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Organotitanium Polydyes Derived from Phenylsulfonphthalein Dyes, and Congo Red, Eriochrome Black T, Nigrosine and Indigo Carmine-Synthesis and Doping Characteristics

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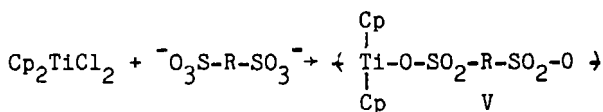
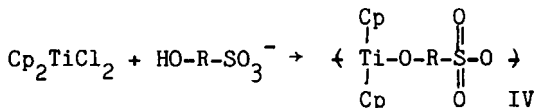
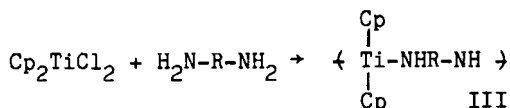
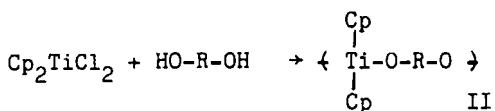
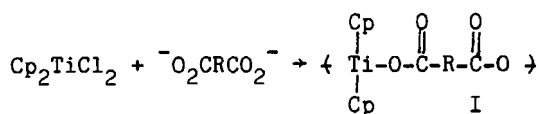
ABSTRACT

The synthesis of titanium polydyes emphasizing the interfacial technique is described. Emphasis is placed on applications of the polydyes taking advantage of the potential permanent, nonleaching nature of such materials compared with the monomeric dyes themselves. The polydyes are fluorescent and can be impregnated into paper, cloth and paint and "doped" into plastics giving fluorescent materials.

INTRODUCTION

Carraher and co-workers have reported the synthesis of titanium polyesters (I), polyethers (II) and polyamines (III) (for instance 1-6). The reactivity of the RSO_3^- moiety appears analogous to that of RCO_2^- towards metal halides. Here we report the synthesis of titanium polydyes derived from se-

veral dyes including phenylsulfonphthalein dyes (IV), Nigrosine (III), Indigo Carmine (V), Eriochrome Black T, Congo Red and 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p, p'-disulfonic acid (PDTD, V).



EXPERIMENTAL

The following chemicals were used as received: Cp_2TiCl_2 (Strem Chemicals, Inc.; Danvers, Mass.), Nigrosin (certified; Matheson, Coleman and Bell; Norwood, Ohio), Bromophenol Blue (Fisher Scientific Co.; Fairlawn, N.J.), Eriochrome Black T (Eastman Chem. Corp., Rochester, N.Y.); Bromothymol Blue (Fisher Sci. Co.; Fairlawn, N.J.), Indigo Carmine (MCB,

Norwood, Ohio), Congo Red (MCB) and Ethidium Bromide (Chemalog).

Polycondensations were carried out as described in ref. 1. Briefly aqueous solutions containing dye and any added base were added to rapidly stirred aqueous (for aqueous solution systems) or organic (for interfacial systems) solutions containing Cp_2TiCl_2 . The polymerization equipment, a one pint Kimex Emulsifying Jar fitted onto a Waring Blendor (700 model 31BL46, is fully described in reference 6.

Infrared spectra were obtained using KBr pellets and Perkin-Elmer 621 and 457 Grating Infrared Spectrophotometers. Ultraviolet-visible spectra were obtained utilizing a Cary Model 14 Spectrophotometer.

