. Acetone was added to the reaction mixture and the white solid was collected by filtration, washed with acetone and dried in air (yield—99.0 g). The disodium salt was dissolved in water (250 mL) by stirring. Acidification with conc. HCl to a pH of about 3.0 gave a slightly sticky product which solidified in a few minutes. The pale yellow granular solid was collected by filtration, washed with water and dried in air (yield—58.0 g). FDMS indicated the structure to be that of the coupler used in Example 87a.

EXAMPLE 88

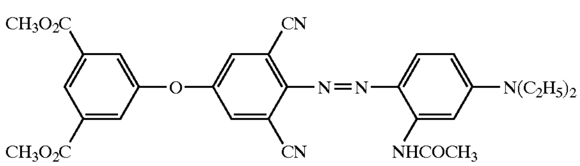
[0247] A mixture of the diacid azo compound (0.70 g, 0.0013 mole) having the structure



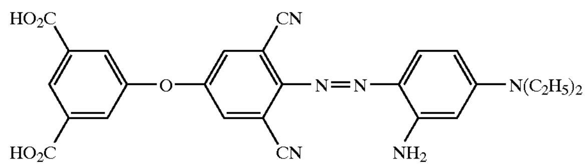
[0248] 1,6-hexanediol, dimethanesulfonate (0.36 g, 0.0013 mole), potassium carbonate (0.35 g) and DMF (5.0 mL) was heated at about 95° C. with occasional stirring for 2.0 hours. The reaction mixture was drowned into methanol (50 mL) and the polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—0.55 g). GPC indicated a Mw of 7,353, a Mn of 2,431 and a Mw/Mn of 3.02. An absorption maximum at 537 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 88a

[0249] To a mixture of the diester dye (1.75 g, 0.0013 mole) having the structure



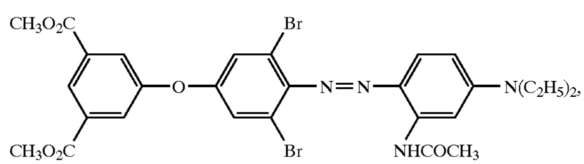
[0250] and 2-ethoxyethanol (20 mL) was added aqueous 50% NaOH solution (1.2 g) and the hydrolysis mixture was heated at about 10 minutes at about 95° C. The reaction mixture was drowned into acetone and the solid material collected by filtration. The acetone-wet material was dissolved by stirring in water (200 mL) and the diacid dye precipitated by adding acetic acid. The product was collected by filtration washed with water and dried in air (yield—1.35 g). FDMS showed the product to be mostly



[0251] indicating hydrolysis of the acetamido group in addition to the ester group. All of the product was added to acetic acid (8.0 mL) and acetic anhydride (1.0 mL). The reaction mixture was heated at 95° C. for 30 minutes with occasional stirring. A bathochromic shift in color from red to magenta was observed as the amine group was acetylated. The reaction mixture was allowed to cool, whereupon a solid dark red product crystallized, and then was drowned into methanol (40 mL). The product was collected by filtration, washed with water and dried in air (yield—0.90 g). FDMS indicated the structure to be that of the diacidic azo dye in Example 88.

EXAMPLE 88b

[0252] A mixture of the dibromo azo dye (3.00 g, 0.0044 mole) having the structure



[0253] sodium dicyanocuprate (0.69 g, 0.005 mole) and DMF (30 mL) was heated at 95° C. for 1.0 hour. The reaction mixture was drowned into methanol (150 mL) and the dye was collected by filtration, washed with methanol and dried in air (yield—1.91 g). FDMS indicated the structure to be that of the dicyano dye used in Example 88a.

EXAMPLE 88c

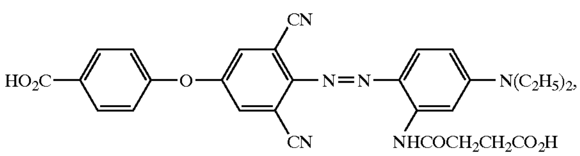
[0254] To conc. H_2SO_4 (7.5 mL) was added dry $NaNO_2$ (1.08 g) portionwise with stirring and the temperature allowed to rise. The nitrosyl sulfuric acid mixture was cooled and 1:5 acid (15 mL) was added at less than 10° C. with stirring. To this mixture was added at 0-5° C. with stirring dimethyl 5-(4'-amino,2',6'-dibromophenoxy)isophthalate (6.86 g, 0.015 mole), followed by an additional 15 mL of 1:5 acid. The diazotization reaction mixture was stirred at 0-5° C. for 2.0 hours and then an aliquot (0.0075 mole) was added to a solution of 3-acetamido-N,N-diethylaniline (1.54 g, 0.0075 mole) dissolved in 1:5 acid (75 mL) at 0-5° C. Ammonium acetate was added with stirring to the coupling mixture until neutral to Congo Red test paper. Coupling was allowed to continue at 0-5° C. for 1.0 hour and the dye then precipitated by addition of water, collected by filtration, washed with water and dried in air. FDMS indicated the structure to be that of the starting dibromo azo dye in Example 88b. An absorption maximum at 546 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 88d

[0255] A mixture of the dimethyl 5-(4'-aminophenoxy-)isophthalate (15.0 g, 0.05 mole). (Example 12c), anhydrous sodium acetate (9.6 g) and acetic acid (85 mL) was treated with stirring with bromine (17.4 g, 0.11 mole) allowing the temperature to rise. The reaction mixture was heated at 70-80° C. for 1.5 hours, allowed to cool, and then drowned into ice water (350 mL). The product was collected by filtration, washed with water and dried in air (yield—21.9 g). FDMS indicated the structure to be that of the amine compound diazotized in Example 88c.

EXAMPLE 89

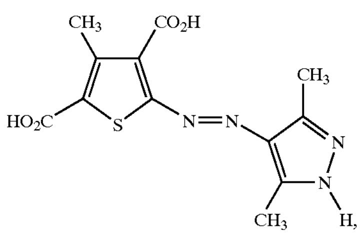
[0256] A mixture of the diacidic azo compound (1.39 g, 0.0025 mole) having the structure



[0257] 1,6-hexanediol, dimethanesulfonate (0.68 g, 0.0025 mole), potassium carbonate (1.0 g) and DMF (8.0 mL) was heated at 95° C. for 2.5 hrs with occasional stirring. The reaction mixture was drowned into methanol (100 mL) and the red polydye was collected by filtration, washed with water containing acetic acid, hot water and dried in air (0.85 g). GPC analysis indicated a Mw of 2,772, a Mn of 1,306 and a Mw/Mn of 2.12. An absorption maximum was observed at 538 nm in the visible light absorption spectrum in DMF.

EXAMPLE 90

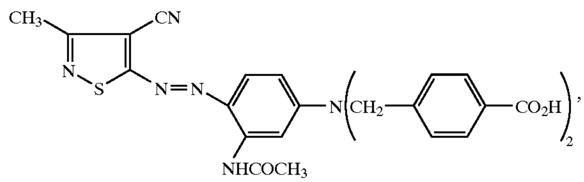
[0258] A mixture of the diacidic azo compound (1.23 g, 0.004 mole) having the formula



[0259] 1,2-hexanediol, dimethanesulfonate (1.1 g, 0.004 mole), potassium carbonate (0.55 g) and DMF (8.0 mL) was heated at 95° C. for 1 hour. The reaction mixture was drowned into water (250 mL) containing acetic acid (5.0 mL). The yellow polydye was collected by filtration, washed with water and dried in air (yield—1.21 g). GPC analysis indicated a Mw of 1,726, a Mn of 1,079 and a Mw/Mn of 1.6. An absorption maximum at 400 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 91

[0260] A mixture of the diacidic azo compound (1.71 g, 0.003 mole) having the formula



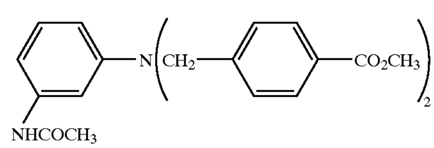
[0261] 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.85 g) and DMF (8.0 mL) was heated with occasional stirring at 95° C. for 2.0 hours. The reaction mixture was drowned into methanol (100 ml) and the red polydye was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—1.5 g). GPC indicated a Mw of 2,090, a Mn of 1,235 and a Mw/Mn of 1.69. An absorption maximum was observed at 545 nm in the visible light absorption spectrum in DMF.

EXAMPLE 91a

[0262] To conc. H_2SO_4(5.0 mL) was added dry $NaNO_2$ (0.72 g) portionwise with stirring, allowing the temperature to rise. The nitrosyl sulfuric acid solution was stirred and cooled and 1:5 acid (10 ml was added below about 15° C., followed by 5-amino-4-cyano-3-methylisothiazole (1.39 g, 0.01 mole) and 1:5 acid (10 ml) both added at 0-5° C. After being stirred at 0-5° C. for 2.0 hours an aliquot (0.005 mole) of the diazonium solution was added to a stirred solution of 3-acetamido-N,N-bis-(4-carboxyphenylmethyl)aniline (2.09 g, 0.005 mole) dissolved in 1:5 acid (30 ml) at 0-5° C. Ammonium acetate was added to neutralize the coupling mixture until neutral to Congo Red test paper. Water was added to the coupling mixture to precipitate the red dye, which was collected by filtration and dried in air (yield—2.67 g). The product was reslurried in hot methanol, allowed to cool and the solid collected by filtration, washed with methanol and dried in air (yield—2.10 g). FDMS indicated the structure to be that of the diacid azo compound used as a starting material for Example 91.

EXAMPLE 91b

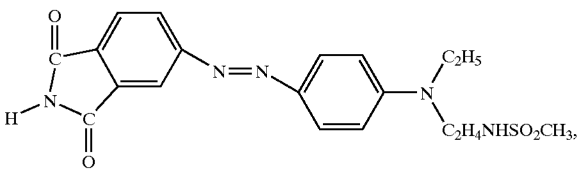
[0263] To a slurry of the diester compound (12.00 g, 0.0269 mole) having the structure



[0264] in water (150 ml) was added aqueous 50% NaOH solution (10.80 g) and 2-ethoxyethanol (20 ml). The reaction mixture was heated at about 70-80° C. for 2.0 hours and allowed to cool. The cloudy reaction mixture was clarified by filtering through Celite filter aid and the filtrate was drowned into ice/water mixture (150 g). Conc. HCl was added dropwise with stirring to bring the pH to about 2.5. The tan solid was collected by filtration, washed with water and dried at 40° C. under nitrogen (yield—10.04 g). FDMS indicated the product to have the structure of the coupler used in Example 91a.

EXAMPLE 92

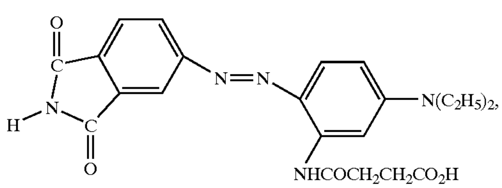
[0265] A mixture of the diacidic azo compound (0.83 g, 0.002 mole) having the structure



[0266] 1,2-ethanediol, dimethanesulfonate (0.44 g, 0.002 mole), potassium carbonate (0.5 g) and DMF (7.5 ml) was heated at about 95° C. for 3.0 hours. The polydye was isolated by drowning the reaction mixture into water and acidifying with acetic acid, followed by filtering, washing with water and drying in air. GPC analysis indicated a Mw of 2,379, a Mn of 1,363 a Mw/Mn of 1.74. An absorption maximum was observed-in DMF in the visible absorption spectrum at 480 nm.

EXAMPLE 93

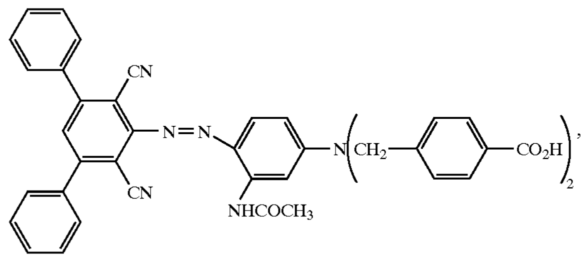
[0267] A mixture of the diacidic azo compound (1.26 g, 0.003 mole) having the structure



[0268] 1,6-hexanediol, dimethanesulfonate (0.82 g, 0.003 mole), potassium carbonate (0.50 g) and DMF (8.0 mL) was heated at about 95° C. for 1.5 hours. The reaction mixture was drowned into methanol (100 mL) and acetic acid (1.0 mL) was added The initially sticky polydye solidified after standing for about 1.0 hour and was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—0.60 g). GPC analysis indicated a Mw of 2,667, a Mn of 1,695 and a Mw/Mn of 1.57. An absorption maximum at 508 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLE 93a

[0269] A mixture of the diacidic azo compound (3.62 g, 0.005 m) having the structure



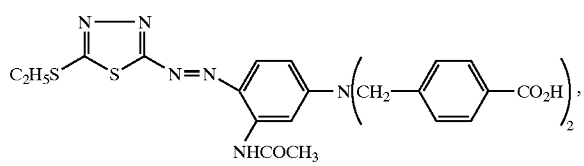
[0270] 1,2-ethanediol, dimethanesulfonate (1.10 g, 0.005 m), potassium carbonate (1.50 g) and DMF (30 mL) was heated at about 95° C. with stirring for 2.0 hours. The reaction mixture was drowned into methanol (100 mL) and the red polydye was collected by vacuum filtration and washed with methanol, water containing acetic acid, hot water and dried in air (yield—3.08 grams). GPC analysis indicated a Mw of 7,176, a Mn of 3,533 and a Mw/Mn of 2.02. An absorption maximum was observed in the visible light absorption spectrum at 525 nm.

EXAMPLE 93b

[0271] To conc. H_2SO_4 (5.0 mL) was added dry $NaNO_2$ (0.72 g) portionwise with stirring, allowing the temperature to rise. The nitrosyl sulfuric acid solution was stirred and cooled and 1:5 acid (1 part propionic:5 parts acetic acid) (10 mL) was added below about 15° C., followed by 2,6-dicyano-3,5-diphenylaniline (2.95 g, 0.01 m) and 1:5 acid (10 mL) both added at 0-5° C. After being stirred for 2.0 hours at 0-5° C., the diazonium solution was added to a stirred solution of 3-acetamido-N,N-bis (4-carboxyphenyl-methyl)aniline (4.18 g, 0.01 m) dissolved in a mixture of 1:5 acid (75 mL) plus 15% aqueous sulfuric acid (15 mL) at 0-5° C. Ammonium acetate was added portionwise until the coupling mixture was neutral to Congo Red test paper. After about 1.0 hour, water was added to the coupling mixture and the resulting slurry heated to about 60° C. The red product was collected by filtration, washed well with hot water and dried in air (yield—5.43 g). FDMS analysis indicated the structure to be that of the starting material for Example 93-1.

EXAMPLE 93c

[0272] A mixture of the diacidic azo compound (1.80 g, 0.003 m) having the structure



[0273] 1,2-ethanediol, dimethanesulfonate (0.66 g, 0.003 m), potassium carbonate (1.0 g) and DMF (8 mL) was heated at about 95° C. with occasional stirring. The polydye was isolated by drowning the reaction mixture into methanol (100 mL) followed by filtration and washing with methanol, water containing acetic acid, water and was then dried in air (yield—0.52 g). GPC analysis using NMP (N-methyl-2-pyrrolidinone) solvent indicated a Mw of 5,413, a Mn of 2,196 and a Mw/Mn of 2.46. An absorbance maximum at 517 nm was observed in the visible absorption maximum in DMF.

EXAMPLE 93d

[0274] A sample of 2-amino-5-ethylthio-1,3,4-thiadiazole (1.61 g, 0.01 m) was diazotized and coupled with 3-acetamido-N,N-bis(4-carboxyphenylmethyl)aniline (4.18 g, 0.01 m) and the red product isolated using the procedure described above in Example 93-1a. FDMS indicated the structure of the azo compound to be that of the starting material for Example 93-2.

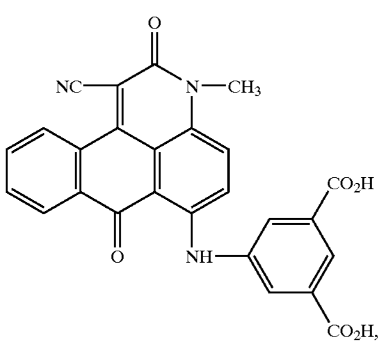
EXAMPLES 94-118

[0275] Colored EASTAR® PETG 6763 film was produced by melt blending the polydyes of Examples 69-93 and extruding according to the following procedures to produce Examples 94-118 (Table 2).

[0276] EASTAR® PETG polyester 6763, a poly(ethylene-cyclohexanedimethylene) terephthalate, (Eastman Chemical Company) (300 g of previously dried pellets) was dry blended with the azo dye composition (0.12 g) and the blend extruded and finally a 18-20 mil thick film prepare as described above for Examples 37-66.

EXAMPLE 119

[0277] A mixture of the diacidic anthrapyridone compound (0.93 g, 0.002 mole) having the structure



[0278] 1,2-ethandiol, dimethanesulfonate (0.44 g, 0.002 mole), potassium carbonate. (0.5 g) and DMF (8.0 mL) was heated at about 95° C. for 3.0 hours with occasional stirring. The reaction mixture was drowned into methanol (100 mL) and the violet polydye was collected by filtration, washed with methanol, water containing acetic acid, water and dried in air (yield—1.09 g). A number average molecular weight of 1,228 was obtained by GPC analysis. Absorption maxima at 544 and 583 nm were observed in the visible light absorption spectrum in DMF.

EXAMPLE 119a

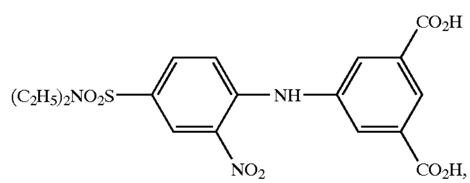
[0279] To a mixture of 1-cyano-6-(3',5'-dicarbomethoxyphenylamino)-3-methyl-3H-dibenz[f,ij]isoquinoline-2,7-dione (2.00 g, 0.00405 mole) stirred in 2-ethoxyethanol (50 mL) was added aqueous 50% NaOH solution (2.47 g). The reaction mixture was heated at 90-95° C. for 50 minutes and then was drowned into water. The mixture was acidified by addition of acetic acid and the solid product was collected by filtration, washed with water and dried in air (yield—1.78 g). FDMS indicated the product to be the diacidic anthrapyridone compound reacted in Example 119.

EXAMPLE 119b

[0280] A mixture of 6-bromo-1-cyano-3-methyl-3H-dibenz[f,ij]isoquinoline-2,7-dione (11.0 g, 0.03 mole), dimethyl 5-aminoisophthalate (25.1 g, 0.12 mole), cupric acetate (3.6 g), potassium carbonate (3.0 g) and DMF (90 mL) was heated and stirred under nitrogen to about 135-40° C. The reaction mixture became very thick and turned violet. Additional DMF (40 mL) was added and heating was continued at 135-40° C. for 2.0 hours. The reaction mixture was allowed to cool to about 60° C. and poured on a coarse fritted glass funnel for vacuum filtration. The product was washed with DMF and water and the water-wet cake was reslurried in boiling acetone (250 mL). After cooling, the product was collected by filtration, washed with acetone and dried in air (yield—10.8 g). FDMS indicated the product to be the diester anthrapyridone compound used in Example 119a.

EXAMPLE 120

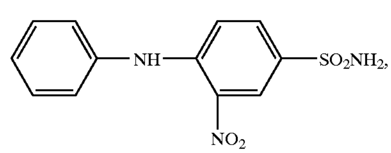
[0281] A mixture of the diacidic nitroarylamine compound (2.50 g, 0.0057 mole) having the structure



[0282] 1,2-ethanediol, dimethanesulfonate (1.25 g, 0.0057 mole), potassium carbonate (1.6 g) and DMF (15 mL) was heated at 95° C. for 2.5 hours. The reaction mixture was drowned into methanol (200 mL) and the yellow polydye was collected by filtration, washed containing acetic acid, water and dried at 40° C. (yield—0.77 g). An absorption maximum was observed at 412 nm in the visible absorption spectrum in DMF.

EXAMPLE 121

[0283] A mixture of the diacidic nitroarylamine compound (4.40 g, 0.015 mole) having the structure



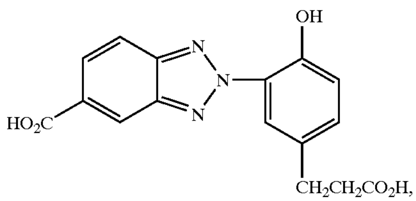
[0284] 1,2-ethanediol, dimethanesulfonate (3.27 g, 0.015 mole), potassium carbonate (2.0 g) and DMF 40 mL) was heated at 90-95° C. with stirring for 4.0 hours. The reaction mixture was drowned into methanol (200 mL) and the yellow polydye was collected by filtration, washed with methanol, water containing acetic acid, water and dried in air (yield—1.80 g). GPC analysis indicated a Mw of 1,585, a Mn of 1,024, a Mw/Mn of 1.54. An absorption maximum at 416 nm was observed in the visible light absorption spectrum in DMF.

EXAMPLES 122-124

[0285] Colored polyester film was produced by melt blending and extruding EASTAR® PETG polyester 6763 (Eastman Chemical Company) (300 g previously dried pellets) which had dry blended with the polydyes of Examples 119, 120, 121 to produce Examples 122-124, respectively, according to the procedure used to produce Examples 37-66. The film of Example 122 was violet and those of Examples 123 and 124 were bright yellow.

EXAMPLE 125

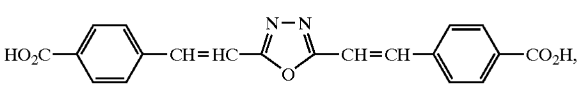
[0286] A mixture of the benzotriazole UV light absorbing compound. (3.27 g, 0.01 mole) having the structure



[0287] 1,2-ethanediol, dimethanesulfonate (2.18 g, 0.01 mole), potassium carbonate (2.76 g) and DMF (25 mL) was heated at about 95° C. for 6.0 hours. The reaction mixture was drowned into methanol (200 mL) and a little acetic acid added. The polymeric UV light absorbing compound was collected by filtration, washed with water containing a little acetic acid, hot water and then dried in air (yield—2.88 g). GPC analysis indicated a Mw of 7,561, a Mn of 2,632 and a Mw/Mn of 2.87. An absorption maximum was observed at 350 nm in the UV light absorption spectrum in methylene chloride.

EXAMPLE 126

[0288] A benzylidene type UV light fluorescent compound (1.0 g, 0.0028 mole) having the structure



[0289] 1,6-hexenediol, dimethanesulfonate (0.0028 mole), potassium carbonate (0.97 g) and DMF (10 mL) were mixed and the reaction mixture was heated at for 3.0 hours at about 120-130° C. The reaction mixture was drowned into methanol (100 mL) and the polymer was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—0.69 g). GPC indicated a Mw of 50,717, a Mn of 16,044 and a MW/Mn of 3.16.

EXAMPLE 127

[0290] EASTAPAK® PET 7352, a poly(ethyleneterephthalate) (Eastman Chemical Company) (400 g of previously dried pellets) was dry blended with the polymeric UV light fluorescent material of Example 126 (0.16 g). The blend was extruded with a C. W. Brabender ¾ inch extruder, equipped with a mixing screw, at 285° C. into a water bath and the extrudate pelletized. The pellets which contained about 400 ppm of the UV light absorber showed a strong blue white fluorescence under UV light.

EXAMPLE 128

[0291] Example 127 was repeated except that 8 mg of the UV light fluorescent material of Example 126 was added to the EASTAPAK® PET 7352. The resulting pellets showed a strong blue-white fluorescence under UV light and appeared very white in sunlight.

EXAMPLE 129

[0292] A mixture of Pc-Al—O—C_6H_3-3,5-diCO_2H (Pc=phthalocyanine) (1.74 g, 0.0024 mole), 1,6-hexanediol, dimethanesulfonate (0.66 g, 0.0024 mole), potassium carbonate (0.83 g) and DMF (10 mL) was heated and stirred at about 125° C. for 1 hour and then at about 140° C. for 1 hour. The reaction mixture was drowned into methanol (50 mL) and the polymeric product was collected by filtration, washed with methanol, water containing acetic acid, hot water and dried in air (yield—1.48 g).

EXAMPLE 130

[0293] EASTAPAK® PET 7352, a poly(ethyleneterephthalate) (Eastman Chemical Company) (400 g of previously dried pellets) was dry blended with the polymeric phthalocyanine compound of Example 129 (0.12 g). The blend was extruded with a C. W. Brabender ¾ inch extruder, equipped with a mixing screw, at 2850 into a water bath and the extrudate pelletized. The cyan pellets were redried at 70° C. for about 17 hrs at a pressure of about 1-5 torr. A portion of the dried pellets (1.40 g) was pressed into a film at 285° C. using a 2-inch diameter circular mold in a Pasadena Hydraulic, Inc. press using 12,000 pounds ram force (4-inch ram). A transparent cyan film was produced by quenching in water and had an absorption maximum at 684 nm in the light absorption spectrum.

EXAMPLE 131

[0294] Example 130 was repeated except that 4 mg of the polymeric phthalocyanine compound of Example 129 was added to the PET. The final film contained-about 10 ppm and had a light absorption maximum at 685 nm.

EXAMPLE 132

[0295] EASTAPAK® PET 7352, a poly(ethyleneterephthalate) (Eastman Chemical Company) (400 g of dried pellets) was dry blended with the polydye of Example 18 (0.6 g). The blend was extruded with a C. W. Brabender ¾ inch extruder, equipped with a mixing screw, at 285° C. into a water bath and the extrudate pelletized. Good color production resulted with no evidence of color loss by sublimation to give dark red pellets containing about 0.15% by weight of the polydye.

EXAMPLE 133

[0296] Example 132 was repeated using 0.6 g of the polydye of Example 75 as the colorant to give yellow pellets having about 0.15% by weight of the polydye. No loss of color by sublimation was observed.

EXAMPLES 134-182

[0297] The diacidic azo compounds of Formula VI in Table 3 are reacted with essentially equimolar amounts of 1,2-ethanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 134-182 in Table 3.

EXAMPLES 183-193

[0298] The diacidic diazo compounds of Formula VII in Table 4 are reacted with essentially equimolar amounts of 1,4-butanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 183-193 in Table 4.

EXAMPLES 194-202

[0299] The diacidic bisazo compounds of Formula VIIa in Table 5 are reacted with essentially equimolar amounts of 1,3-propanediol, dimethanesulfonate in DMF in the presence of sodium carbonate to yield the polydyes of Examples 194-202 in Table 5.

EXAMPLES 203-211

[0300] The diacidic benzylidene (methine) compounds in Table 6 are reacted with essentially equimolar amounts of 1,4-cyclohexanedimethanol, dimethanesulfonate in DMF in the presence of sodium carbonate to yield the polydyes of Examples 203-211 in Table 6.

EXAMPLES 212-220

[0301] The diacidic 3-aryl-2,5-dioxypyrroline compounds of Formula X in Table 7 are reacted with essentially equimolar amounts of diethylene glycol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 212-220 in Table 7.

EXAMPLES 221-230

[0302] The diacidic 3-aryl-5-dicyanomethylene-2-oxypyrroline compounds of Formula XI in Table 8 are reacted with essentially equimolar amounts of triethylene glycol, dimethanesulfonate to yield the polydyes of Examples 221-230 in Table 8.

EXAMPLES 231-239

[0303] The diacidic azo-methine compounds of Formula XIII in Table 9 are reacted with essentially equimolar amounts of 1,4-butanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 231-239 in Table 9.

EXAMPLES 240-269

[0304] The diacidic anthraquinone compounds of Formula XIV in Table 10 are reacted with essentially equimolar amounts of 2,2,4,4-tetramehtyl-1,3-cyclobutanediol, dimethanesulfonate in N,N-dimethylacetamide in the presence of potassium carbonate to yield the polydyes of Examples 240-269 in Table 10.

EXAMPLES 270-326

[0305] The diacidic anthraquinone compounds of Formula XV in Table 11 are reacted with essentially equimolar amounts of 1,2-ethanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 270-326 in Table 11.

EXAMPLES 327-344

[0306] The diacidic anthraquinone compounds of Formula XVI in Table 12 are reacted with essentially equimolar amounts of 1,6-hexanediol, dimethanesulfonate in N-methyl-2-pyrrolidinone in the presence of sodium carbonate to yield the polydyes of Examples 327-344 in Table 12.

EXAMPLES 345-361

[0307] The diacidic anthrapyridine compounds of Formula XVIII in Table 13 are reacted with essentially equimolar amounts of 1,4-butanediol, di-p-toluenesulfonate in the presence of DMF to yield the polydyes of Examples 345-361 in Table 13.

EXAMPLES 362-381

[0308] The diacidic anthraquinone compounds of Formula XIX in Table 14 are reacted with 2,2-dimethyl-1,3-propanediol, dimethanesulfonate in essentially equimolar amounts in DMF in the presence of potassium carbonate to yield the polydyes of Examples 362-381 in Table 14.

EXAMPLES 382-396

[0309] The diacidic anthraquinone compounds of Formula XIXc of Table 15 are reacted with essentially equimolar amounts of 1,2-ethanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 382-396 in Table 15.

EXAMPLES 397-414

[0310] The diacidic anthraquinone compounds of Formula XIXd in Table 16 are reacted with essentially equimolar amounts of 1,6-hexanediol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 397-414 in Table 16.

EXAMPLES 415-435

[0311] The diacidic anthraquinone compounds of Formula XIXe in Table 17 are reacted in essentially equimolar amounts with ethylene glycol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 414-435 in Table 17.

EXAMPLES 436-449

[0312] The diacidic anthraquinone compounds of Formula XIXf in Table 18 are reacted in essentially equimolar amounts with 1,4-cyclohexanedimethanol, dimethanesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 436-449 in Table 18.

EXAMPLES 450-455

[0313] The diacidic anthrapyridine compounds of Table 19 are reacted with essentially equimolar amounts of 1,6-hexanediol, di-p-toluenesulfonate in DMF in the presence of potassium carbonate to yield the polydyes of Examples 450-455 in Table 19.

EXAMPLES 456-465

[0314] The diacidic nitroarylamine compounds of Table 20 are reacted with 1,4-butanediol, dimethanesulfonate in essentially equimolar amounts in DMF in the presence of potassium carbonate to yield the polydyes of Examples 456-465 in Table 20.

EXAMPLES 466-505

[0315] The miscellaneous diacidic compounds of Table 21 are reacted with essentially equimolar amounts of the disulfonate compounds of Table 21 in DMF in the presence of potassium carbonate to yield the polydyes of Examples 466-505 in Table 21.

EXAMPLES 506-522

[0316] The diacidic UV light absorbing compounds of Table 22 are reacted with essentially equimolar amounts of the disulfonate compounds of Table 22 in DMF in the presence of potassium carbonate to yield the polymeric UV absorbers of Examples 506-522 in Table 22.

EXAMPLES 523-536

[0317] The diacidic infrared light absorbing compounds of Table 23 are reacted with essentially equimolar amounts of the disulfonate compounds of Table 23 in DMF in the presence of potassium carbonate to yield the polymeric infrared light absorbing compounds of Examples 523-536 in Table 23.

TABLE 1

Anthraquinone Polydyes in EASTAR ® PETG (300 ppm)		
Example No.	Polydye Melt Blended and Extruded With EASTAR ® PETG	Color of Film
37	Polydye of Example 7	Blue
38	Polydye of Example 8	Blue
39	Polydye of Example 9	Blue
40	Polydye of Example 10	Blue
41	Polydye of Example 11	Blue
42	Polydye of Example 12	Blue
43	Polydye of Example 13	Greenish-blue
44	Polydye of Example 14	Reddish-blue
45	Polydye of Example 15	Blue
46	Polydye of Example 16	Green
47	Polydye of Example 17	Bright blue
48	Polydye of Example 18	Bluish-red
49	Polydye of Example 19	Yellow
50	Polydye of Example 20	Orange

TABLE 1-continued

Anthraquinone Polydyes in EASTAR ® PETG (300 ppm)		
Example No.	Polydye Melt Blended and Extruded With EASTAR ® PETG	Color of Film
51	Polydye of Example 21	Red
52	Polydye of Example 22	Green
53	Polydye of Example 23	Yellow
54	Polydye of Example 24	Yellow
55	Polydye of Example 25	Yellow
56	Polydye of Example 26	Yellow
57	Polydye of Example 27	Blue
58	Polydye of Example 28	Red
59	Polydye of Example 29	Greenish-yellow
60	Polydye of Example 30	Yellow
61	Polydye of Example 31	Greenish-yellow
62	Polydye of Example 32	Blue
63	Polydye of Example 33	Yellow
64	Polydye of Example 34	Yellow
65	Polydye of Example 35	Greenish-blue
66	Polydye of Example 36	Greenish-blue

[0318]

TABLE 2

Azo Polydyes in EASTAR ® PETG 6763 (300 ppm)		
Example No.	Polydye Melt Blended and Extruded With EASTAR ® PETG	Color of Film
94	Polydye of Example 69	Violet
95	Polydye of Example 70	Blue
96	Polydye of Example 71	Yellow-brown
97	Polydye of Example 72	Red
98	Polydye of Example 73	Orange
99	Polydye of Example 74	Yellow
100	Polydye of Example 75	Greenish-yellow
101	Polydye of Example 76	Scarlet
102	Polydye of Example 77	Yellow
103	Polydye of Example 78	Scarlet
104	Polydye of Example 79	Yellow
105	Polydye of Example 80	Red
106	Polydye of Example 81	Orange
107	Polydye of Example 82	Reddish-brown
108	Polydye of Example 83	Red
109	Polydye of Example 84	Reddish-blue
110	Polydye of Example 85	Blue
111	Polydye of Example 86	Brown
112	Polydye of Example 87	Reddish-brown
113	Polydye of Example 88	Magenta
114	Polydye of Example 89	Magenta
115	Polydye of Example 90	Yellow
116	Polydye of Example 91	Red
117	Polydye of Example 92	Orange
118	Polydye of Example 93	Scarlet

[0319]

TABLE 3

Polydyes From Diacidic Compounds of Formula VI
R_6—N═N—Z

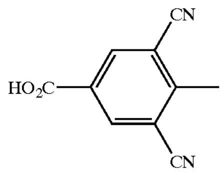
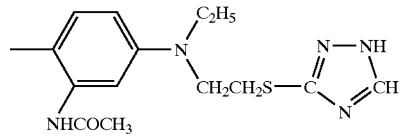
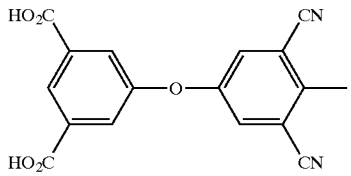
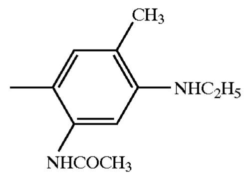
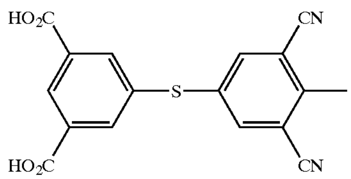
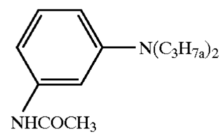
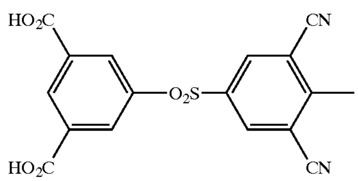
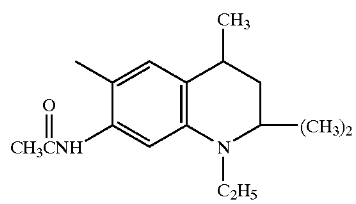
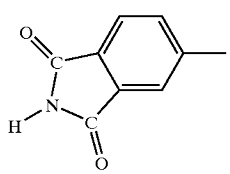
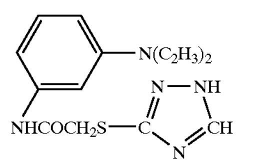
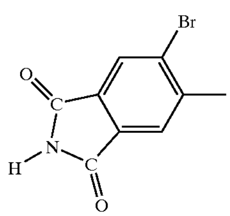
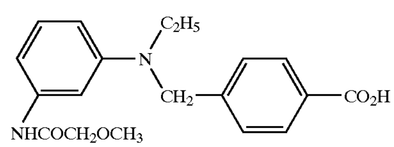
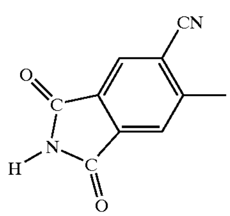
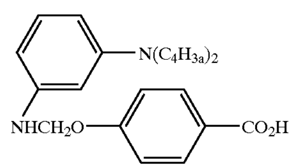
Example No.	R_4	Z	Color
134			violet
135			red
136			magenta
137			violet
138			scarlet
139			red
140			violet

TABLE 3-continued

Polydyes From Diacidic Compounds of Formula VI
R_6—N=N—Z

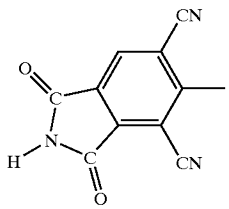
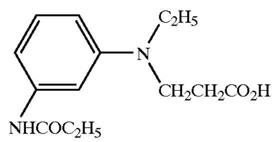
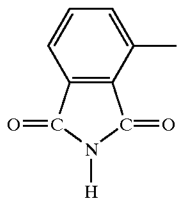
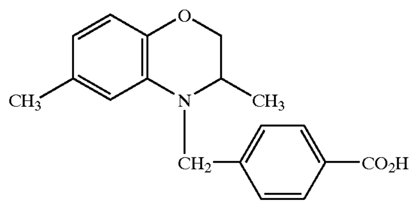
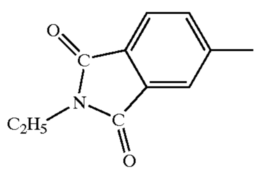
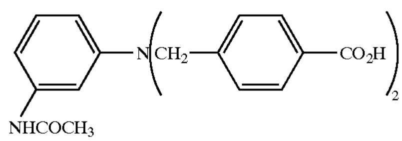
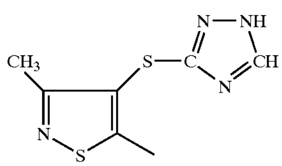
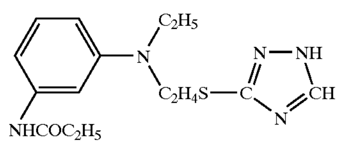
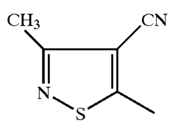
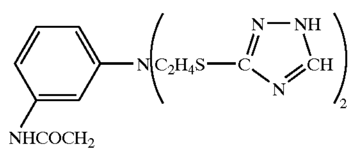
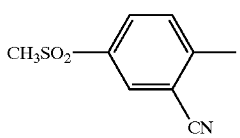
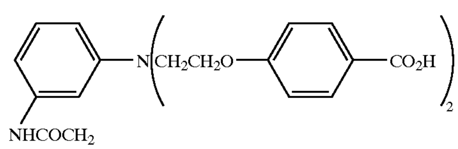
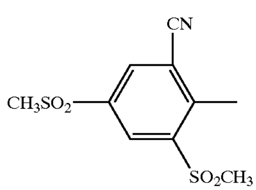
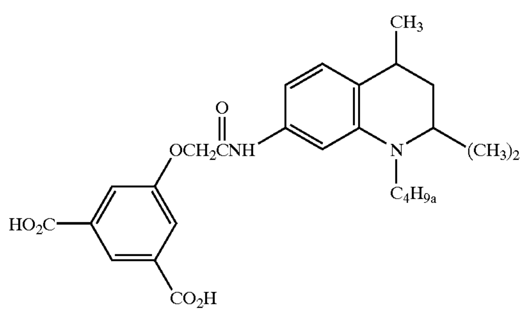
Example No.	R_4	Z	Color
141			blue
142			orange
143			scarlet
144			magenta
145			magenta
146			bluish-red
147			violet

TABLE 3-continued

Polydyes From Diacidic Compounds of Formula VI
R_6—N=N—Z

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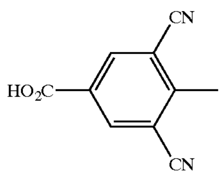
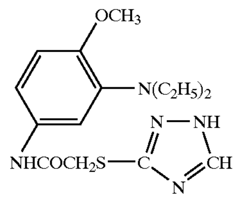
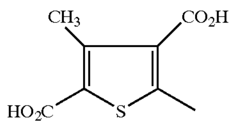
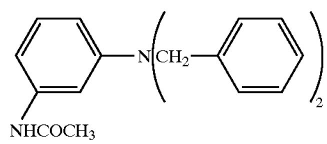
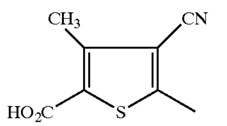
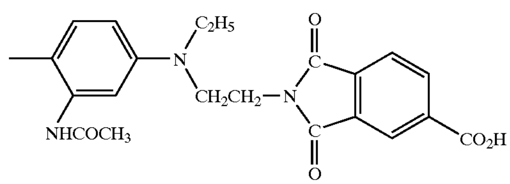
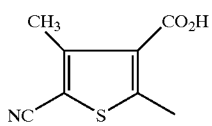
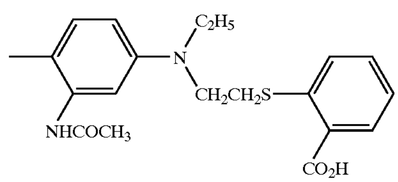
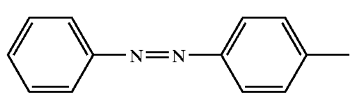
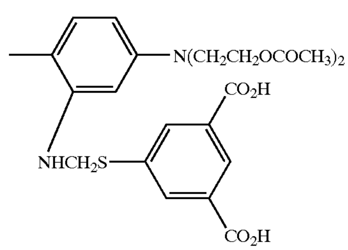
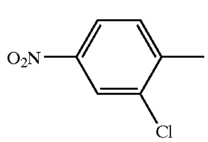
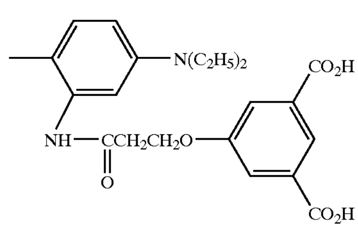
148			blue
149			red
150			violet
151			violet
152			orange
153			red

TABLE 3-continued

Polydyes From Diacidic Compounds of Formula VI
$R_6—N{=}N—Z$

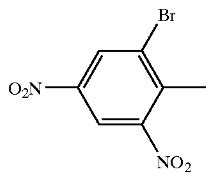
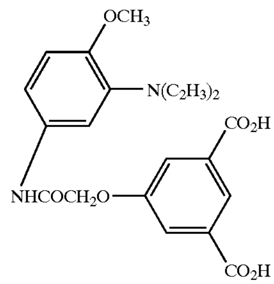
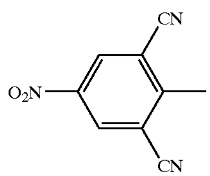
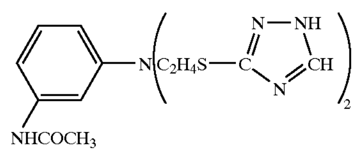
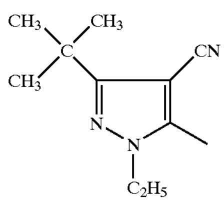
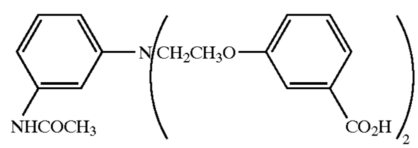
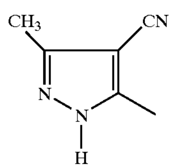
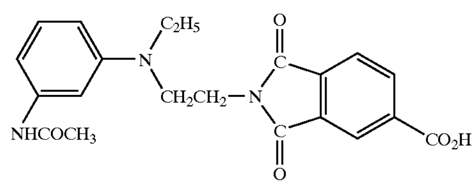
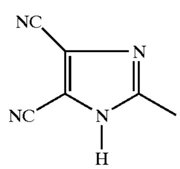
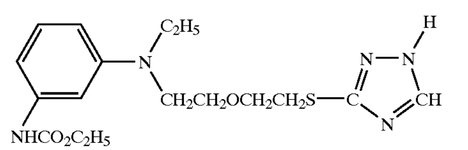
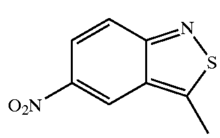
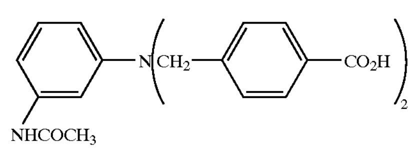
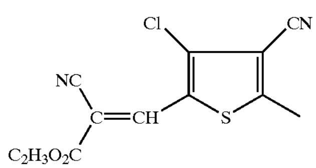
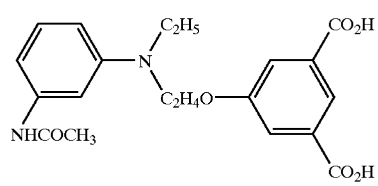
Example No.	R_4	Z	Color
154			navy blue
155			blue
156			red
157			orange
158			red
159			blue
160			blue

TABLE 3-continued

Polydyes From Diacidic Compounds of Formula VI
R_6—N=N—Z

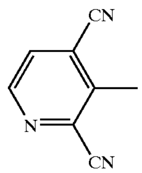
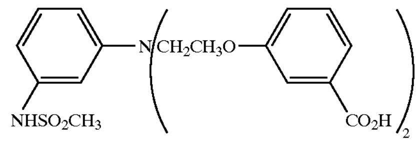
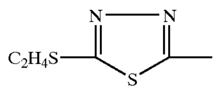
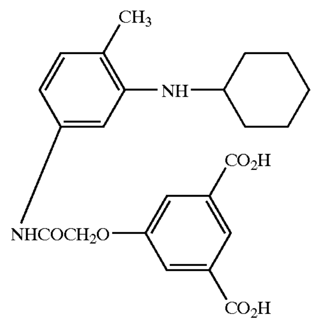
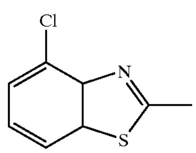
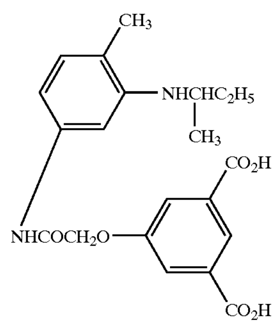
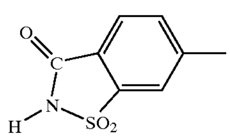
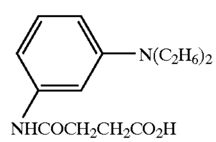
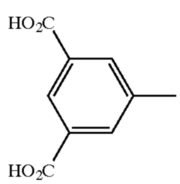
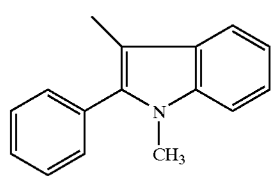
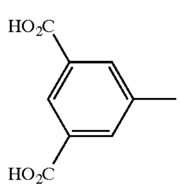
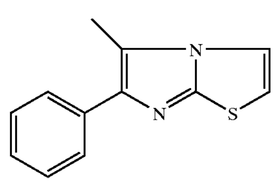
Example No.	R_4	Z	Color
161			red
162			red
163			red
164			orange
165			yellow
166			yellow

TABLE 3-continued

Polydyes From Diacidic Compounds of Formula VI

$R_6—N═N—Z$

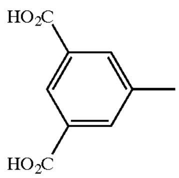
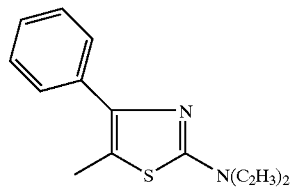
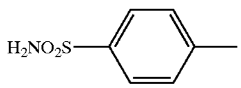
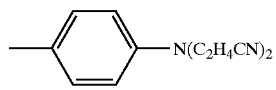
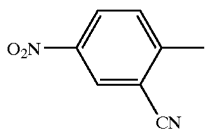
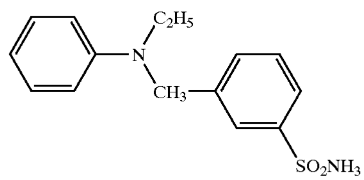
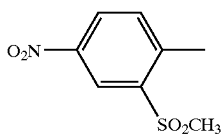
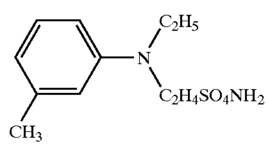
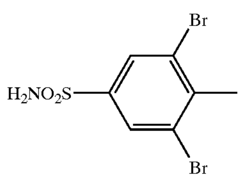
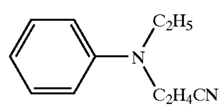
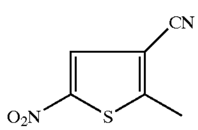
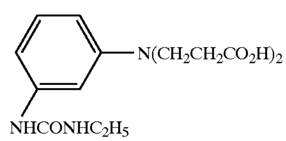
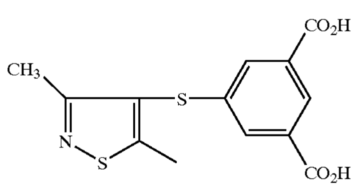
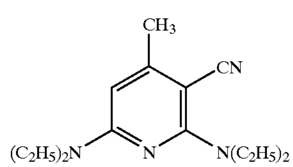
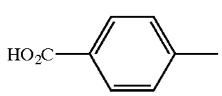
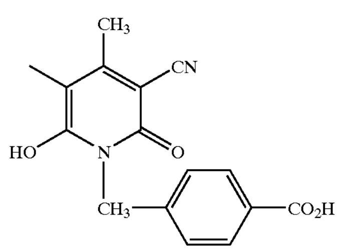
Example No.	R_4	Z	Color
167			orange
168			yellow
169			red
170			red
171			orange
172			blue
173			red
174			yellow

TABLE 3-continued

Polydyes From Diacidic Compounds of Formula VI
$R_6—N=N—Z$

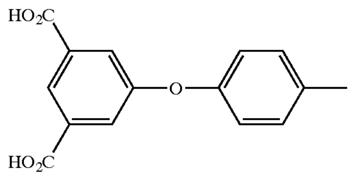
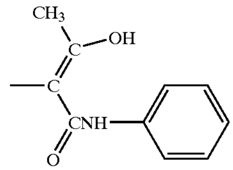
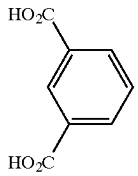
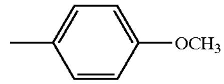
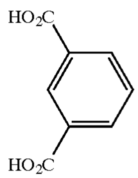
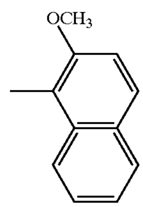
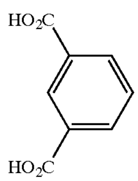
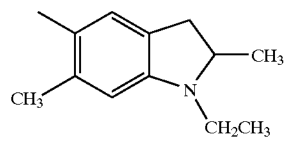
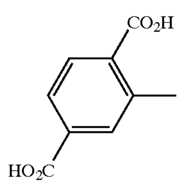
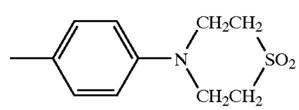
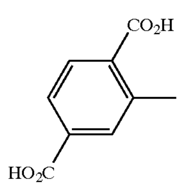
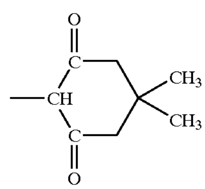
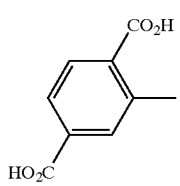
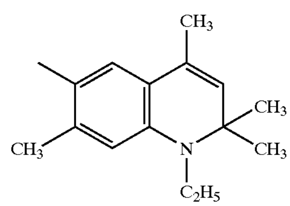
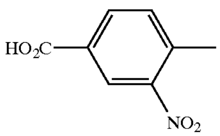
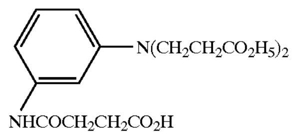
Example No.	R_4	Z	Color
175			yellow
176			yellow
177			yellow
178			orange
179			yellow
180			yellow
181			orange

TABLE 3-continued

Polydyes From Diacidic Compounds of Formula VI
R6—N=N—Z

Example No.	R_4	Z	Color
182			red

[0320]

TABLE 4

Polydyes From Diacidic Compounds of Formula VII
R6—N=N—R7—N=N—Z

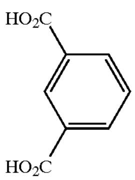
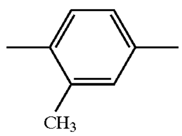
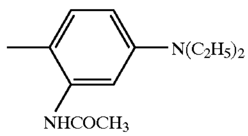
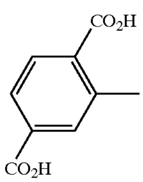
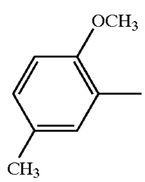
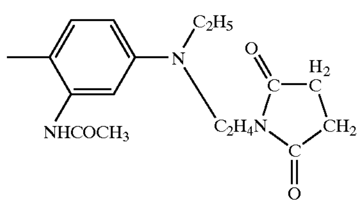
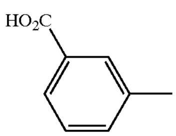
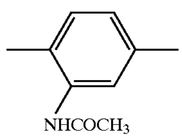
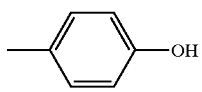
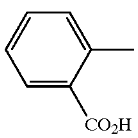
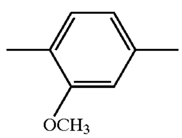
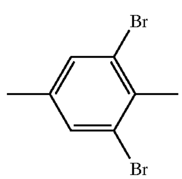
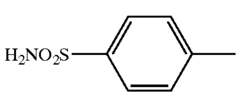
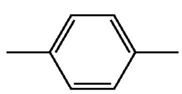
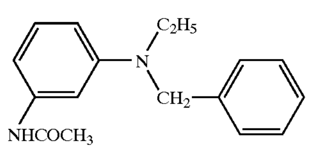
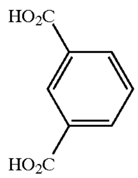
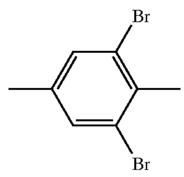
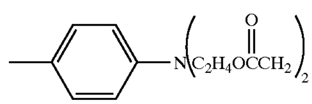
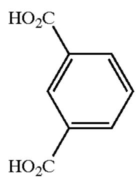
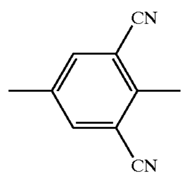
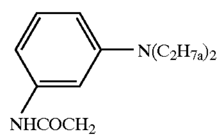
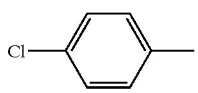
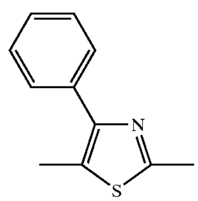
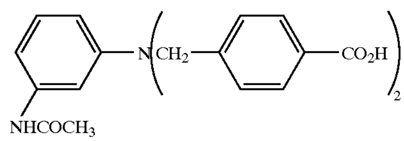
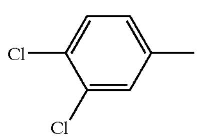
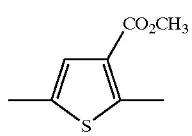
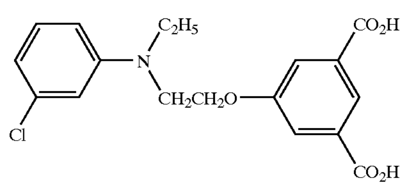
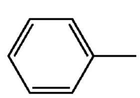
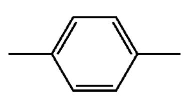
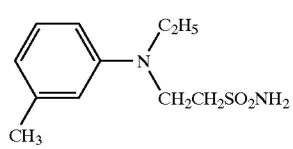
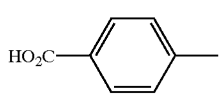
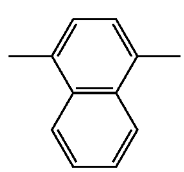
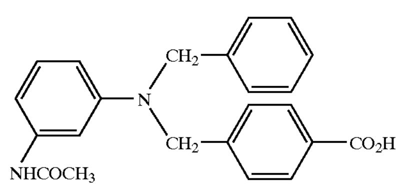
Example No.	R_6	R_7	Z	Color
183				red
184				red
185				reddish yellow
186				reddish yellow
187				red

TABLE 4-continued

Polydyes From Diacidic Compounds of Formula VII

R$_6$—N═N—R$_7$—N═N—Z

Example No.	R_6	R_7	Z	Color
188				yellow brown
189				blue
190				red
191				red
192				reddish yellow
193				red

[0321]

TABLE 5

Polydyes From Diacidic Compounds of Formula VIIa
$R_6—N=N—Y_1—N=N—R_6$

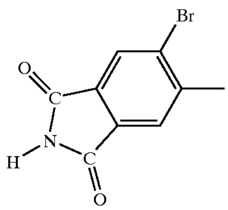
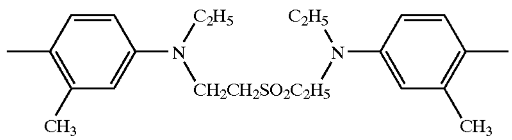
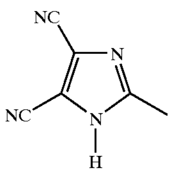
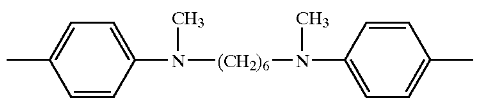
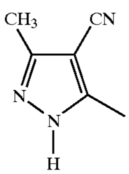
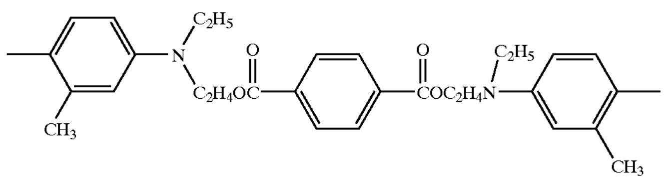
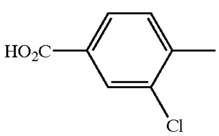
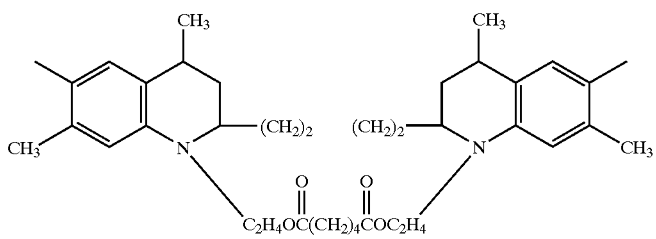
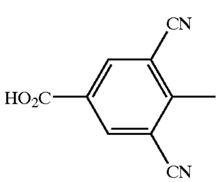
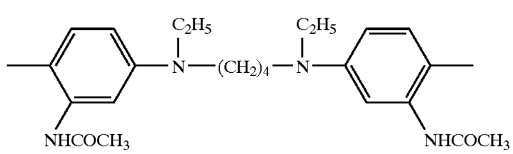
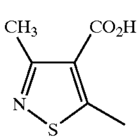
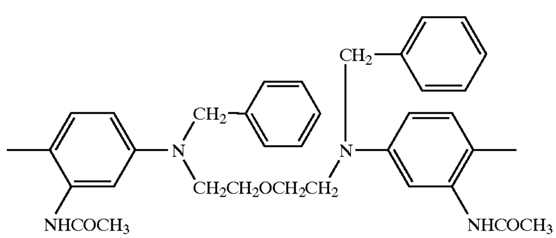
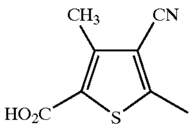
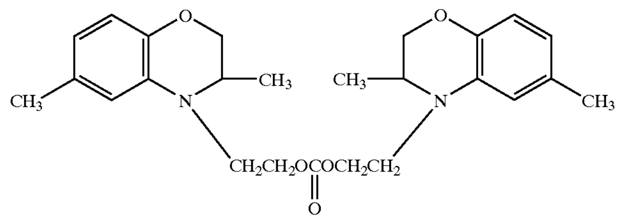
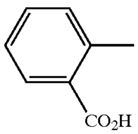
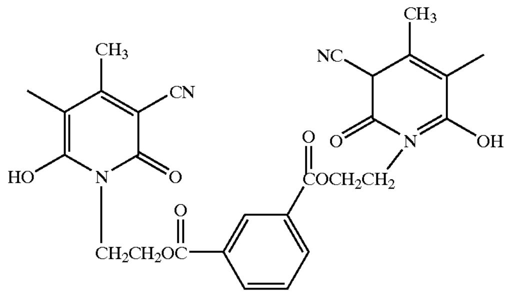
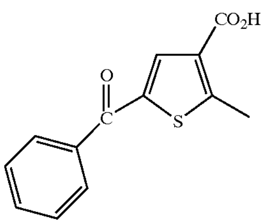
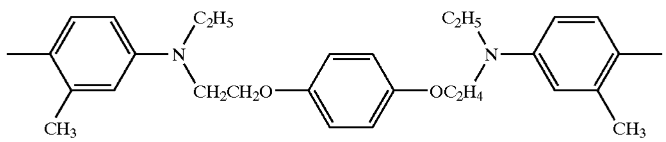
Example No.	R_6	Y_1	Color
194			red
195			orange
196			orange
197			orange
198			violet
199			red

TABLE 5-continued

Polydyes From Diacidic Compounds of Formula VIIa

$R_6—N═N—Y_1—N═N—R_6$

Example No.	R_6	Y_1	Color
200			violet
201			yellow
202			blue

[0322]

TABLE 6

Polydyes From Diacidic Compounds of Formula VIII

$R_{11}—CH═D$

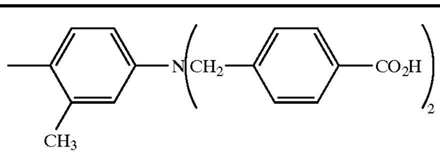
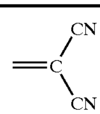
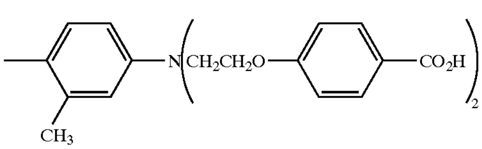
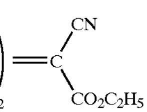
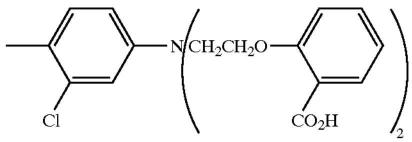
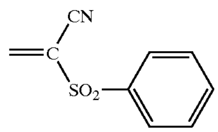
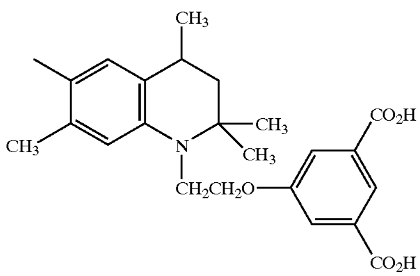
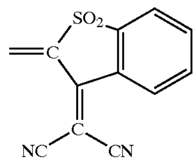
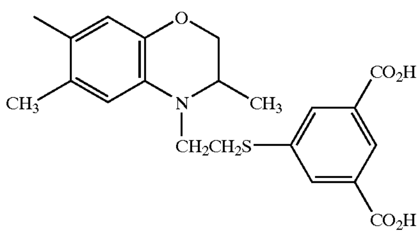
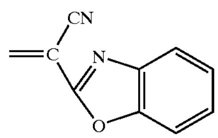
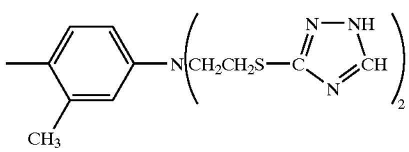
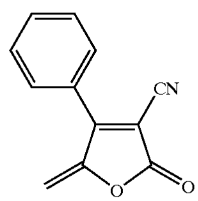
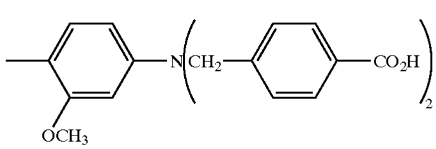
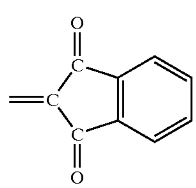
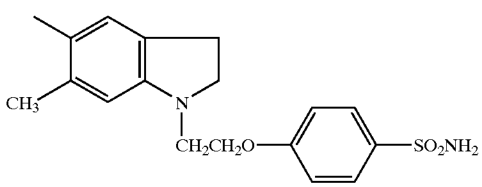
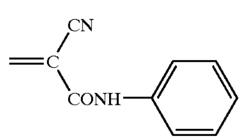
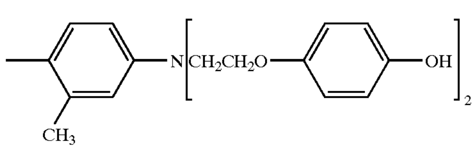
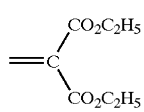
Example No.	R_{11}	D	Color
203			yellow
204			yellow

TABLE 6-continued

Polydyes From Diacidic Compounds of Formula VIII

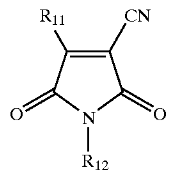
R_{11}—CH═D

Example No.	R_{11}	D	Color
205			yellow
206			blue
207			yellow
208			red
209			red
210			yellow
211			yellow

[0323]

TABLE 7

Polydyes From Diacidic Compounds of Formula X



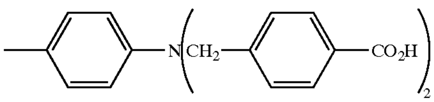
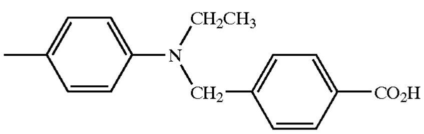
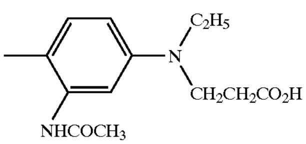
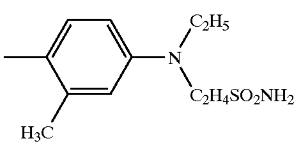
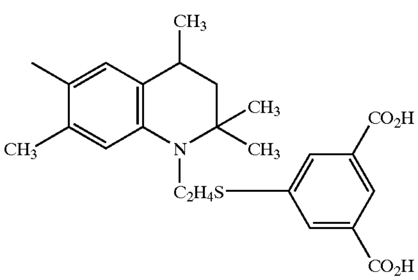
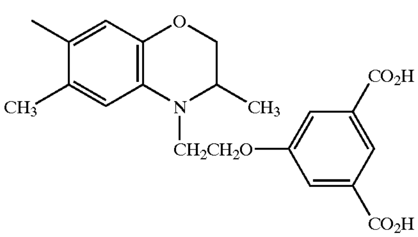
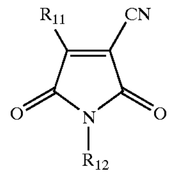
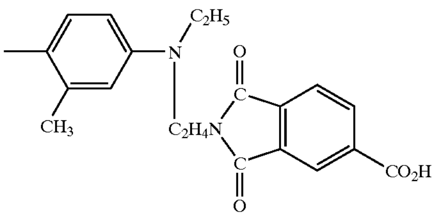
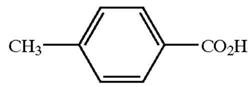
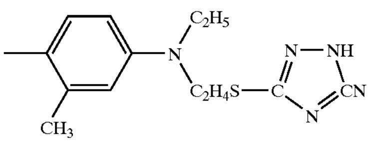
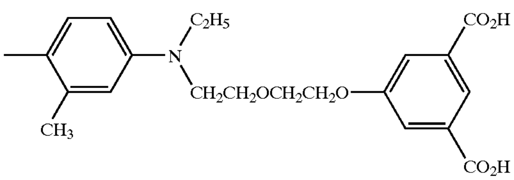
Example No.	R_{11}	R_{12}	Color
212		C_2H_5	red
213		H	red
214		H	red
215		$CH_2C_6H_5$	red
216		CH_3	violet
217		CH_2CH_2OH	violet

TABLE 7-continued

Polydyes From Diacidic Compounds of Formula X

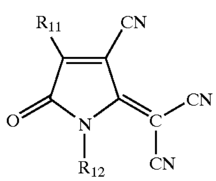


Example No.	R_{11}	R_{12}	Color
218			red
219		$CH_2CH_2CO_2H$	red
220		H	red

[0324]

TABLE 8

Polydyes From Diacidic Compounds of Formula XI



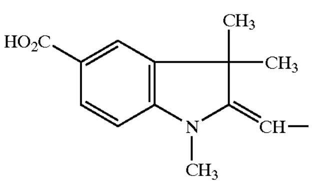
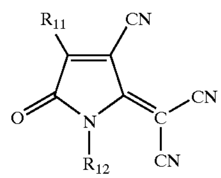
Example No.	R_{11}	R_{12}	Color
221		H	blue

TABLE 8-continued

Polydyes From Diacidic Compounds of Formula XI



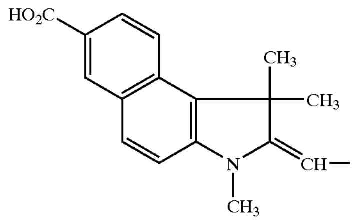
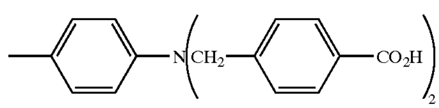
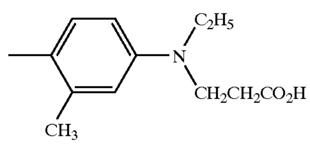
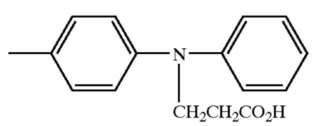
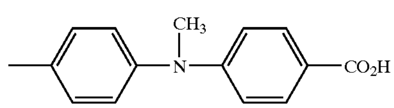
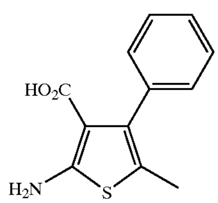
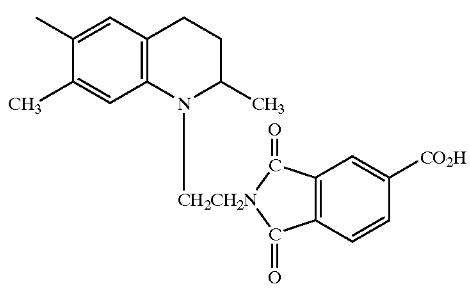
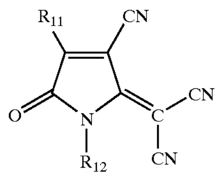
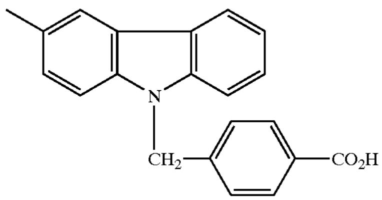
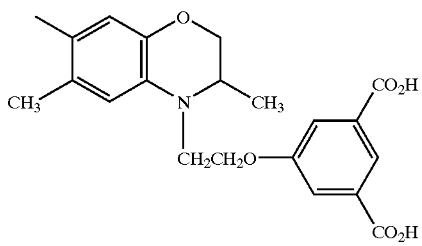
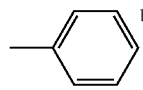
Example No.	R_{11}	R_{12}	Color
222		H	greenish blue
223		$CH_2CH{=}CH_2$	reddish blue
224		$CH_2C_5H_{11}$	blue
225		H	blue
226		H	blue
227		H	blue
228		H	blue

TABLE 8-continued

Polydyes From Diacidic Compounds of Formula XI



Example No.	R_{11}	R_{12}	Color
229		H	blue
230			blue

[0325]

TABLE 9

Polydyes From Diacidic Compounds of Formula XIII

D═HC—R_7—N═N—Z

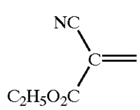
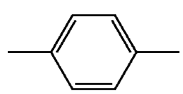
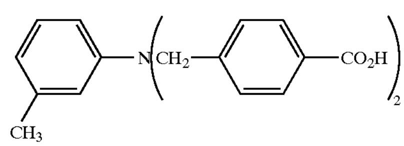
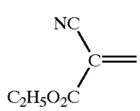
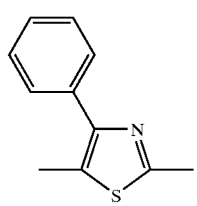
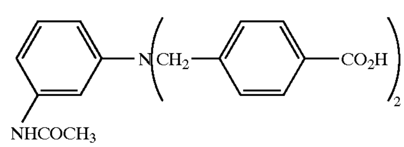
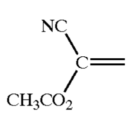
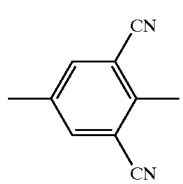
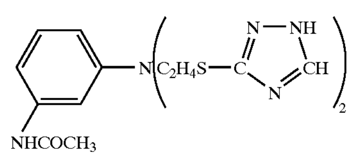
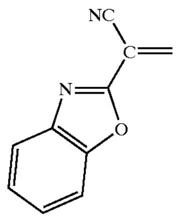
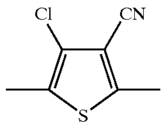
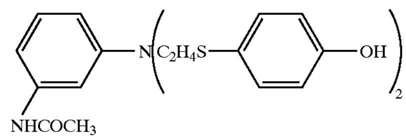
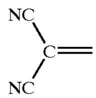
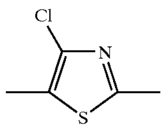
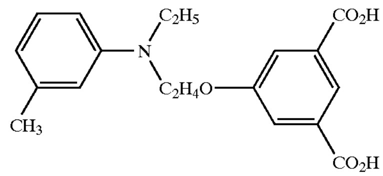
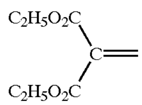
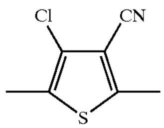
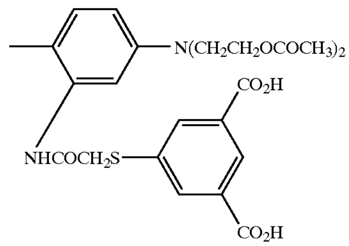
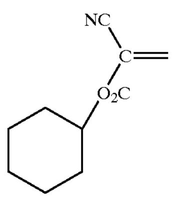
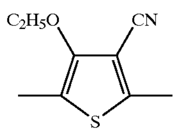
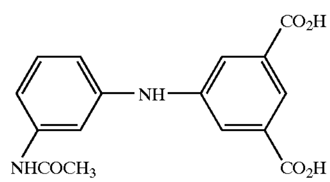
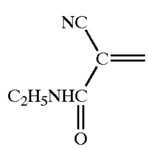
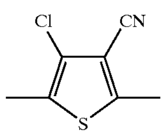
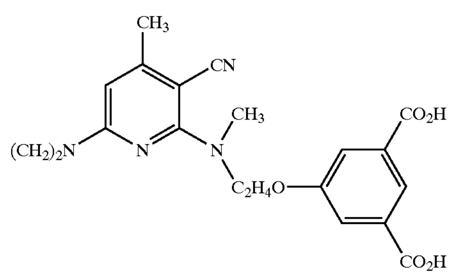
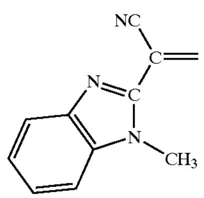
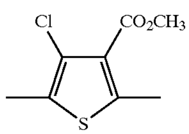
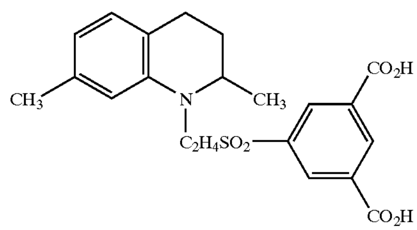
Example No.	D	R_7	Z	Color
231				red
232				blue
233				blue

TABLE 9-continued

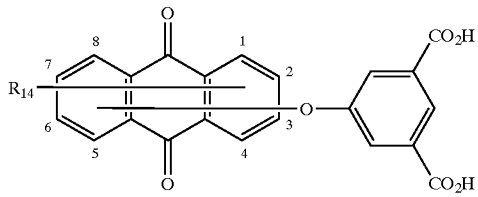
Polydyes From Diacidic Compounds of Formula XIII
$D{=}HC{-}R_7{-}N{=}N{-}Z$

Example No.	D	R_7	Z	Color
234				blue
235				blue
236				blue
237				blue
238				blue
239				blue

[0326]

TABLE 10

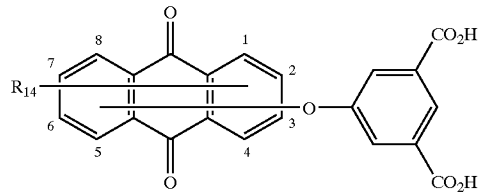
Polydyes From Diacidic Anthraquinone Compounds of Formula XIV

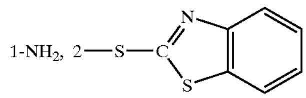
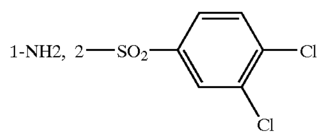


Example No.	Q	R_{14}	Color
240	5-S	1,4-diNHCH$_2$C(CH$_3$)$_2$CH$_2$OH	blue
241	2-O—	1-NH$_2$, 4-OH	red
242	2-S—	1-NH$_2$, 4-NHSO$_2$CH$_3$	violet
243	2-S—	1-NH$_2$, 4-NHSO$_2$C$_6$H$_5$	violet
244	2-SO$_2$—	1-NH$_2$, 4-NHC$_6$H$_5$	blue
245	2-SO$_2$—	1-NH$_2$, 4-NHC$_6$H$_4$-4-CH$_3$	blue
246	2-SO$_2$—	1-NH$_2$, 4-SC$_6$H$_5$	violet
247	2-S—	1-NH$_2$, 4-NHCOC$_2$H$_5$	violet
248	4-S—	1-NH$_2$	red
249	4-S—	1-NHC$_6$H$_{11}$	violet
250	4-S—	1-NHC$_6$H$_5$	violet
251	4-NH—	1-NH$_2$, 2-OCH$_3$	violet
252	4-NH—	1-NHC$_6$H$_5$	green
253	4-NH—	1-NHC$_6$H$_5$-2,6-diC$_2$H$_5$	blue
254	4-NH—	1-OH	violet
255	2-S—	1,4-di-OH	orange
256	2-SO$_2$—	1,4-di-OH	orange
257	4-S—	1-NHCH$_3$	violet
258	4-S—	1-NHCH$_2$CH(C$_2$H$_5$)C$_4$H$_9$	violet
259	6(7)S—	1,4-diNHC$_6$H$_3$-2,5-diC$_2$H$_5$	cyan
260	6(7)S—	1,4-diNHC$_6$H$_2$-2,4,6-triCH$_3$	cyan
261	6(7)SO$_2$—	1,4-diNHC$_6$H$_3$-2-CH$_3$, 6-C$_2$H$_5$	cyan
262	4-NH—	1,8-diOH, 5-NO$_2$	blue
263	4-NH—	1,8-diOH, 5-NH$_2$	blue

TABLE 10-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XIV

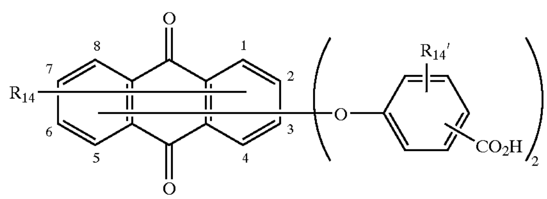


Example No.	Q	R_{14}	Color
264	4-NH—	1,8-diOH, 5-NHC$_6$H$_5$	blue
265	4-NH—	1,5-diOH, 8-NO$_2$	blue
266	4-NH—	1-NH$_2$, 2-CN	cyan
267	4-NH—	1-NH$_2$, 2-S—C$_6$H$_5$	blue
268	4-NH—		blue
269	4-NH—		blue

[0327]

TABLE 11

Polydyes From Diacidic Anthraquinone Compounds of Formula XV



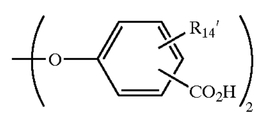
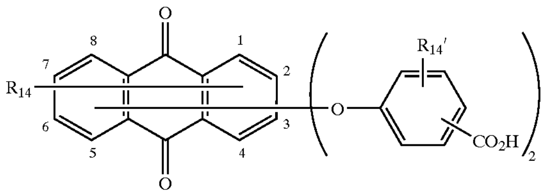
Example No.		R_{14}	Color
270	2,4-di-S—C$_6$H$_4$-3-CO$_2$H	1-NH$_2$	red
271	2,3-di-S—C$_2$H$_4$-4-CO$_2$H	1,4-diNH$_2$	blue
272	2,4-di-S—C$_6$H$_4$-2-CO$_2$H	1-NHCH$_3$	violet
273	2-SO$_2$C$_6$H$_4$-2-CO$_2$H, 4-NHC$_6$H$_4$-2-CO$_2$H	1-NH$_2$	blue
274	2-OC$_6$H$_4$-4-CO$_2$H, 4-NHC$_6$H$_4$-2-CO$_2$H	1-NH$_2$	violet
275	2-OC$_6$H$_4$-3-CO$_2$H, 4-S—NHC$_6$H$_4$-2-CO$_2$H	1-NH$_2$	red
276	2,4-di-S—C$_6$H$_4$-2-CO$_2$H	1-OH	orange
277	4,5-di-S—C$_6$H$_4$-2-CO$_2$H	1,8-diNHCH$_3$	blue

TABLE 11-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XV



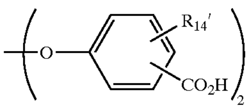
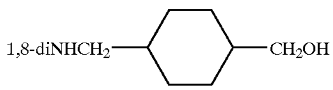
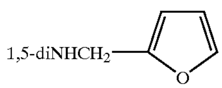
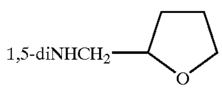
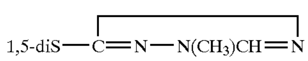
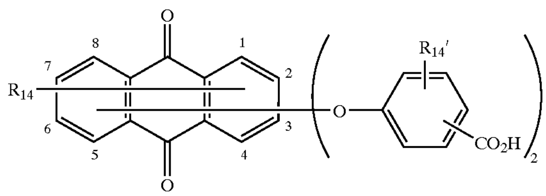
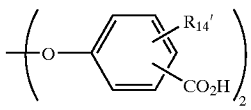
Example No.		R_{14}	Color
278	4,5-di-S—C_6H_4-3-CO_2H	1,8-diNHCH$_2$CH(CH$_3$)$_2$	blue
279	4,5-di-S—C_6H_4-4-CO_2H	1,8-diNH(CH$_2$)$_7$CH$_3$	blue
280	4,5-di-S—C_6H_4-2-CO_2H	1,8-diNHCH$_2$(C$_2$H$_5$)C$_2$H$_{9\text{-}n}$	blue
281	4,5-di-S—C_6H_4-2-CO_2H	1,8-diNHC$_6$H$_4$-4-CH$_3$	blue
282	4,5-di-S—C_6H_4-2-CO_2H	1,8-diNHC$_6$H$_{11}$	blue
283	4,5-di-S—C_6H_4-2-CO_2H	1,8-diNH(CH$_2$)$_3$OH	blue
284	4,5-di-S—C_6H_4-2-CO_2H	1,8-diNHCH$_2$C(CH$_3$)$_2$CH$_2$OH	blue
285	4,5-di-S—C_6H_4-2-CO_2H	1,8-diNHCH$_2$C$_6$H$_5$	blue
286	4,5-di-S—C_6H_4-2-CO_2H	1,8-diNHCH$_2$CH$_2$C$_6$H$_5$	blue
287	4,5-di-S—C_6H_4-2-CO_2H	1,8-diNHCH$_2$CH═CH$_2$	blue
288	4,5-di-S—C_6H_4-2-CO_2H	1,8-diNHCH$_2$C≡CH	blue
289	4,5-di-S—C_6H_4-2-CO_2H		blue
290	4,8-di-S—C_6H_4-2-CO_2H	1,5-diNHC$_2$H$_5$	blue
291	4,8-di-S—C_6H_4-2-CO_2H	1,5-diNHCH$_2$CH(CH$_3$)CN	blue
292	4,8-di-S—C_6H_4-4-CO_2H	1,5-diNHCH$_2$CH$_2$NHCOCH$_3$	blue
293	4,8-di-S—C_6H_4-2-CO_2H	1,5-diNH(CH$_2$)$_3$OC$_2$H$_5$	blue
294	4,8-di-S—C_6H_4-2-CO_2H	1,5-diNHCH$_2$C$_6$H$_{10}$-4-CH$_3$	blue
295	4,8-di-S—C_6H_4-2-CO_2H		blue
296	4,8-di-S—C_6H_4-2-CO_2H		blue
297	4,8-di-S—C_6H_4-2-CO_2H	1,5-diNH(CH$_2$)$_3$OC$_6$H$_5$	blue
298	4,8-di-S—C_6H_4-2-CO_2H	1,5-diNHCH(CH$_3$)(CH$_2$)$_2$C$_6$H$_5$	blue
299	4,8-di-S—C_6H_4-2-CO_2H	1,5-diNHCH(CH$_2$CH$_3$)$_2$	blue
300	4,8-di-S—C_6H_4-2-CO_2H	1,5-diSCH$_2$CH$_2$OH	red
301	4,8-di-S—C_6H_4-2-CO_2H	1,5-diSCH$_2$C$_6$H$_5$	red
302	4,8-di-S—C_6H_4-2-CO_2H	1,5-diSC$_6$H$_5$	red
303	4,8-di-S—C_6H_4-2-CO_2H	1,5-diSC$_6$H$_{11}$	red
304	4,8-di-S—C_6H_4-2-CO_2H	1,5-diSC$_6$H$_4$-4-OCH$_3$	red
305	4,8-di-S—C_6H_4-2-CO_2H	1,5-diSC$_6$H$_4$-4-Cl	red
306	4,5-di-S—C_6H_4-3-CO_2H	1,8-diSC$_6$H$_4$-4-CH$_3$	red
307	4,5-di-S—C_6H_4-2-CO_2H	1,8-diSC$_6$H$_3$-3,4-diCl	red
308	4,5-di-S—C_6H_4-2-CO_2H	1,8-diSC$_6$H$_4$-2-NHCOCH$_3$	red
309	4,5-di-S—C_6H_4-2-CO_2H	1,8-diSC$_6$H$_4$-4-NHCOC$_6$H$_5$	red
310	4,5-di-S—C_6H_4-2-CO_2H	1,8-diSCH$_2$CH$_2$OCOCH$_3$	red
311	4,8-di-S—C_6H_4-2-CO_2H	1,5-diSC$_6$H$_4$-4-C(CH$_3$)$_3$	red
312	4,8-di-S—C_6H_4-2-CO_2H	1,5-dibenzothiazol-2-ylthio	red
313	4,8-di-S—C_6H_4-2-CO_2H	1,5-dibenzoxazol-2-ylthio	red
314	4,8-di-S—C_6H_4-2-CO_2H		red
315	2,6-di-S—C_6H_4-2-CO_2H	1,5-diNH$_2$, 4,8-diOH	blue
316	2,6-di-O—C_6H_4-2-CO_2H	1,4,5,8-tetra NH$_2$	blue
317	4,8-di-S—C_6H_4-2-CO_2H	1,5-diNH$_2$, 2,6-diBr	blue

TABLE 11-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XV

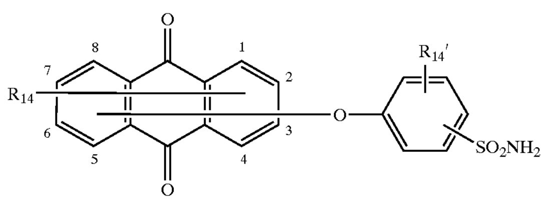


Example No.		R_{14}	Color
318	2,7-di-S—C_6H_4-2-CO_2H	1,8-diNH_2, 4,5-di$NHCO_2CH_3$	blue
319	2,7-di-SO_2—C_6H_4-2-CO_2H	1,8-diNH_2, 4,5-diOH	cyan
320	4,5-di-S—C_6H_4-2-CO_2H	1,8-di$NHCOCH_3$	orange
321	2,7-di-S—C_6H_4-2-CO_2H	1,8-diNH_2, 4,5-diNHC_6H_5	cyan
322	2,6-di-O—C_6H_4-2-CO_2H	1,8-diNH_2, 4,5-diNHC_6H_{11}	blue
323	2,8-di-SO_2—C_6H_4-4-CO_2H	1,4,5,8-tetra NH_2	cyan
324	4,8-di-S—C_6H_4-2-CO_2H	1,5-$NHCHCH_2SO_2CH_2CH$	blue
325	2,3-di-O—C_6H_4-4-CO_2H	1,4-diNH_2	violet
326	2,3-di-SO_2—C_6H_4-2-CO_2H	1,4-diNH_2	blue

[0328]

TABLE 12

Polydyes From Diacidic Anthraquinone Compounds of Formula XVI



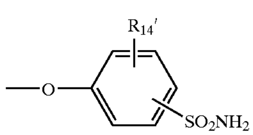
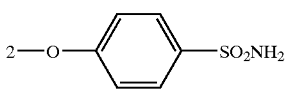
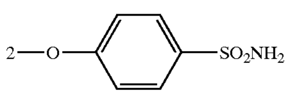
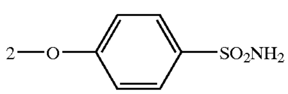
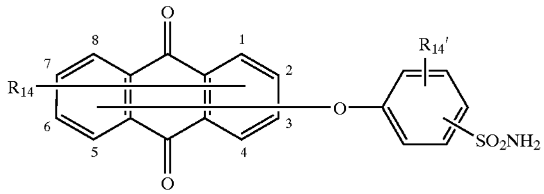
Example No.		R_{14}	Color
327		1,4-diOH	orange
328		1-di-NH_2	violet
329		1-NH_2, 4-OH	red

TABLE 12-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XVI



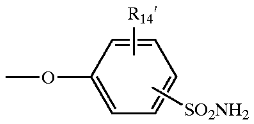
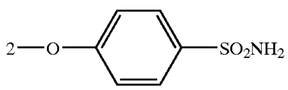
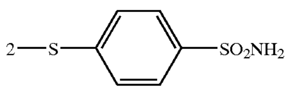
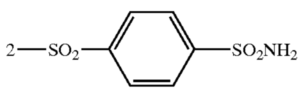
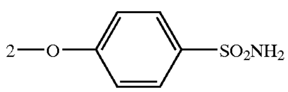
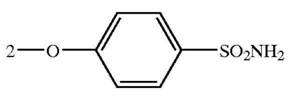
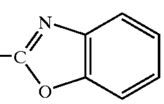
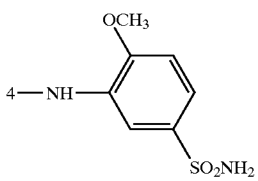
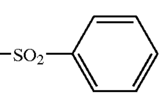
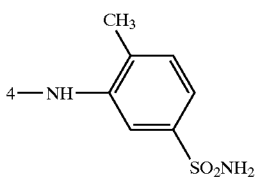
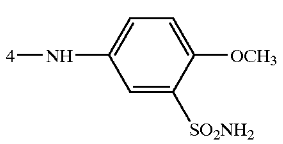
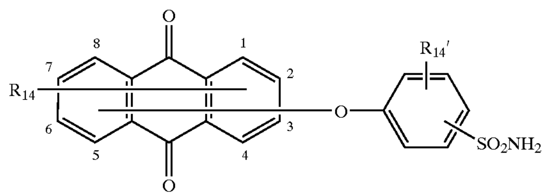
Example No.		R_{14}	Color
330		1-NH_2, 4-NHC_6H_5	violet
331		1-NH_2, 4-NHC_6H_4-4-Cl	blue
332		1-NH_2, 4-NHC_6H_4-4-OCH_3	blue
333		1-NH_2, 4-$NHSO_2C_4H_{9\text{-}n}$	red
334		1-NH_2, 4— 	red
335		1-NH_2, 2— 	blue-green
336		1-NH_2, 2-Br	blue
337		1-$NH_2SO_2C_6H_3$-3,4-diCl	blue

TABLE 12-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XVI



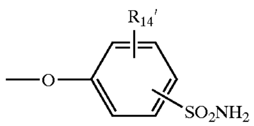
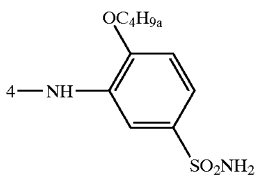
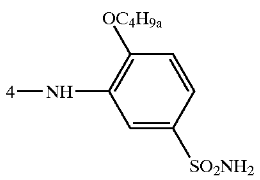
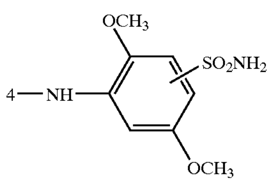
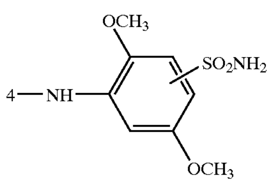
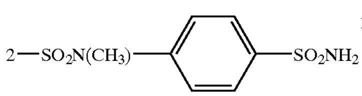
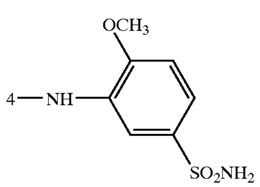
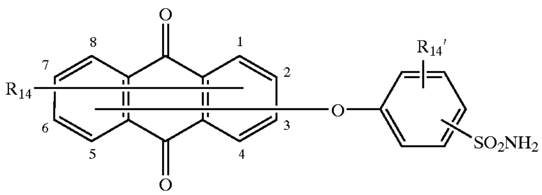
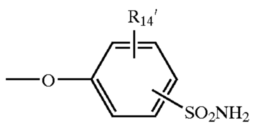
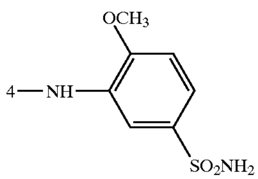
Example No.		R_{14}	Color
338		1-NH_2, 2-CN	cyan
339		1-NH_2, 2-NO_2	cyan
340		1-NH_2, 2-Br	blue
341		1-NH_2, 2-$SO_2N(C_2H_5)_2$	blue
342		1-NH_2, 4-NHC_6H_4-3-Cl	blue
343		1,8-diOH, 5-NO_2	blue

TABLE 12-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XVI

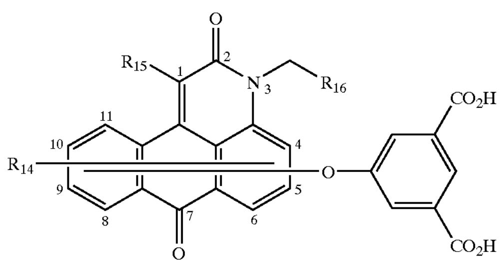


Example No.		R_{14}	Color
344		1,5-diOH, 8-NH_2	blue

[0329]

TABLE 13

Polydyes From Diacidic Anthrapyridone Compounds of Formula XVIII



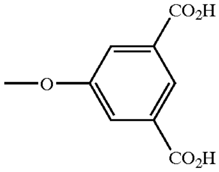
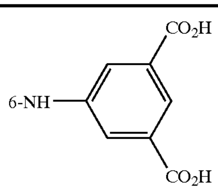
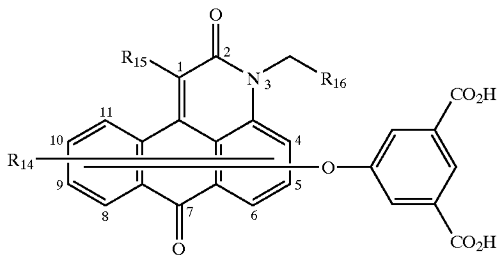
Example No.		R_{14}	R_{15}	R_{16}	Color
345		H	$CO_2C_2H_5$	CH_3	red

TABLE 13-continued

Polydyes From Diacidic Anthrapyridone Compounds of Formula XVIII



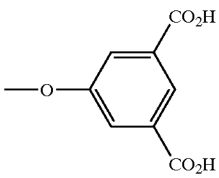
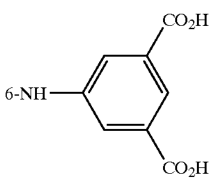
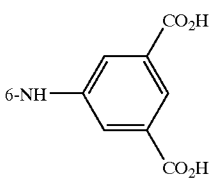
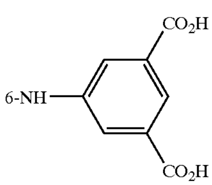
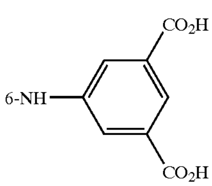
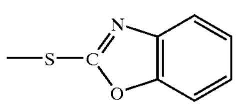
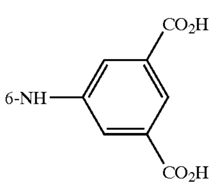
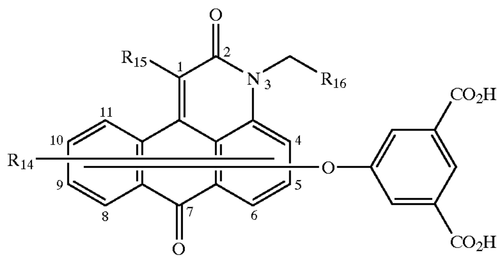
Example No. 		R_{14}	R_{15}	R_{16}	Color
346		H	CN	$CH_2CH(CH_3)_2$	violet
347		H	H	C_4H_{9-n}	red
348		H	Cl	C_6H_{11}	red
349		H		CH_3	red
350		H	CN	C_6H_5	violet

TABLE 13-continued

Polydyes From Diacidic Anthrapyridone Compounds of Formula XVIII



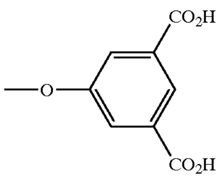
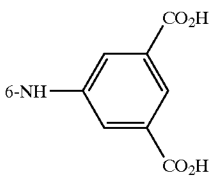
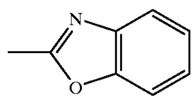
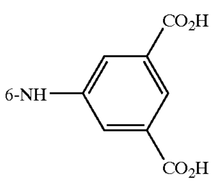
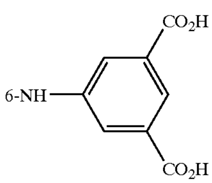
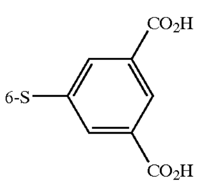
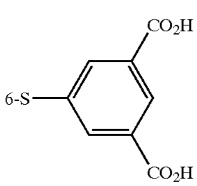
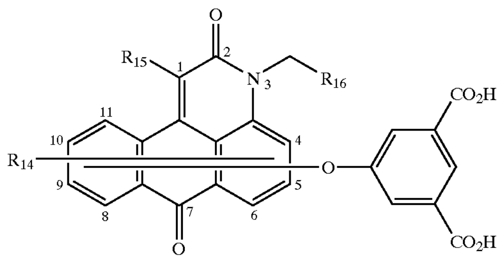
Example No.		R_{14}	R_{15}	R_{16}	Color
351		H		CH_3	violet
352		H	$SO_2C_6H_5$	CH_3	reddish blue
353		4-CH_3	$CO_2C_2H_5$	H	red
354		H	$CO_2C_2H_5$	H	orange
355		H	CN	CH_3	scarlet

TABLE 13-continued

Polydyes From Diacidic Anthrapyridone Compounds of Formula XVIII



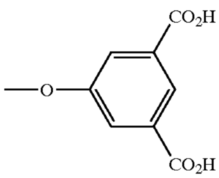
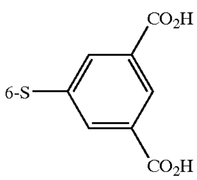
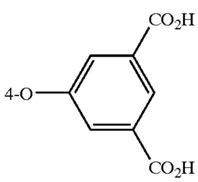
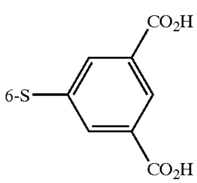
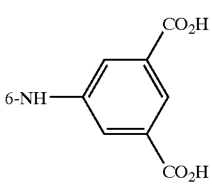
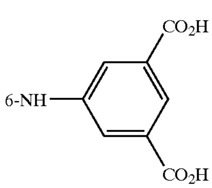
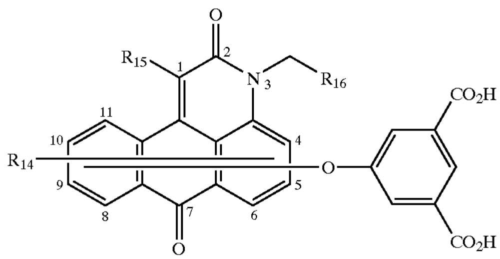
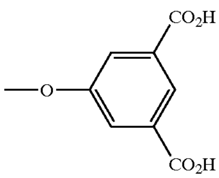
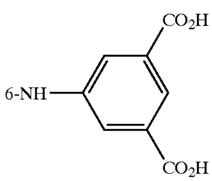
Example No. 	R_{14}	R_{15}	R_{16}	Color
356 	6-NHC_6H_5	CN	CH_3	violet
357 	6-NHC_6H_4-4-CH_3	$CO_2C_2H_5$	CH_3	red
358 	6-NHC_6H_5	H	CH_3	red
359 	H	COC_6H_5	$CH_2CH_2OC_2H_5$	red
360 	H	CN	$(CH_2)_7CH_3$	violet

TABLE 13-continued

Polydyes From Diacidic Anthrapyridone Compounds of Formula XVIII

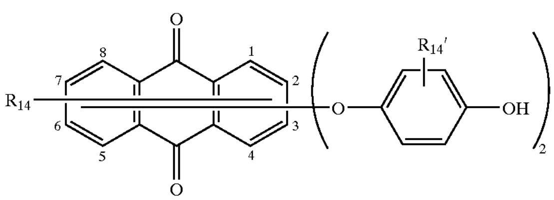


Example No.		R_{14}	R_{15}	R_{16}	Color
361		4-Br	CN	CH_3	violet

[0330]

TABLE 14

Polydyes From Diacidic Anthraquinone Compounds of Formula XIX



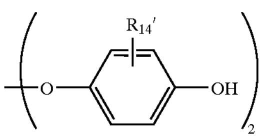
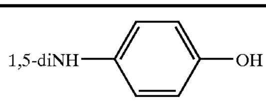
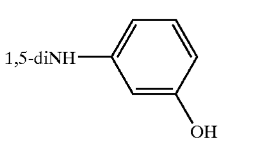
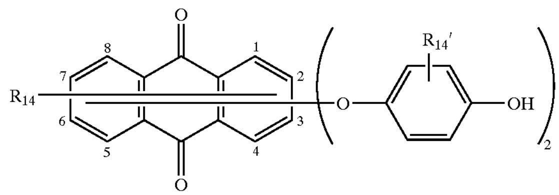
Example No.		R_{14}	Color
362		H	red
363		H	red

TABLE 14-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XIX



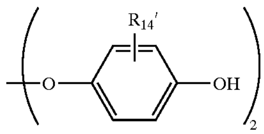
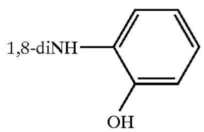
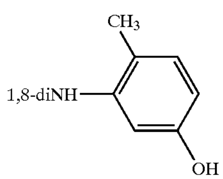
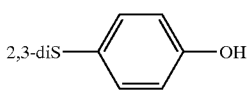
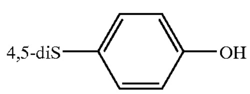
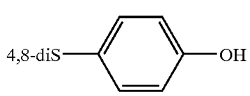
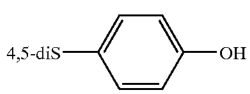
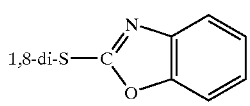
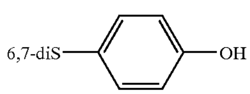
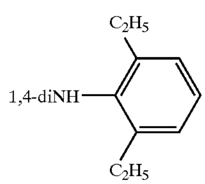
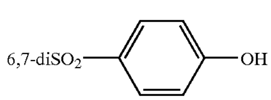
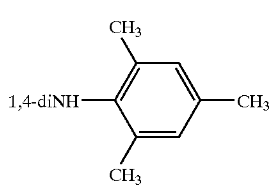
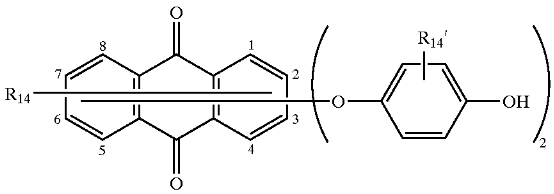
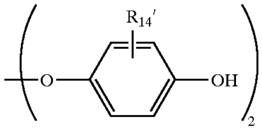
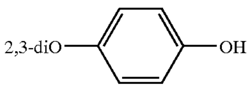
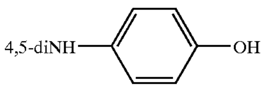
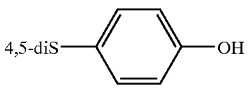
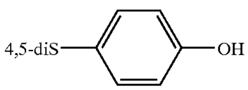
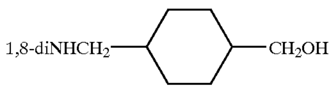
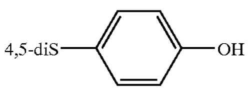
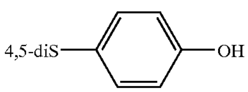
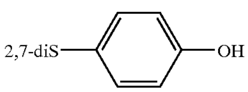
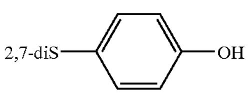
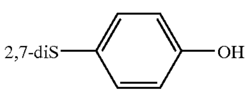
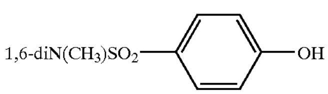
Example No.		R_{14}	Color
364		H	red
365		H	red
366		1,4-diNH_2	blue
367		1,8-di$NHCH_2CH(CH_3)_2$	blue
368		1,5-diSC_6H_5	red
369			red
370			cyan
371			cyan

TABLE 14-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XIX

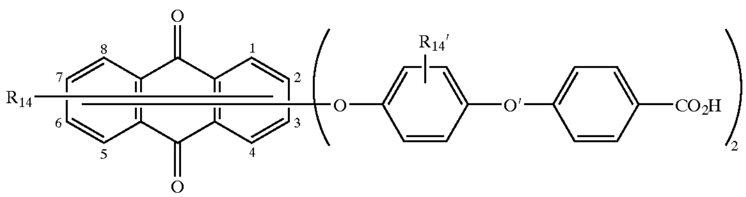


Example No.		R_{14}	Color
372		1,4-diNH$_2$	violet
373		1,8-diOH	blue
374		1,8-diNHC$_6$H$_{11}$	blue
375			blue
376		1,8-diNHCH$_2$C(CH$_3$)$_2$CH$_2$OH	blue
377		1,8-diNHCH$_2$CH(C$_2$H$_5$)C$_4$H$_{9-n}$	blue
378		1,4,5,8-tetra NH$_2$	blue
379		1,8-diNH$_2$, 4,5-diOH	blue
380		1,8-diNH$_2$, 4,5-diNHC$_6$H$_5$	cyan
381		H	yellow

[0331]

TABLE 15

Polydyes From Diacidic Anthraquinone Compounds of Formula XIXc



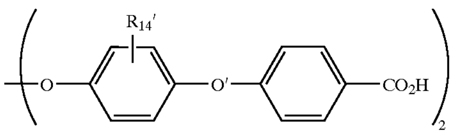
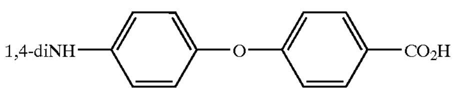
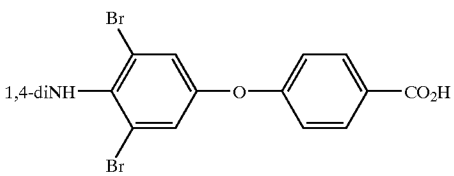
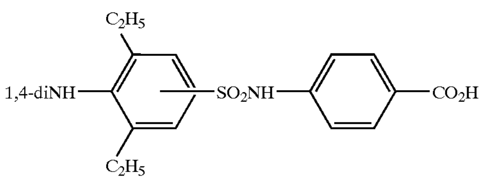
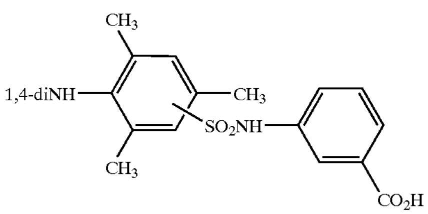
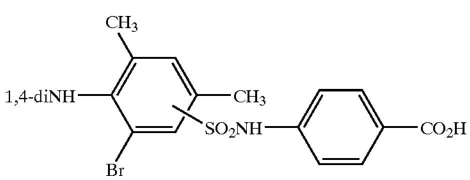
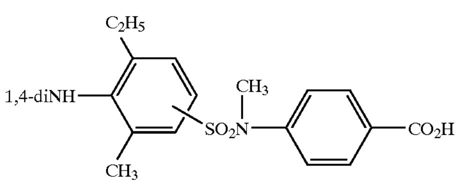
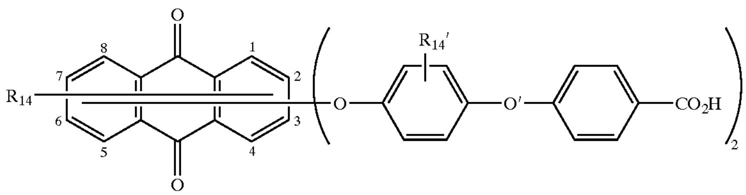
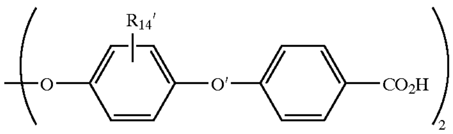
Example No.		R_{14}	Color
382		H	green
383		H	blue
384		H	blue
385		H	blue
386		H	blue
387		H	blue

TABLE 15-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XIXc





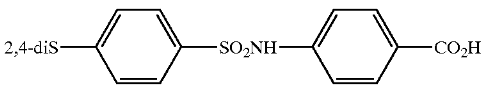
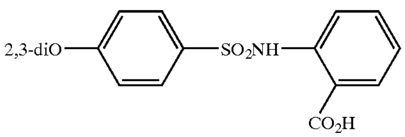
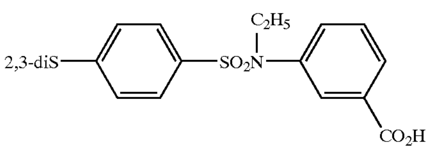
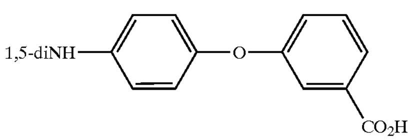
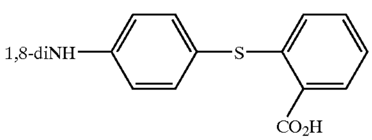
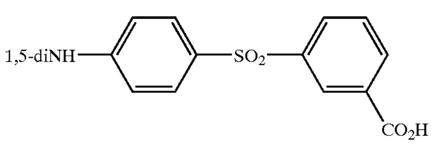
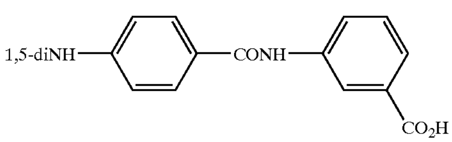
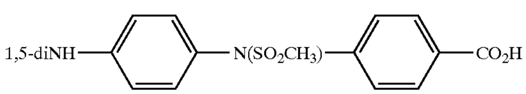
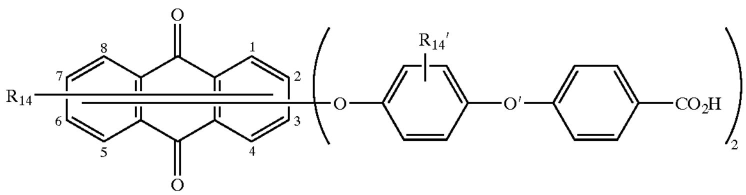
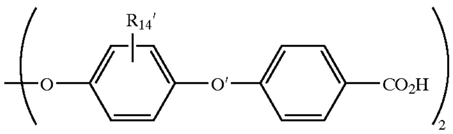
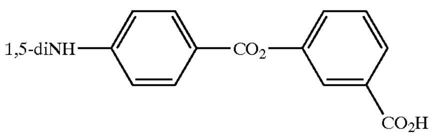
Example No.		R_{14}	Color
388		1-NH_2	red
389		1,4-diNH_2	violet
390		1,4-diNH_2	blue
391		H	red
392		H	red
393		H	red
394		H	red
395		H	red

TABLE 15-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XIXc



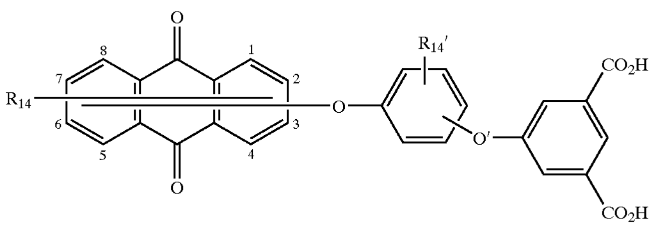


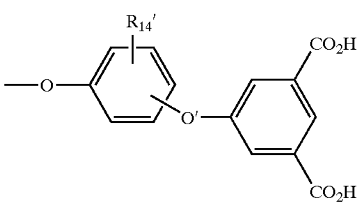
Example No.		R_{14}	Color
396		H	red

[0332]

TABLE 16

Polydyes From Diacidic Anthraquinone Compounds of Formula XIXd





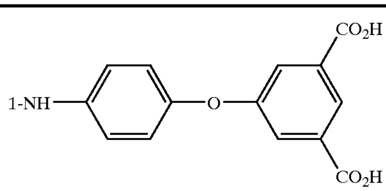
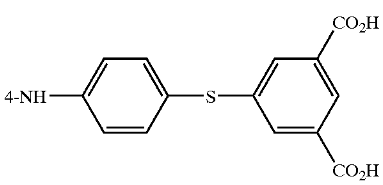
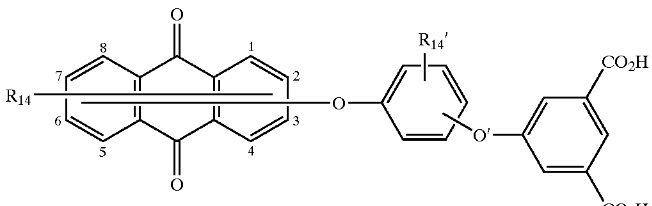
Example No.		R_{14}	Color
397		H	red
398		1-NHC_4H_{9-n}	blue

TABLE 16-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XIXd



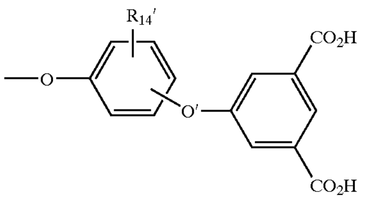
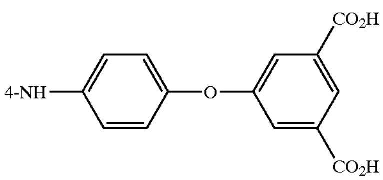
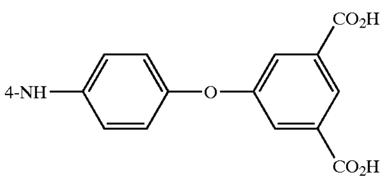
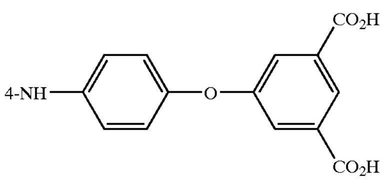
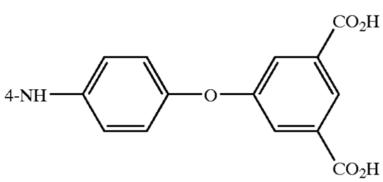
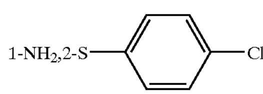
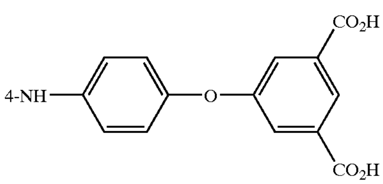
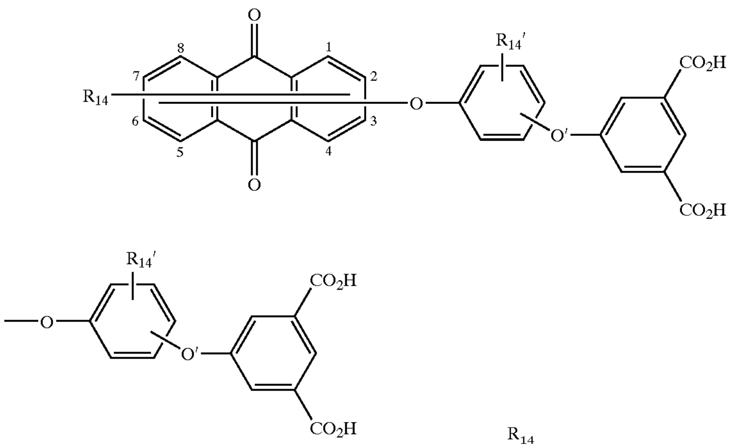
Example No.		R_{14}	Color
399		1-NH_2, 2-CN	cyan
400		1-NH_2, 2-$SO_2N(CH_3)C_6H_5$	blue
401		1-NH_2, 2-CF_2	cyan
402			blue
403		1-NH_2-2-$OCH_2CH_2$2OH	violet

TABLE 16-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XIXd



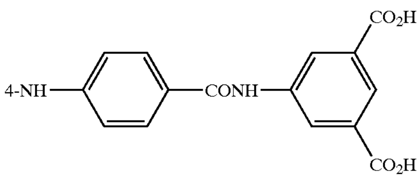
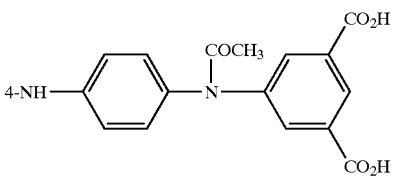
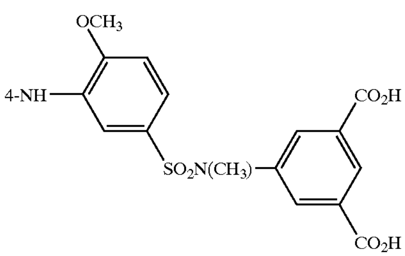
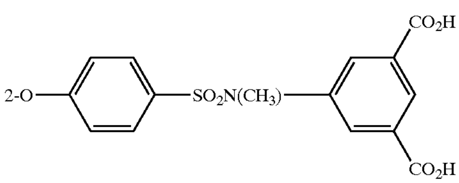
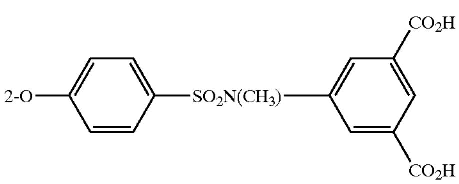
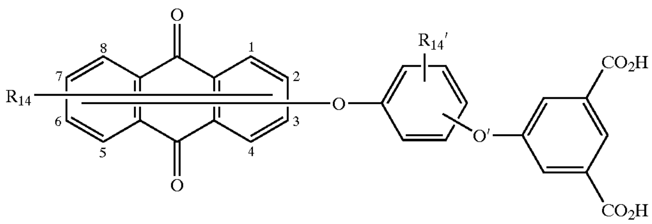
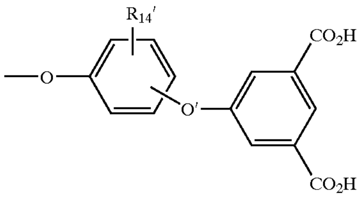
Example No.		R_{14}	Color
404		1-NH_2-2-Br	blue
405		1-NH_2, 2-$SO_2C_6H_5$	blue
406		1-NH_2-2-Br	blue
407		1-NH_2-4-OH	red
408		1,4-diNH_2	violet

TABLE 16-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XIXd





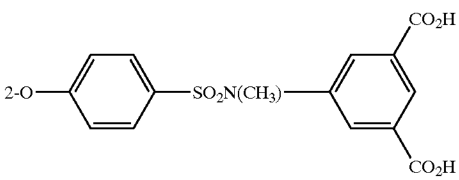
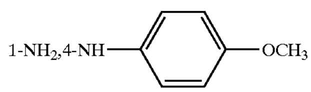
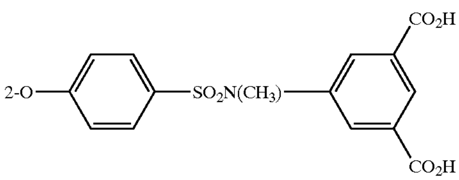
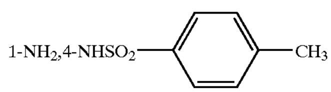
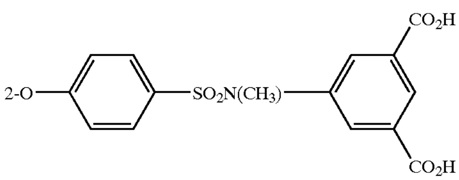
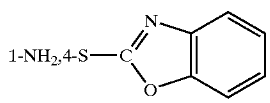
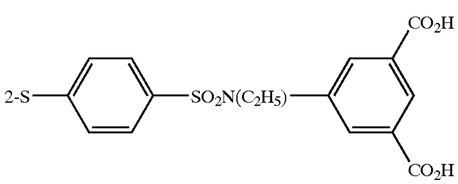
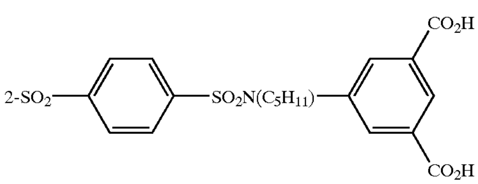
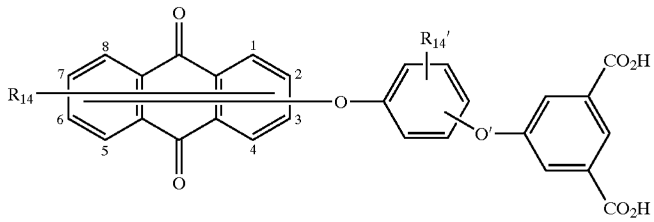
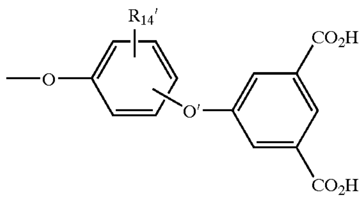
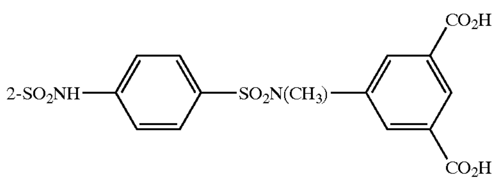
Example No.		R_{14}	Color
409			violet
410			red
411			red
412		$1\text{-}NH_2$, $4\text{-}NHC_6H_5$	blue
413		$1\text{-}NH_2$, $4\text{-}NHC_6H_{11}$	blue

TABLE 16-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XIXd

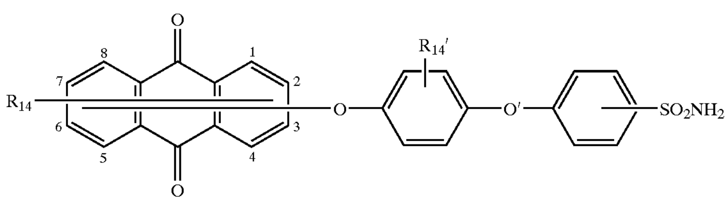


Example No.		R_{14}	Color
414		1-NH_2, 4-NHC_6H_5	blue

[**0333**]

TABLE 17

Polydyes From Diacidic Anthraquinone Compounds of Formula XIXe



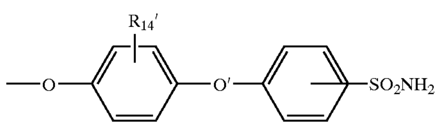
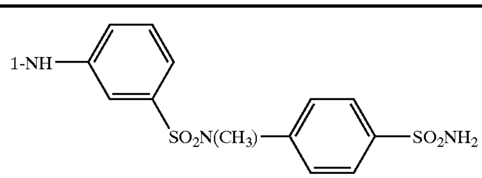
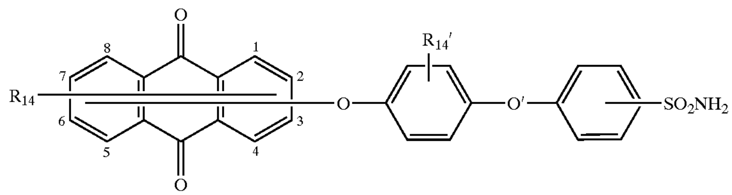
Example No.		R_{14}	Color
415		H	red

TABLE 17-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XIXe



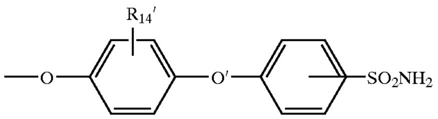
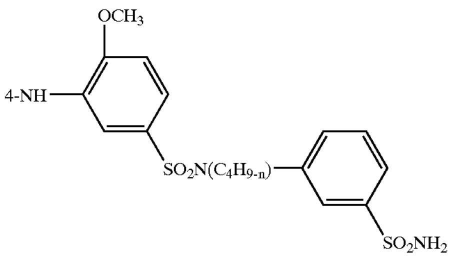
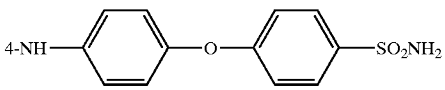
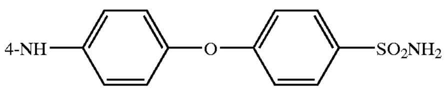
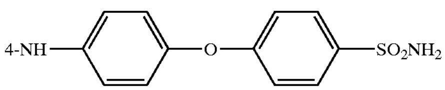
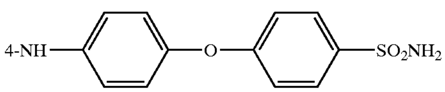
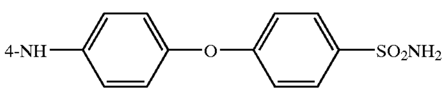
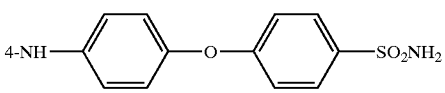
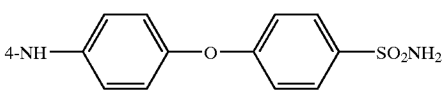
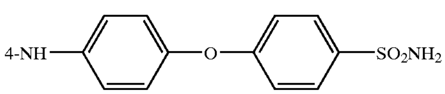
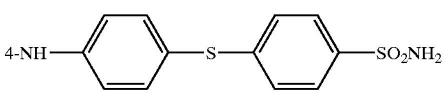
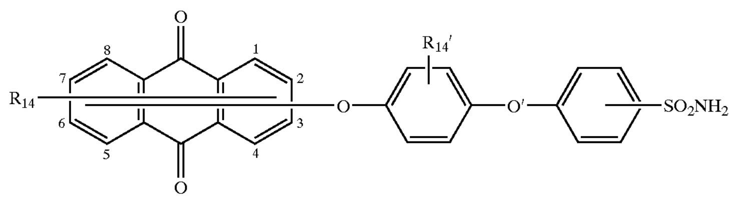
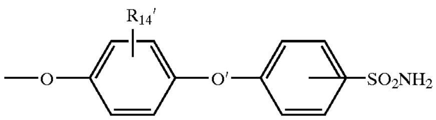
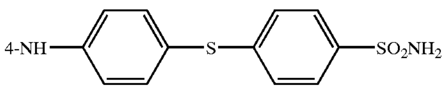
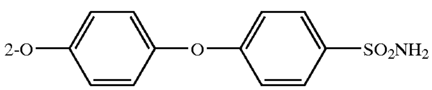
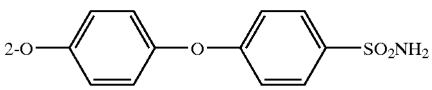
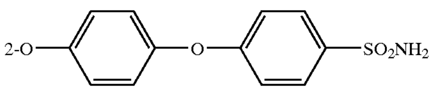
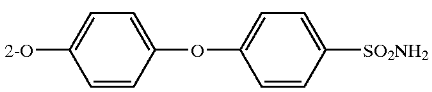
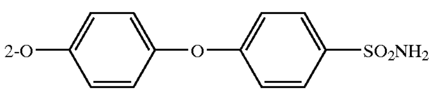
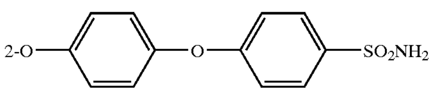
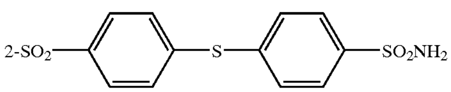
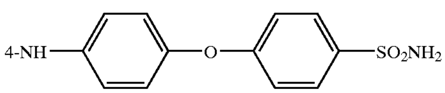
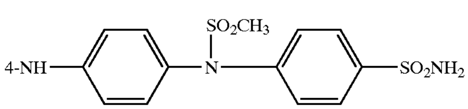
Example No.		R_{14}	Color
416		1-$NHCH_3$	blue
417		1-OH	violet
418		1-NH_2-2-Br	blue
419		1-NH_2-2-OC_6H_5	violet
420		1-NH_2-2-SO_2CH_3	blue
421		1-NH_2-2-COC_6H_5	blue
422		1-NH_2-2-CF_3	cyan
423		1-NH_2-2-$CONH_2$	blue
424		1-NH_2-2-$SO_2N(CH_3)_2$	blue
425		1-NHC_6H_{11}	blue

TABLE 17-continued

Polydyes From Diacidic Anthraquinone Compounds of Formula XIXe

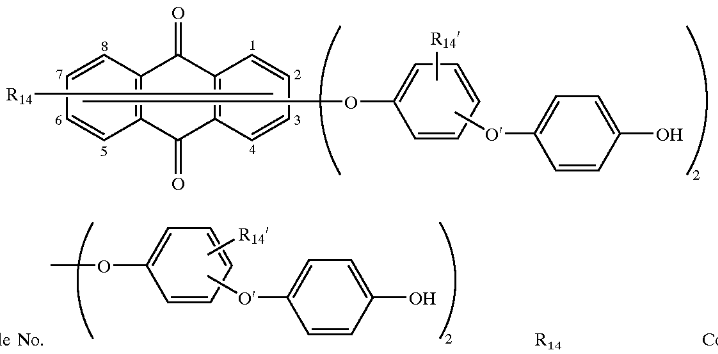


Example No.		R_{14}	Color
426		1-NHC_6H_5	green
427		1-NH_2, 4-OH	red
428		1-NH_2, 4-$NHSO_2CH_3$	red
429		1-NH_2-4-$NHCO_2C_2H_5$	red
430		1-NH_2-4-$NHSO_2C_6H_5$	red
431		1-NH_2-4-$NHCOC_2H_5$	red
432		1,4-diNH_2	violet
433		1-NH_2-4-NHC_6H_5	blue
434		1,8-diOH, 5-NO_2	blue
435		1-NH_2-2-$SO_2C_6H_5$	blue

[0334]

TABLE 18

Polydyes From Diacidic Anthraquinones of Formula XIXf



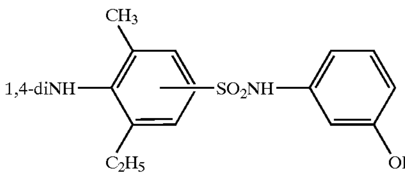
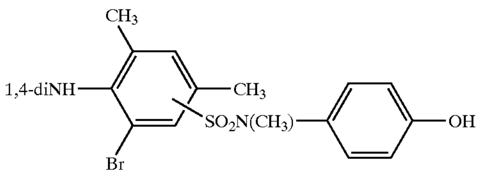
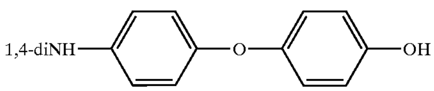
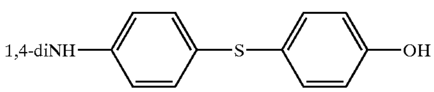
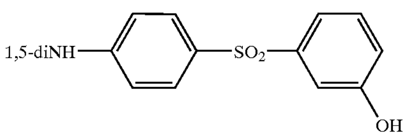
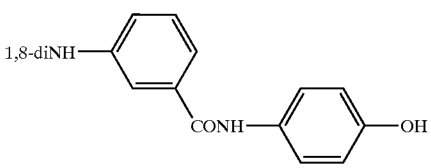
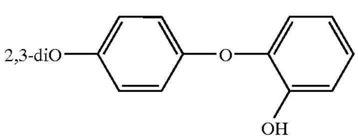
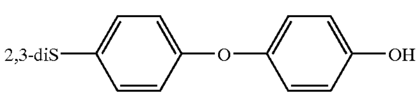
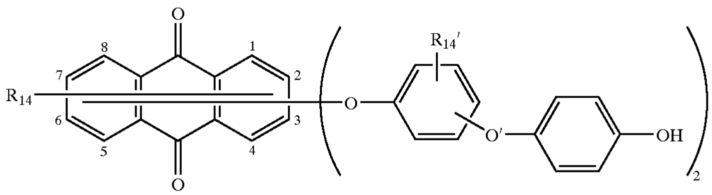
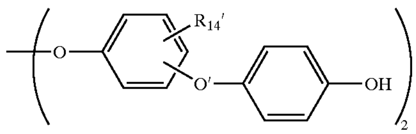
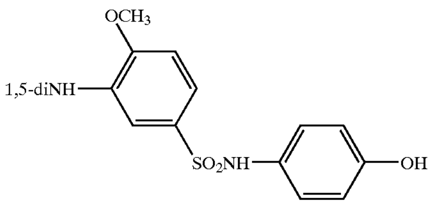
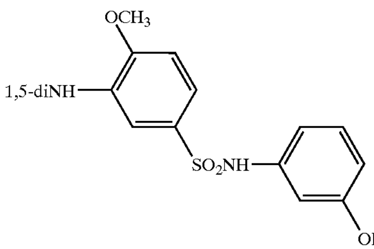
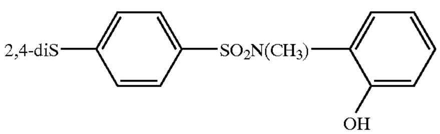
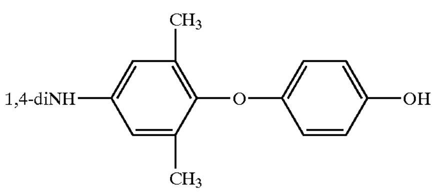
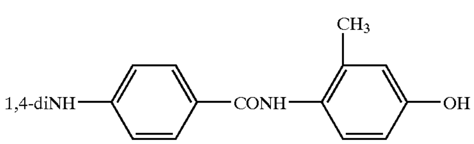
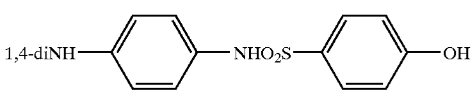
Example No.		R_{14}	Color
436		H	blue
437		H	blue
438		H	green
439		H	green
440		H	red
441		H	red
442		1,4-diNH_2	violet
443		1,4-diNH_2	blue

TABLE 18-continued

Polydyes From Diacidic Anthraquinones of Formula XIXf



Example No.		R_{14}	Color
444		H	red
445		4,8-diNH_2, 3,7-diBr	blue
446		1-NH_2	red
447		6,7-diCl	cyan
448		H	blue
449		H	blue

[0335]

TABLE 19

Polydyes From Diacidic Anthrapyridines

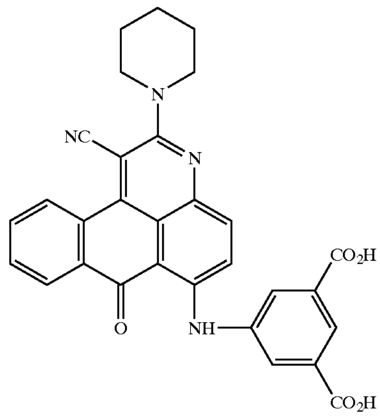
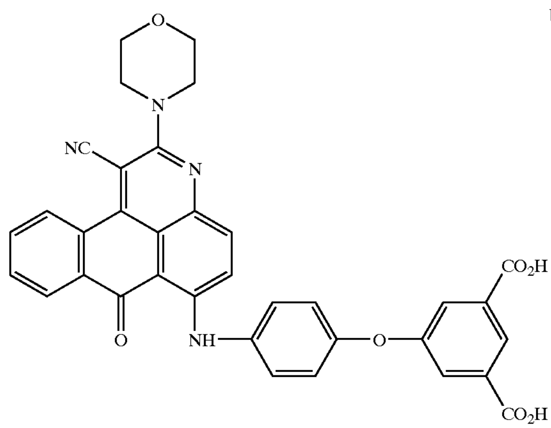
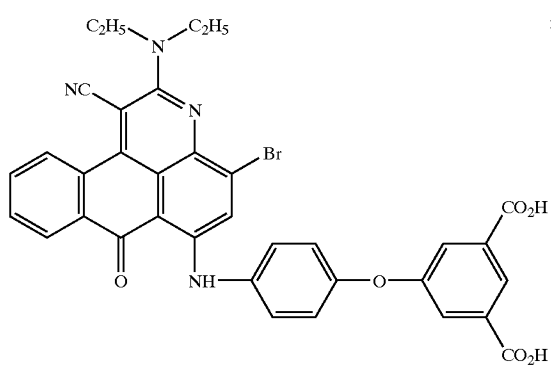
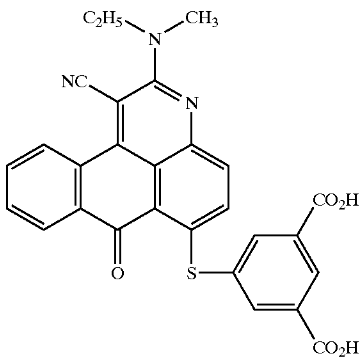
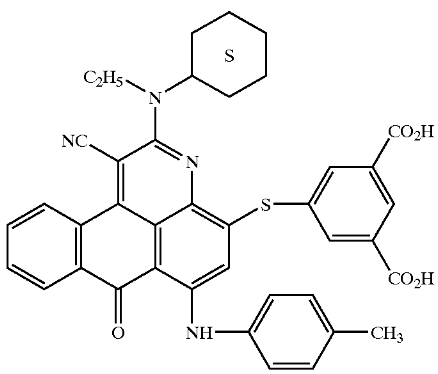
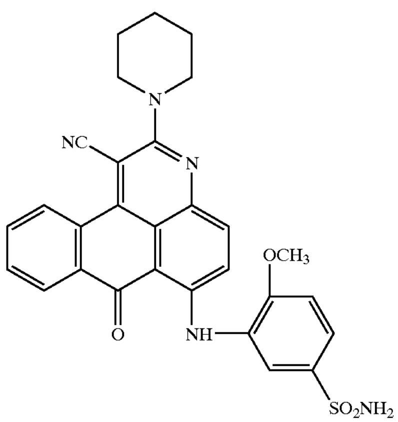
Example No.	Anthrapyridines	Color
450		red
451		bluish-red
452		red

TABLE 19-continued

Polydyes From Diacidic Anthrapyridines

Example No.	Anthrapyridines	Color
453		orange
454		violet
455		red

[**0336**]

TABLE 20

Polydyes From Diacidic Nitroarylamines

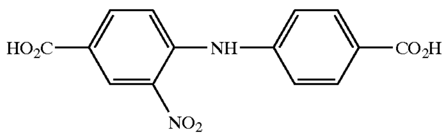
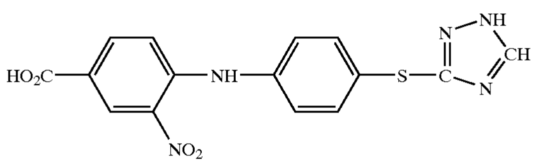
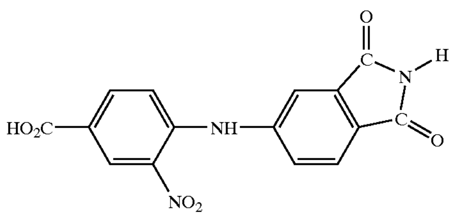
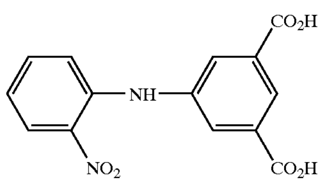
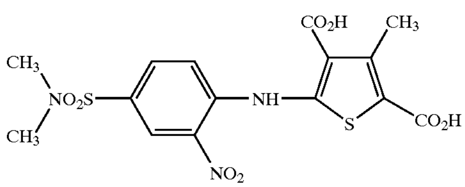
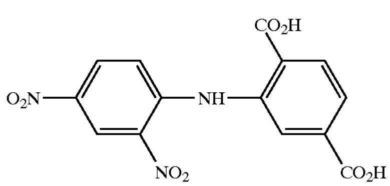
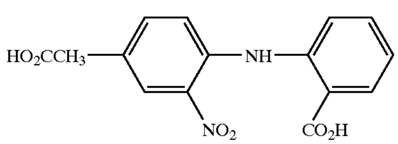
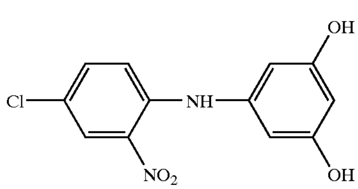
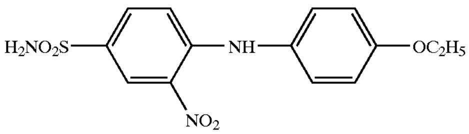
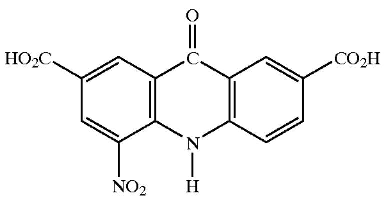
Example No.	Nitroarylamine Compound	Color
456		yellow
457		yellow
458		yellow
459		yellow
460		yellow
461		yellow
462		yellow
463		yellow

TABLE 20-continued

Polydyes From Diacidic Nitroarylamines

Example No.	Nitroarylamine Compound	Color
464		yellow
465		yellow

[0337]

TABLE 21

Miscellaneous Polydyes

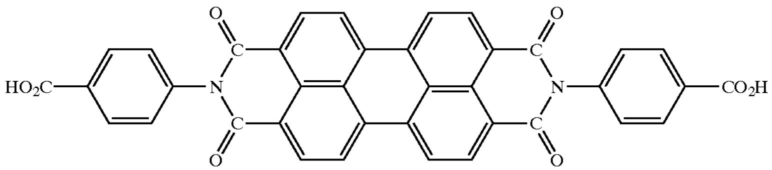
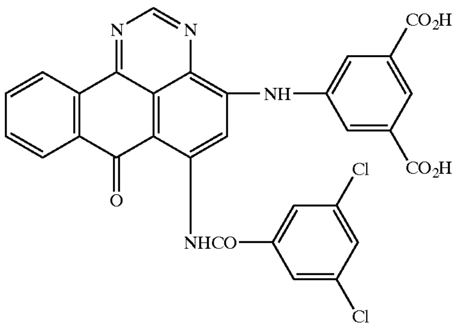
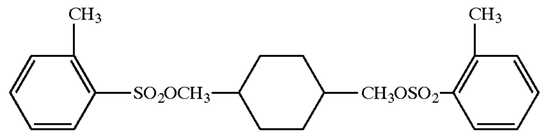
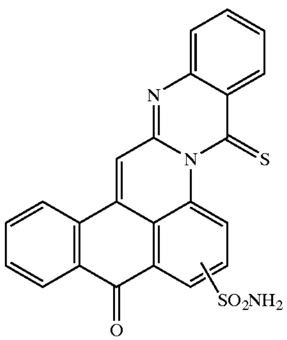
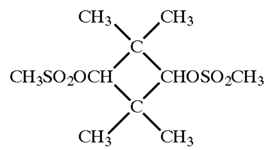
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
466		$CH_3SO_2O(CH_3)_2OSO_2CH_3$	red
467			orange
468			yellow

TABLE 21-continued

Miscellaneous Polydyes

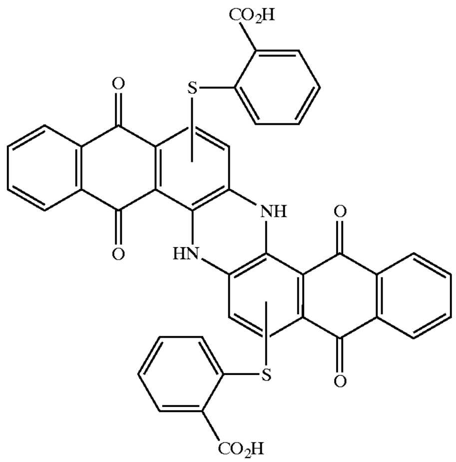
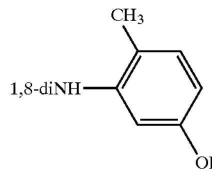
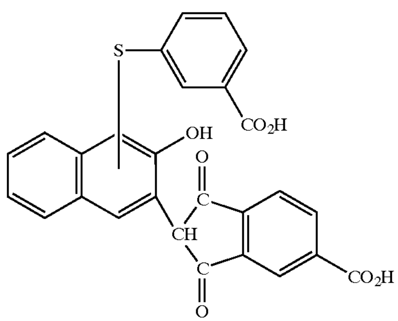
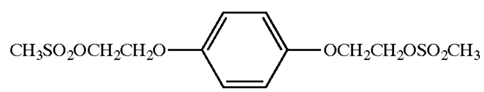
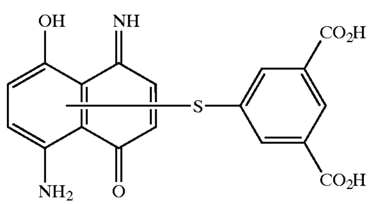
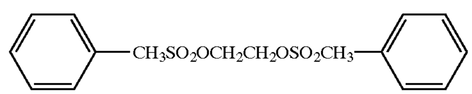
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
469			blue
470			yellow
471			blue

TABLE 21-continued

Miscellaneous Polydyes

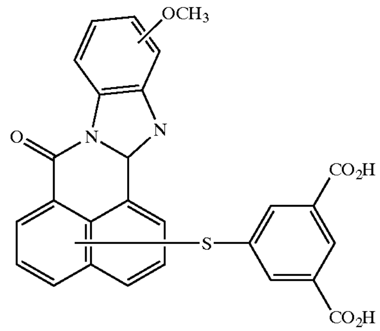
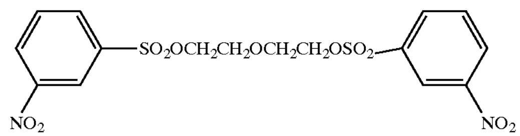
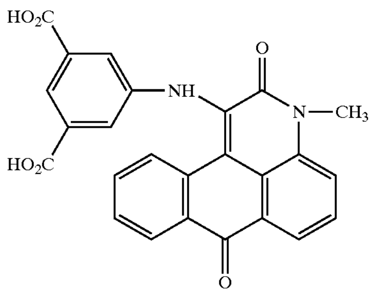
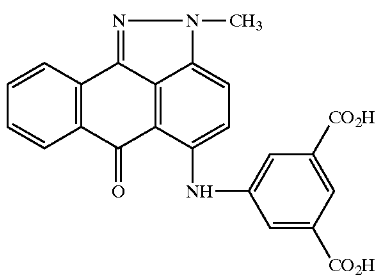
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
472			yellow
473		$CH_3SO_2(OCH_2CH_2)_3OSO_2CH_3$	yellow
474		$CH_3SO_2OCH_2CH_2SCH_2CH_2OSO_2CH_3$	red

TABLE 21-continued

Miscellaneous Polydyes

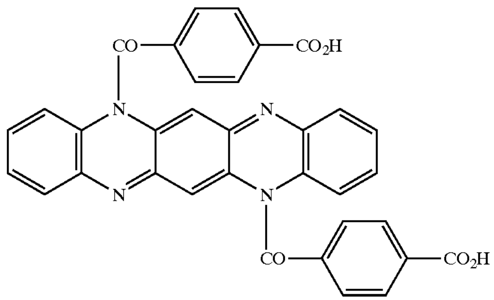
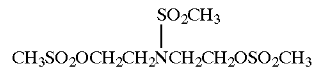
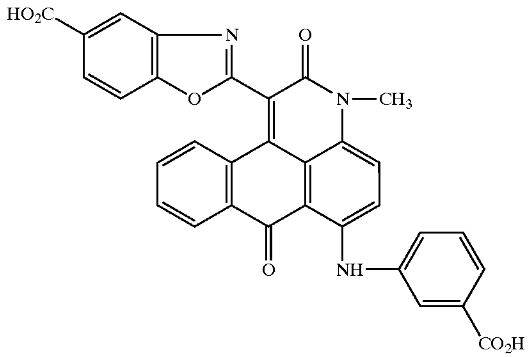
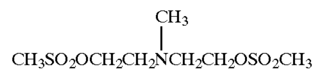
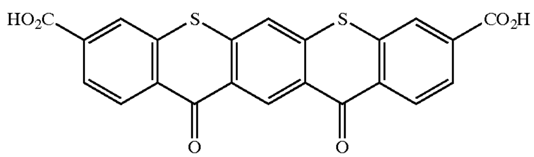
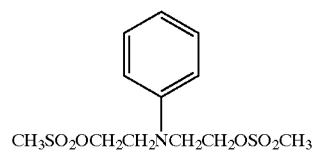
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
475			red
476			violet
477			yellow

TABLE 21-continued

Miscellaneous Polydyes

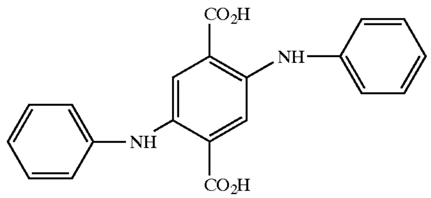
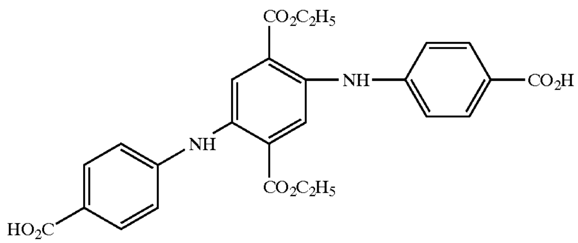
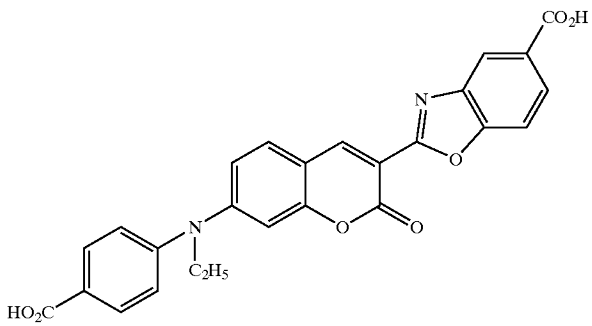
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
478		$CH_3SO_2OCH_2CH_2OSO_2CH_3$	orange
479		$CH_3SO_2OCH_2CH_2OCH_2CH_2OSO_2CH_3$	orange
480		$CH_3SO_2OCH_2CH(CH_3)CH_2OSO_2CH_3$	yellow

TABLE 21-continued

Miscellaneous Polydyes

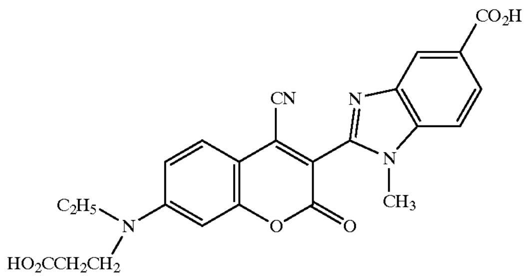
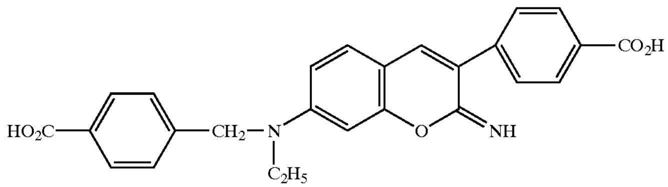
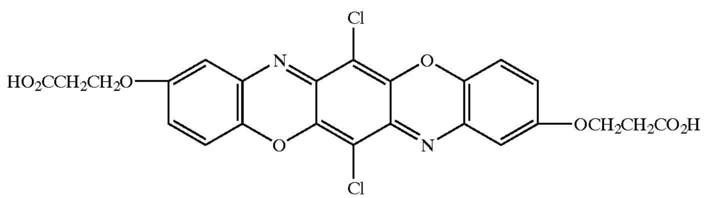
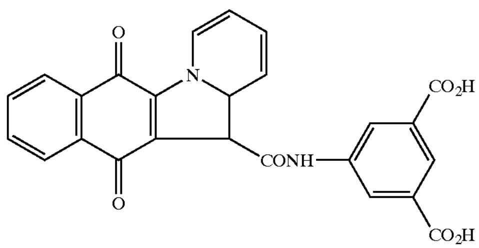
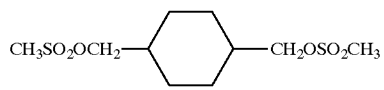
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
481		$CH_3CH_2SO_2OCH_2CH_2CH_2OSO_2CH_2CH_3$	red
482		$n\text{-}C_4H_9SO_2OCH_2CH_2CH_2CH_2OSO_2C_4H_{9\text{-}n}$	yellow
483		$CH_3SO_2(CH_2)_3OSO_2CH_3$	red
484			orange

TABLE 21-continued

Miscellaneous Polydyes

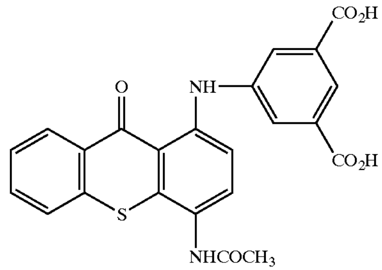
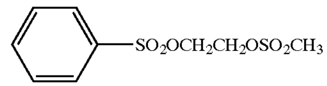
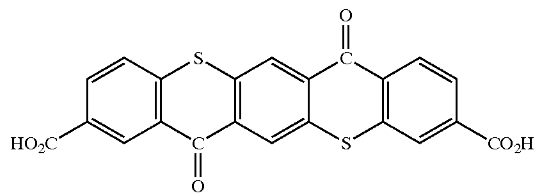
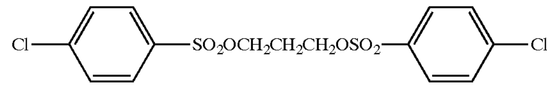
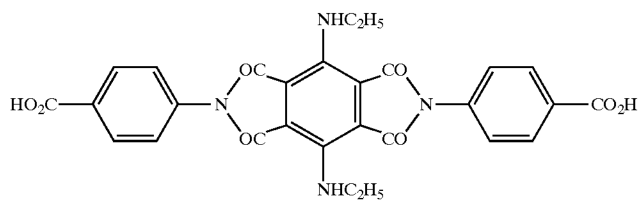
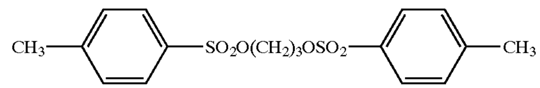
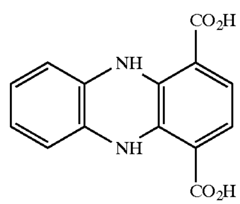
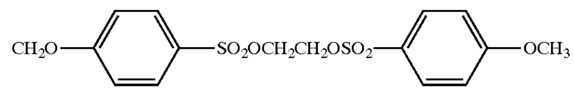
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
485			reddish-yellow
486			yellow
487			blue
488			orange

TABLE 21-continued

Miscellaneous Polydyes

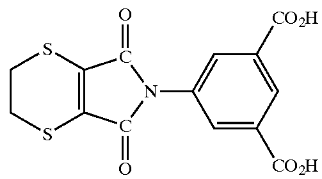
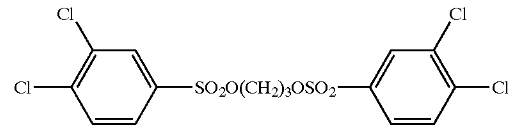
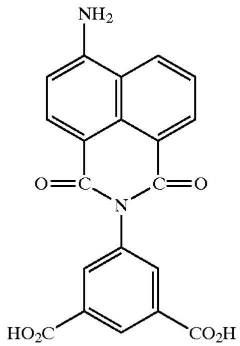
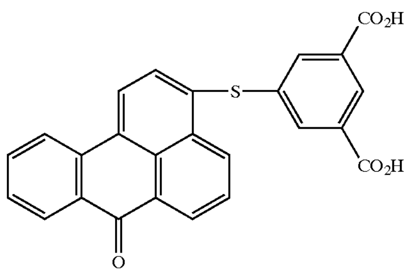
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
489			yellow
490		$CH_3OCH_2SO_2O(CH_2)_3OSO_2CH_2OCH_3$	yellow
491		$ClCH_3SO_2OCH_2CH_2OSO_2CH_2Cl$	yellow

TABLE 21-continued

Miscellaneous Polydyes

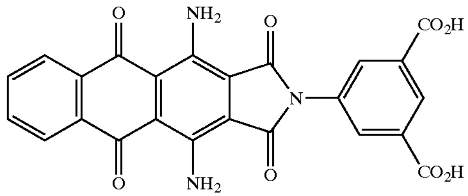
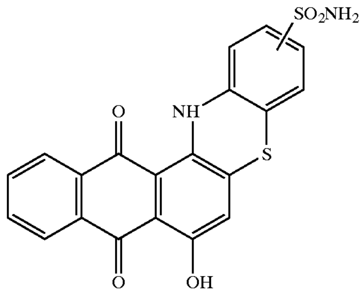
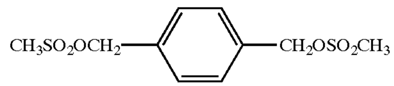
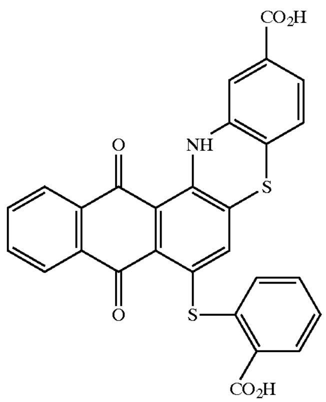
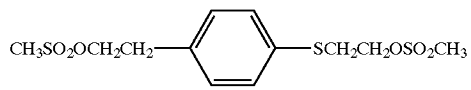
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
492		$CH_3SO_2OCH_2CH_2OCH_2CH_2OSO_2CH_3$	blue
493			greenish-blue
494			greenish-blue

TABLE 21-continued

Miscellaneous Polydyes

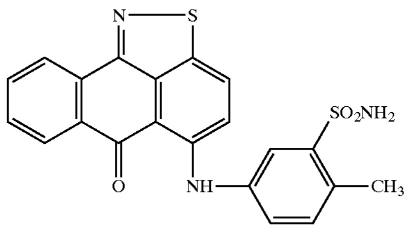
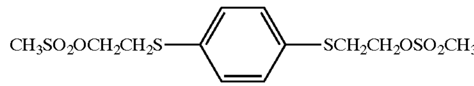
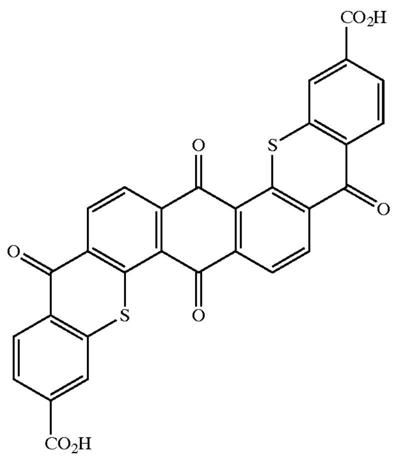
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
495			red
496		$CH_3SO_2OCH_2CH_2SO_2CH_2CH_2OSO_2CH_3$	orange

TABLE 21-continued

Miscellaneous Polydyes

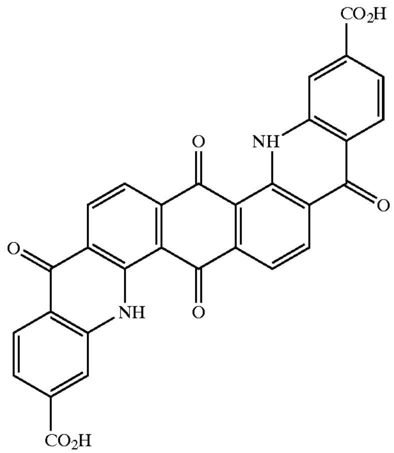
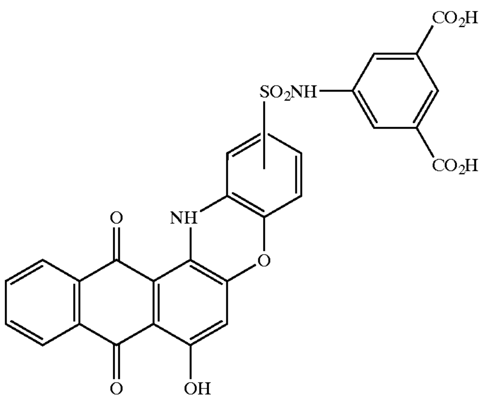
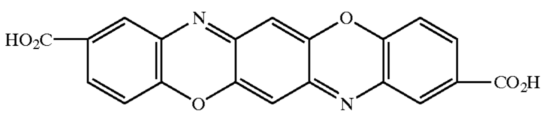
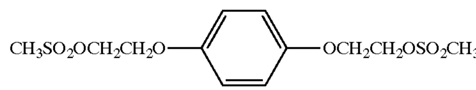
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
497		$CH_3SO_2O(CH_2)_{12}OSO_2CH_3$	red
498		$CH_3SO_2OCH_2C(CH_3)_2CH_2OSO_2CH_3$	blue
499			orange

TABLE 21-continued

Miscellaneous Polydyes

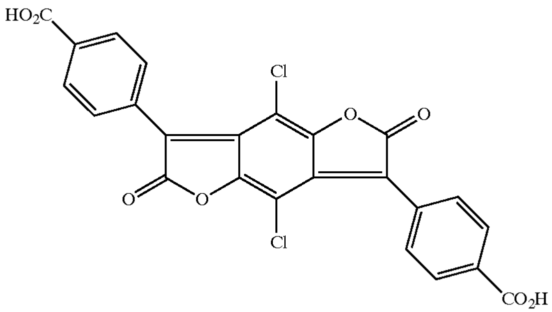
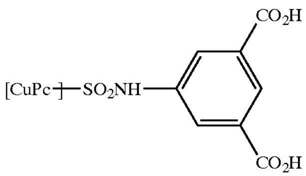
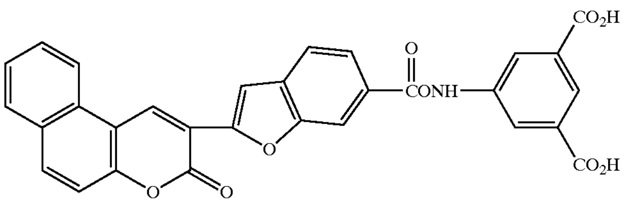
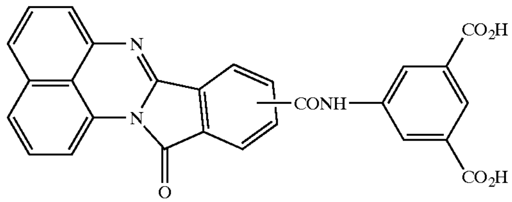
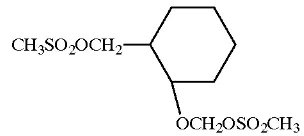
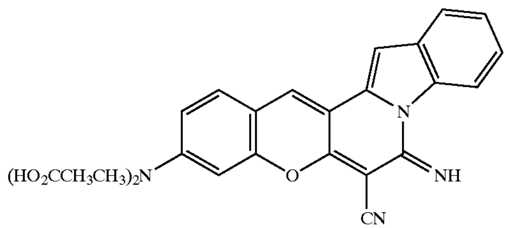
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
500		$CH_3SO_2O(CH_2)_3OSO_2CH_3$	red
501	[CuPc]—SO_2NH_2 Pc = phthalocyanine	$CH_3SO_2OCH_2CH_2OSO_2CH_3$	blue
502		$CH_3SO_2OCH_2CH_2OCH_2CH_2OSO_2CH_3$	blue
503		$CH_3SO_2OCH_2CH_2SCH_2CH_2OSO_2CH_3$	yellow

TABLE 21-continued

Miscellaneous Polydyes

Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted	Color
504			reddish-yellow
505		$CH_3SO_2OCH_2CH_2OSO_2CH_3$	red

[0338]

TABLE 22

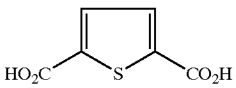
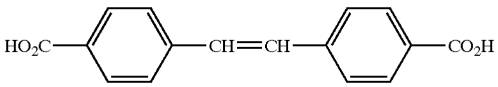
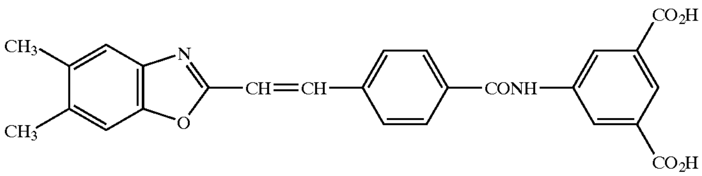
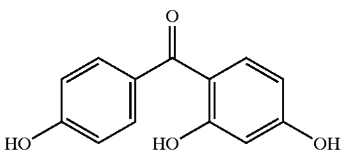
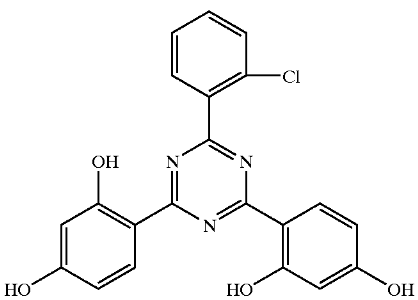
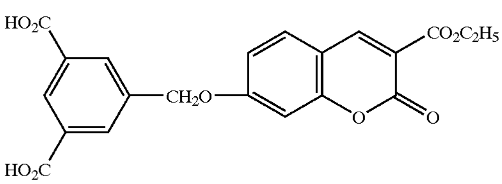
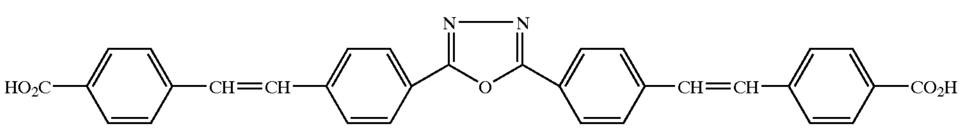
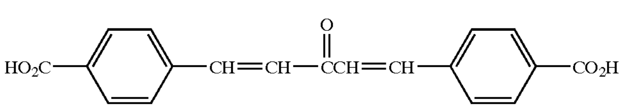
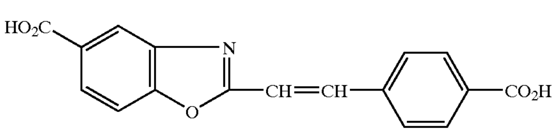
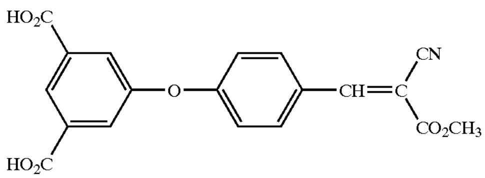
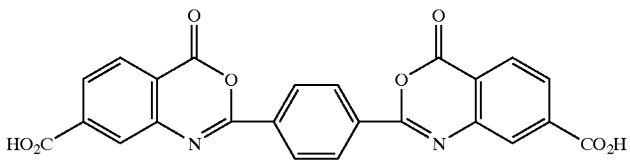
Example No.	Polymeric UV Absorbers Diacidic Compound Reacted
506	
507	
508	
509	
510	
511	
512	
513	
514	

TABLE 22-continued

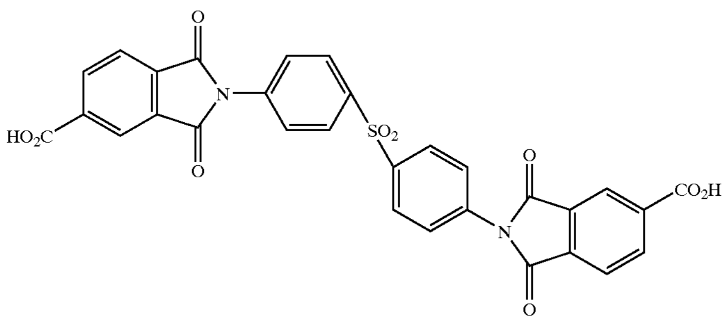
515



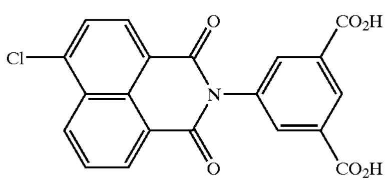
516



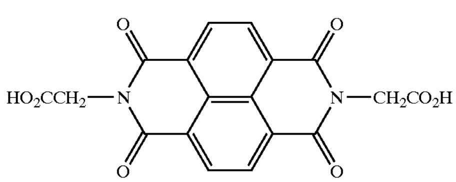
517



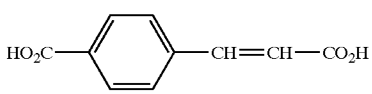
518



519



520



521

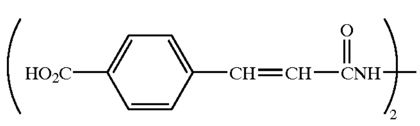
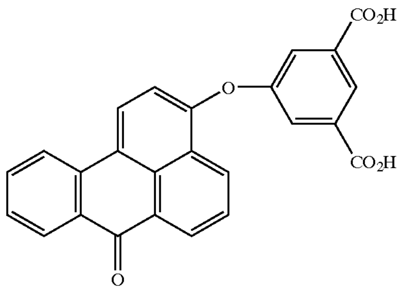
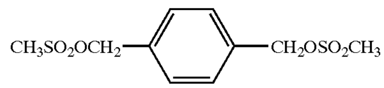


TABLE 22-continued

522	

Example No.	Disulfonate Compound Reacted
506	$CH_3SO_2O(CH_2)_3OSO_2CH_3$
507	$CH_3SO_2OCH_2CH_2OSO_2CH_3$
508	
509	$CH_3SO_2O(CH_2)_4OSO_2CH_3$
510	$CH_3SO_2O(CH_2)_3OSO_2CH_3$
511	$CH_3SO_2O(CH_2)_6OSO_2CH_3$
512	$CH_3SO_2OCH_2CH_2OSO_2CH_3$
513	$CH_3SO_2O(CH_2)_4OSO_2CH_3$
514	$CH_3SO_2O(CH_2)_6OSO_2CH_3$
515	$CH_3SO_2OCH_2CH(CH_3)CH_2OSO_2CH_3$
516	$CH_3SO_2O(CH_2CH_2O)_3SO_2CH_3$
517	$CH_3SO_2OCH_2CH_2OSO_2CH_3$
518	$CH_3SO_2OCH_2CH_2SCH_2CH_2OSO_2CH_3$
519	$CH_3SO_2O(CH_2)_6OSO_2CH_3$
520	$CH_3SO_2OCH_2CH(Cl)CH_2OSO_2CH_3$
521	$CH_3SO_2OCH_2CH(Cl)CH_2OSO_2CH_3$
522	$CH_3SO_2OCH_2CH(Cl)CH_2OSO_2CH_3$

[0339]

TABLE 23

Polymeric Infrared Light Absorbers

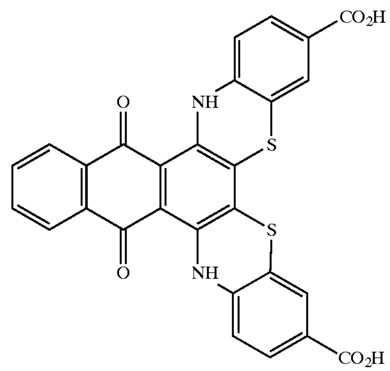
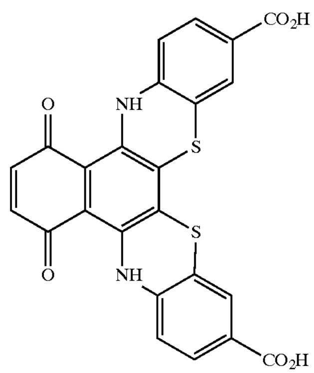
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted
523		$CH_3SO_2OCH_2CH_3OSO_2CH_3$
524		$CH_3SO_2O(CH_2)_3OSO_2CH_3$

TABLE 23-continued

Polymeric Infrared Light Absorbers

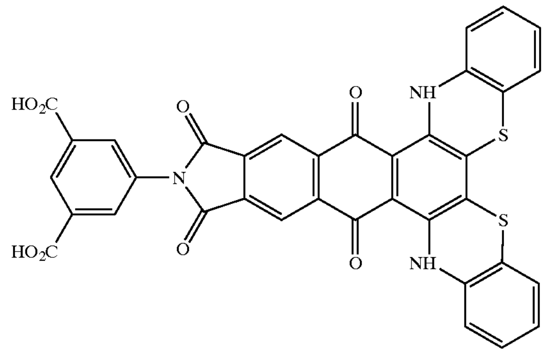
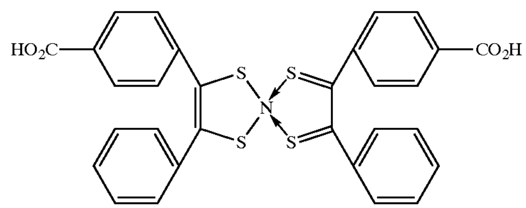
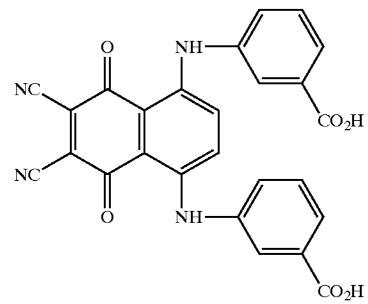
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted
525		$CH_3SO_2O(CH_2)_4OSO_2CH_3$
526		$CH_3SO_2O(CH_2)_6OSO_2CH_3$
527		$CH_3SO_2O(CH_2)_{12}OSO_2CH_3$

TABLE 23-continued

Polymeric Infrared Light Absorbers

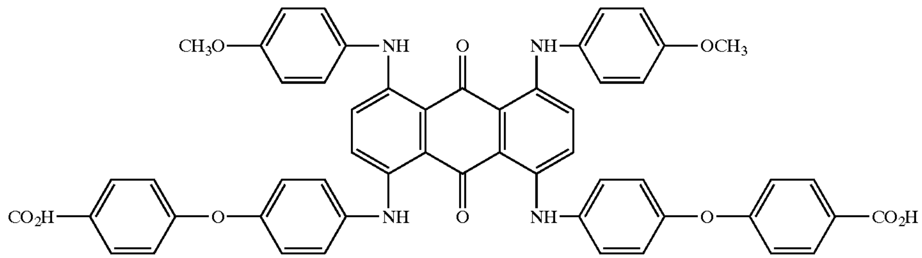
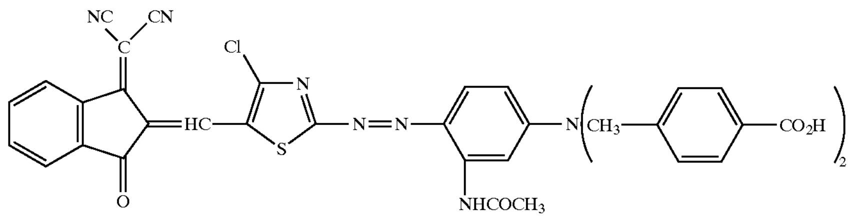
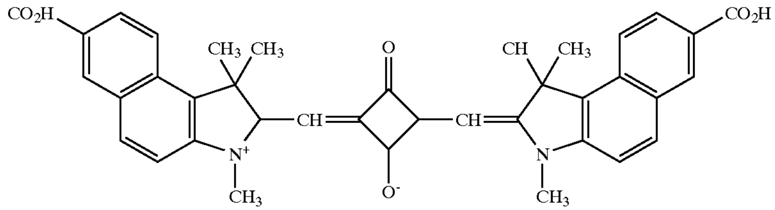
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted
528		$CH_3SO_2OCH_2CH_2OCH_2CH_2OSO_2CH_3$
529		$CH_3SO_2OCH_2CH_2OSO_2CH_3$
530		$CH_3SO_2OCH_2CH_2CH_2OSO_2CH_3$

TABLE 23-continued

Polymeric Infrared Light Absorbers

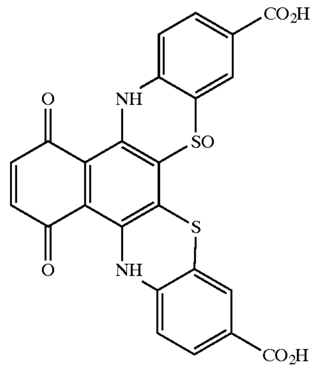
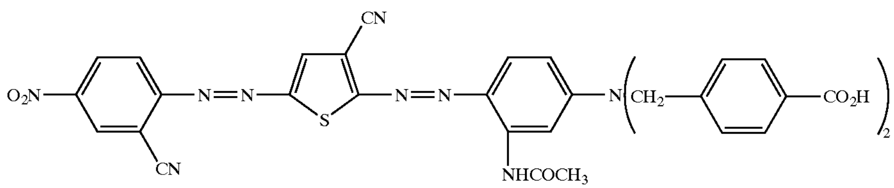
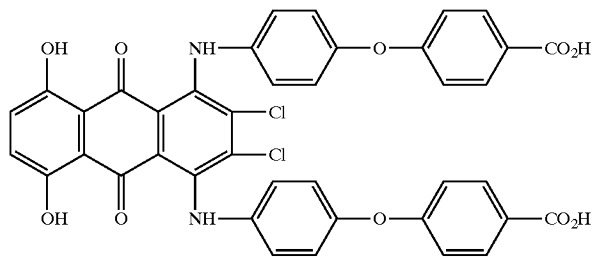
Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted
531		$CH_3SO_2OCH_2CH_2OSO_2CH_3$
532		$CH_3SO_2OCH_2CH_2OSO_2CH_3$

TABLE 23-continued

Polymeric Infrared Light Absorbers

Example No.	Diacidic Compound Reacted	Disulfonate Compound Reacted
533		$CH_3SO_2OCH_2CH_2OSO_2CH_3$
534	$[PcAlOH]$—SO_2NH_3 Pc = phthalocyanine	$CH_3SO_2OCH_2CH_2OSO_2CH_3$
535	$NcSi(OC_4H_{9\text{-}3\text{-}6}\text{-}a(CO_2H)_2$ Nc = naphthalocyanine	$CH_3SO_2OCH_2CH_2OSO_2CH_3$
536	$[PcAlOH](CO_2H)_2$ Pc = phthalocyanine	$CH_3SO_2O(CH_2)_6OSO_2CH_3$

Example 537

[0340] To dimethylfomamide (DMF, 45.0 mL) was added 1,5-bis(2-carboxyphenyl-thio)anthraquinone (17.9 g, 0.035 mole). The mixture was stirred for about 10 minutes and then 1,8-diazabicyclo [5,4,0]undec-7-ene (DBU, 10.4 g, 0.068 mole) was added followed by 1,2-ethanediol, dimethanedisulfonate (7.64 g, 0.035 mole) and additional DMF (10.0 mL). The reaction mixture was stired at about 110° C. for 3.0 hours and allowed to cool to about 55° C. Methanol (35.0 g) was added dropwise with stirring followed by water (20 mL) and acetic acid (3.0 mL). The yellow solid was collected by filtration, washed with methanol (25 mL), warm water (50 mL) and then finally with methanol to facilitate drying. The yield of polymeric and cyclic yellow product was 18.2 g.

Examples 538-543

[0341] The procedure described in Example 537 was repeated exactly except that the reactant X-B-X_1 used in each example was as follows:

[0342] Example 538: 1,3-propanediol, dimethanedisulfonate

[0343] Example 539: 1,4-butanediol, dimethanedisulfonate

[0344] Example 540: diethylene glycol, dimethanedisulfonate

[0345] Example 541: 1,6-hexanediol, dimethanedisulfonate

[0346] Example 542: 1,4-cyclohexanedimethanol, dimethanedisulfonate

[0347] Example 543: 1,12-dodecanediol, dimethanedisulfonate

[0348] The weight yields (Weight, g), percent yields (Yield), weight average molecular weights (Mw), number average molecular weights (Mn), and polydispersities (Mw/Mn, by GPC) for each of the light absorbing (yellow) compositions prepared in Examples 537-543 are presented in Table 24.

[0349] The percent yields were calculated by dividing the actual weight of the polymer

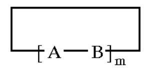
$$\left[A \right]_m$$

[0350] obtained in grams by the theoretical number of moles of repeating unit multiplied by the gram molecular weight of the repeating unit and then multiplying the number thus obtained by 100.

TABLE 24

Example	Weight	Yield	Mw	Mn	Mw/Mn
537	18.2	96.6	7,512	1,106	6.8
538	18.8	97.2	5,224	1,051	5.0
539	19.4	98.0	13,856	1,202	11.5
540	20.1	98.7	9,849	1,840	5.4
541	20.2	97.4	7,396	870	8.5
542	20.7	95.3	3,685	808	4.6
543	22.7	95.5	5,503	1,116	4.9

[0351] The approximate amount of cyclic compounds of formula I-A present in each of the light absorbing compositions produced in Examples 537-543 was determined by a combination of GPC, NMR and FDMS analyses. The weight percentages of the cyclic compounds having the structure



I-A

[0352] wherein m is 1, 2, 3, or 4 present in the compostiion of Examples 537-543 is set forth in Table 25. The remainder or balance of the light absorbing compositions was presumed to be a linear polymer.

TABLE 25

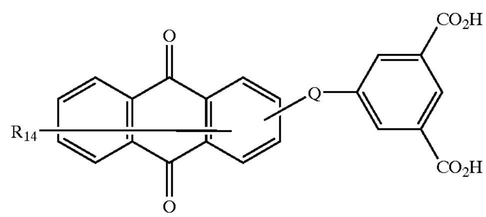
Example	m = 1	m = 2	m = 3	m = 4
537	0.1	3.4	1.5	0.7
538	0.8	3.3	1.3	<0.1
539	6.9	4.1	1.3	0.2
540	9.5	3.1	0.8	<0.1
541	26.7	4.0	1.1	0.2
542	20.4	4.0	0.7	<0.1
543	20.1	2.2*	0.5*	<0.1

*These peaks are unidentified but appear not to be oligomers.

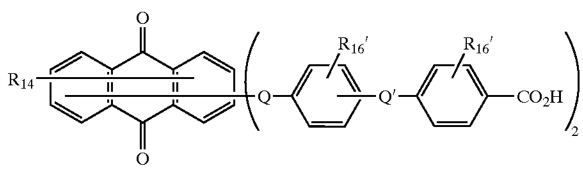
1-58. (canceled)

59. The diacidic anthraquinone compounds having Formulae

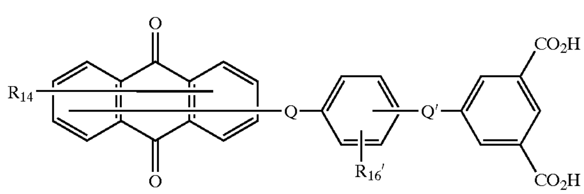
XIV



XIXc

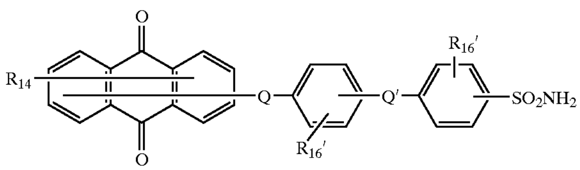


XIXd

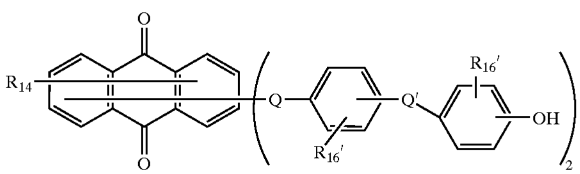


-continued

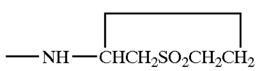
XIXe



XIXf

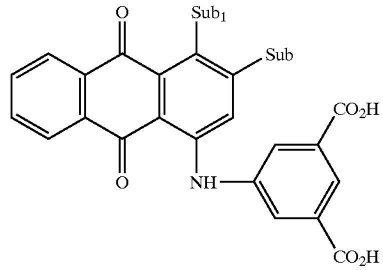


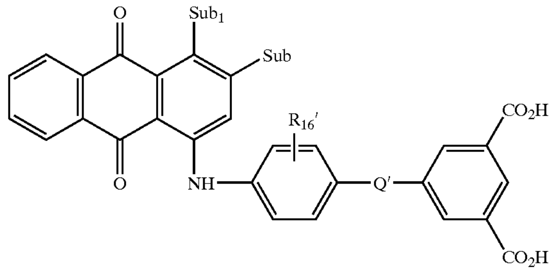
wherein R_{14} is selected from the group consisting of hydrogen, 1-4 groups selected from amino, C_1-C_{10} alkylamino, C_3-C_8 alkenylamino, C_3-C_8 alkynylamino, C_3-C_8 cycloalkylamino, arylamino, halogen, C_1-C_6 alkoxy, C_1-C_6 alkylthio, aryl, aroyl, C_1-C_6 alkanoyl, C_1-C_6 alkanoyloxy, NHCO C_1-C_6 alkyl, NHCOaryl, $NHCO_2$ C_1-C_6 alkyl, $NHSO_2$ C_1-C_6 alkyl, $NHSO_2$ aryl, C_1-C_6 alkoxycarbonyl, aryloxy, arylthio, heteroarylthio, cyano, nitro, trifluoromethyl, thiocyano, SO_2C_1-C_6 alkyl, SO_2 aryl, —SO_2NH C_1-C_6 alkyl, —$SO_2N(C_1$-C_6 alkyl$)_2$, —$SO_2N(C_1$-C_6 alkyl) aryl, CONFH C_1-C_6 alkyl, CON(C_1-C_6 alkyl$)_2$, CON(C_1-C_6 alkyl) aryl, C_1-C_6 alkyl, furfurylamino, tetrahydrofurfurylamino, 4-(hydroxymethyl) cyclohexanemethylamino,



or hydroxy; Q and Q' are independently selected from the group consisting of —O—, —N(COR_{10})—, —N(SO_2R_{10})—, —N(R_{10})—, —S—, —SO_2—, —CO_2—, —CON(R_{10})—, SO_2N (R_{10})—, wherein R_{10} is selected from the group consisting of hydrogen, aryl, C_3-C_8 cycloalkyl, or C_1-C_{10} alkyl; R_{16}' is selected from hydrogen or one or two groups selected from C_1-C_6 alkyl, halogen and C_1-C_6 alkoxy; wherein each C_1-C_6 alkyl group and [[C_1-C_6 alkyl group]] C_1-C_6 alkyoxy group which is a portion of another group may contain at least one substituent selected from the group consisting of hydroxy, cyano, chlorine, fluorine, C_1-C_6 alkoxy, C_3-C_8 cycloalkoxy, C_1-C_6 alkylcyclohexyl, hydroxmethyl cyclohexyl, aryl and heteroaryl; with the provision that two acidic groups containing one acidic proton each or one acidic group containing two acidic hydrogens be present in the compounds of Formula XIV, XIXc, XIXd, XIXe XIXf.

60. The diacidic anthraquinone compounds having the following structures:

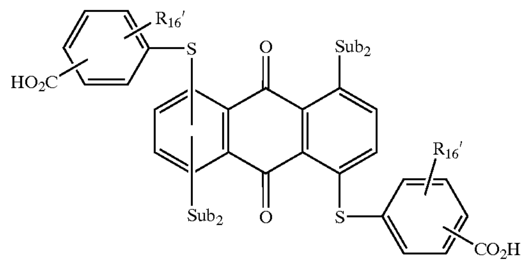


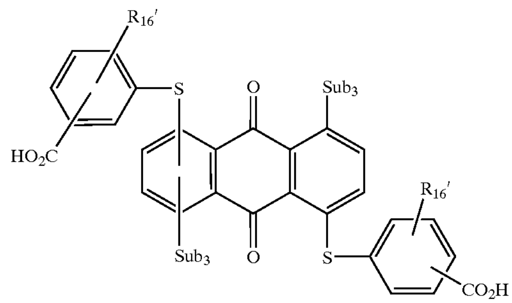


wherein Sub is a substituent selected from the group consisting of halogen, trifluoromethyl, aroyl, C_1-C_6 alkanoyl, C_1-C_6 alkoxycarbonyl, C_1-C_6 alkoxy, C_1-C_6 alkylthio, aryloxy, arylthio, heteroarylthio, cyano, nitro, SO_2NHC_1-C_6 alkyl, SO_2N (C_1-C_6 alkyl$)_2$, SO_2N (C_1-C_6 alkyl) aryl, CONH C_1-C_6 alkyl, CON (C_1-C_6 alkyl$)_2$, CON (C_1-C_6 alkyl) aryl, C_1-C_6 alkyl, SO_2 C_1-C_6 alkylsulfonyl and SO_2 aryl; Sub_1 is a substituent selected from the group consisting of amino, C_1-C_{12} alkylarnino, arylamino and C_3-C_8 cycloalkylamino. Q' is selected from the group consisting of —O—, —N(COR_{10})—, —N(SO_2R_{10})—, —N(R_{10})—, —S—, —SO_2—, —CO_2—, —CON(R_{10})—, SO_2N (R_{10})—, wherein R_{10} is selected from the group consisting of hydrogen, aryl, C_3-C_8 cycloalkyl, or C_1-C_{10} alkyl; and R_{16}' is selected from hydrogen or one or two groups selected from C_1-C_6 alkyl, halogen and C_1-C_6 alkoxy.

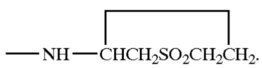
61-62. (canceled)

63. The diacidic anthraquinone compounds having the formulae

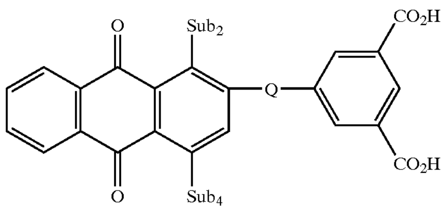


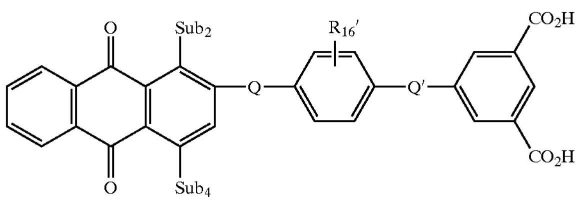


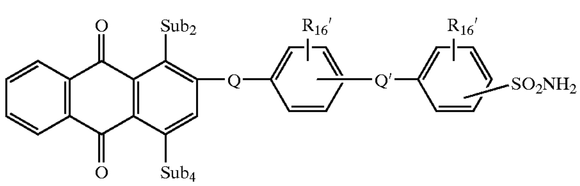
where R_{16}' is selected from the group consisting of hydrogen or one or two groups selected from C_1-C_6 alkyl, halogen and C_1-C_6 alkoxy; and Sub_3 is a substituent selected from C_1-C_6 alkylthio, arylthio and heteroarylthio and Sub_2 is a substituent selected from the group consisting of amino, C_1-C_{10} alkylamino, C_3-C_8 alkenylamino, C_3-C_8 alkynylamino, C_3-C_8 cycloalkylamino, arylamino, furfurylamino, tetrahydrofurfurylamino, 4-(hydroxymethyl) cyclohexanemethylamino, NHCO C_1-C_6 alkyl, NHCO aryl, $NHCO_2$ C_1-C_6 alkyl, $NHSO_2$ C_1-C_6 alkyl, $NHSO_2$ aryl and



64. The diacidic anthraquinone compounds of claim 59 having the formulae:



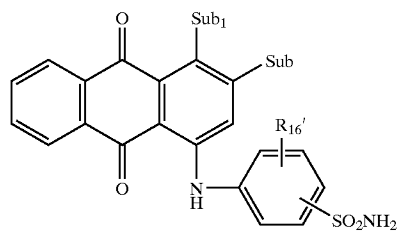




wherein Sub_2 is a substituent selected from the group consisting of amino, C_1-C_{10} alkylamino, C_3-C_8 alkenylamino, C_3-C_8 alkynylamino, C_3-C_8 cycloalkylamino, arylamino, furfurylamino, tetrahydrofurfurylamino, 4-(hydroxymethyl) cyclohexanemethylamino, NHCO C_1-C_6 alkyl, NHCO aryl, $NHCO_2$ C_1-C_6 alkyl, $NHSO_2$ C_1-C_6 alkyl, $NHSO_2$ aryl and

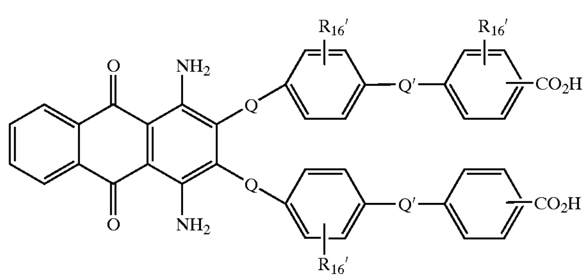
Sub_4 is selected from the group consisting of Sub_2, NHCO C_1-C_6 alkyl, $NHCO_2$ C_1-C_6 alkyl, NHCO aryl, $NHSO_2$ C_1-C_6 alkyl, $NHSO_2$ aryl, C_1-C_6 alkylthio, arylthio, heteroarylthio and hydroxy; Q is selected from the group consisting of —O—, S—, —SO_2—; Q' selected from the group consisting of —O—, —N(COR_{10})—, —N(SO_2R_{10})—, —N(R_{10})—, —S—, —SO_2—, —CO_2—, —CON(R_{10})—, SO_2N (R_{10})—, wherein R_{10} is selected from the group consisting of hydrogen, aryl, C_3-C_8 cycloalkyl, or C_1-C_{10} alkyl.

65. A diacidic anthraquinone compounds having the formula



wherein Sub is a substituent selected from the group consisting of halogen, trifluoromethyl, aroyl, C_1-C_6 alkanoyl, C_1-C_6 alkoxycarbonyl, C_1-C_6 alkoxy, C_1-C_6 alkylthio, aryloxy, arylthio, heteroarylthio, cyano, nitro, SO_2NHC_1-C_6 alkyl, SO_2N (C_1-C_6 alkyl)$_2$, SO_2N (C_1-C_6 alkyl) aryl, CONH C_1-C_6 alkyl, CON (C_1-C_6 alkyl)$_2$, CON (C_1-C_6 alkyl) aryl, C_1-C_6 alkyl, SO_2 C_1-C_6 alkylsulfonyl and SO_2 aryl; Sub_1 is a substituent selected from the group consisting of amino, C_1-C_{12} alkylamino, arylamino and C_3-C_8 cycloalkylamino, and R_{16}' is selected from hydrogen or one or two groups selected from C_1-C_6 alkyl, halogen and C_1-C_6 alkoxy.

66. The diacidic anthraquinone compounds having the structures



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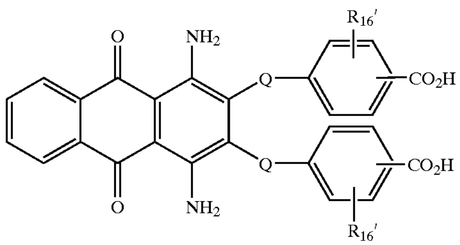

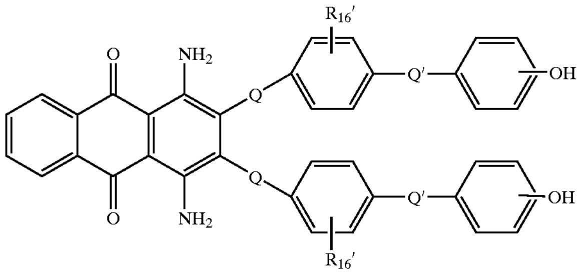

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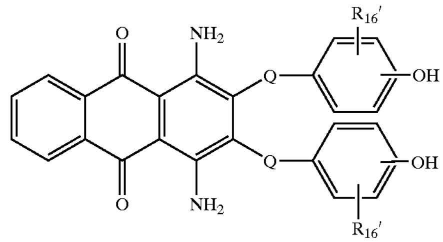
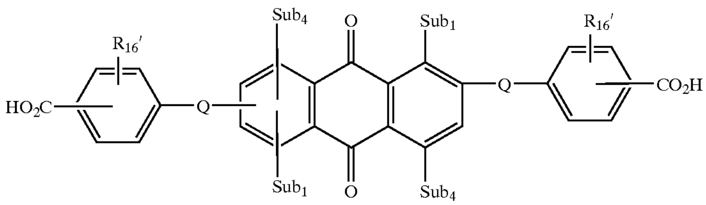
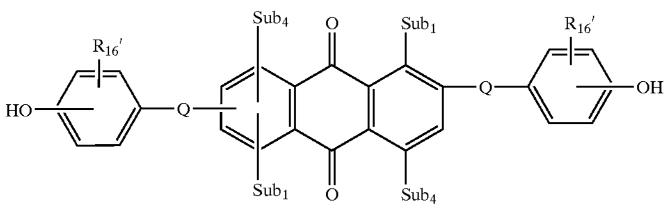
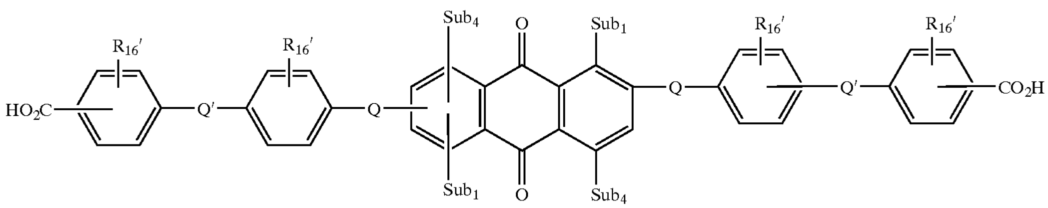


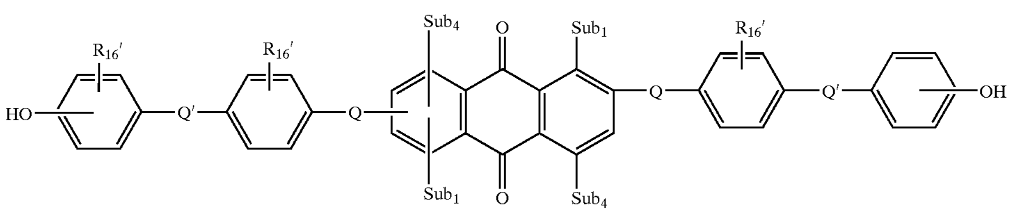
wherein Q is selected from the group consisting of —O—, —S— and —SO_2—; Q' is selected from the group consisting of —O—, —N(COR_{10})—, —N(SO_2R_{10})—, —N(R_{10})—, —S—, —SO_2—, —CO_2—, —CON(R_{10})—, SO_2N (R_{10})—, wherein R_{10} is selected from the group consisting of hydrogen, aryl, C_3-C_8 cycloalkyl, or C_1-C_{10} alkyl; and R_{16}' is selected from the group consisting of hydrogen or one or two groups selected from C_1-C_6 alkyl, halogen and C_1-C_6 alkoxy.

67. The diacidic anthraquinone compounds having the structures:





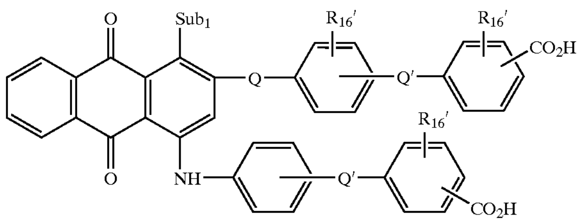




wherein Sub_1 is a substituent selected from the group consisting of amino, C_1-C_{12} alkylamino, arylamino and C_3-C_8 cycloalkylamino: Sub_4 is selected from the group consisting of amino, C_1-C_{10} alkylamino, C_3-C_8 alkenylamino, C_3-C_8 alkynylamino, C_3-C_8 cycloalkylamino, arylaamino, furfurylamino, tetrahydrofurfurylamino, 4-(hydroxymethyl) cyclohexanemethylamino, NHCO C_1-C_6 alkyl, NHCO aryl, $NHCO_2$, C_1-C_6 alkyl, $NHSO_2$ C_1-C_6 alkyl, $NHSO_2$ aryl

NHCO C_1-C_6 alkyl, $NHCO_2$ C_1-C_6 alkyl, NHCO aryl, $NHSO_2$ C_1-C_6 alkyl, $NHSO_2$ aryl, C_1-C_6 alkylthio, arylthio, heteroarylthio and hydroxy: Q is selected from the group consisting of —O—, —S— and —SO_2—; Q' is selected from the group consisting of —O—, —N(COR_{10})—, —N(SO_2R_{10})—, —N(R_{10})—, —S—, —SO_2—, —CO_2—, —CON(R_{10})—, SO_2N (R_{10})—, wherein R_{10} is selected from the group consisting of hydrogen, aryl, C_3-C_8 cycloalkyl, or C_1-C_{10} alkyl; and R_{16}' is selected from the group consisting of hydrogen or one or two groups selected from C_1-C_6 alkyl, halogen and C_1-C_6 alkoxy.

68. The diacidic anthraquinone compounds having the structures:



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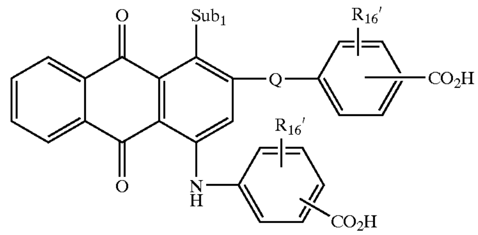

wherein Q is selected from the group consisting of —O—, —S— and —SO_2—; Sub_1 is a substitutent selected from the group consisting of amino, C_1-C_{12} alkylamino, arylamino and C_3-C_8 cycloalkylamino; Q' is selected from the group consisting of —O—, —N(COR_{10})—, —N(SO_2R_{10})—, —N(R_{10})—, —S—, —SO_2—, —CO_2—, —CON(R_{10})—, SO_2N (R_{10})—, wherein R_{10} is selected from the group consisting of hydrogen, aryl, C_3-C_8 cycloalkyl, or C_1-C_{10} alkyl; and R_{16}' is selected from the group consisting of hydrogen or one or two groups selected from C_1-C_6 alkyl, halogen and C_1-C_6 alkoxy.

69-108. (canceled)

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