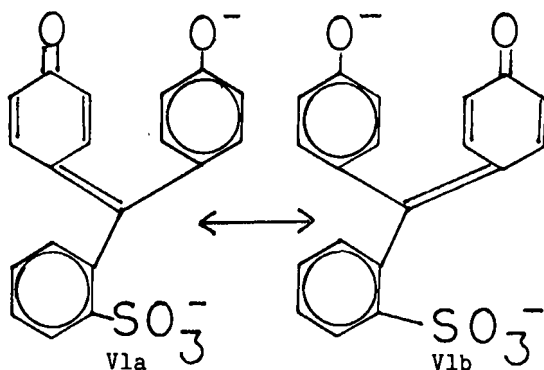
Solubility studies were performed by adding about 1mg of the polydye product to 2ml of solvent contained in a test tube. The tubes were stoppered, periodically shaken, and viewed over a week's period. Elemental analyses for titanium were obtained utilizing a 951 DuPont Thermal Gravimetric Analyzer fitted onto a DuPont 990 Thermal Analyzer console. Softening ranges were obtained using a Fisher-Johns Melting Point Apparatus.

Light scattering was conducted utilizing serial dilutions employing a Brice-Phoenix 2000 Universal Light Scattering Photometer. Refractive index increments were determined using a Bausch and Lomb Abbe Refractometer Model #3-L. Viscometry measurements were obtained employing serial dilutions of polymer solutions using a Cannon-Ubbelohde Semimicro Dilution Viscometer. Timing was accomplished utilizing a Wescan Instruments Inc. (Santa Clara, Calif.) Model 1221 Viscosity timer.

RESULTS AND DISCUSSION

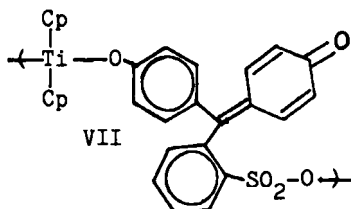
The present study is part of a larger study involving inclusion of dyes into polymers. Selection of dyes was based

on two primary requirements. First, the dye must possess two (acceptable) Lewis base sites (such as alcohol, acid, amine). Second, the dye (in the correct form to allow the desired condensation to occur) was to be water soluble. Phenylsulfonphthalein (PSP) dyes exhibit two nucleophilic sites in water solution over a wide pH range, generally from below a pH of 5 to about 14, existing as noted in form VI.

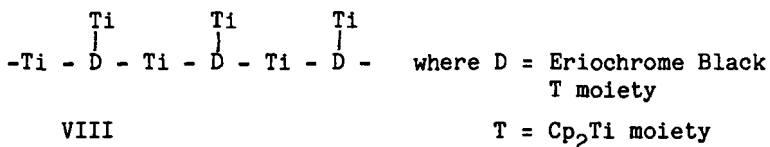


Polymers derived from condensation with Cp_2TiCl_2 and the various dyes will be referred to simply as polydyes.

Polydye structure for condensation with dyes exhibiting only two "active" Lewis base sites will be linear with the connective bonds being the amine and/or imine (for Nigrosine; analogous to form III), sulfone-ether (for PSP dyes, analogous to form IV and depicted by form VII) and sulfone (PDTD, form V).



Polydyes derived from dyes exhibiting more than two reactive sites may contain a complex branched and crosslinked structure. For instance Eriochrome Black T contains three potentially active reactive sites under the employed reaction conditions. The resulting polydye is soluble in such dipolar aproatic solvents as dimethylformamide, triethylphosphate, and dimethylsulfoxide, eliminating the presence of excessive crosslinking. Elemental analysis is consistent with a highly branched structure approaching form VIII.



Indigo Carmine is tetrafunctional and gives products which are insoluble in all tested solvents consistent with the presence of some crosslinking. Thus the structure of products derived from such multifunctional dyes is complex and a mixture of several forms, the proportion and distribution surely dependent on a number of factors including reaction conditions.

The utilized dyes are pictured in Figure 1 with the representative structures depicting the purchased form of the dye.

The infrared spectra of the polydyes are consistent with forms such as V, VII as representing the repeating unit. For instance all of the polydye products exhibit bands at 1440, 1010 and 830 cm⁻¹ characteristic of the Ti-Cp moiety. The PSP dyes react at one alcohol site and the sulfate site. There is a shift in the assymetric stretching band for S=O from a doublet at 1170 cm⁻¹ for the dye to a single band at 1160 cm⁻¹ for the polydye and a shift in the S-O symmetric stretching band

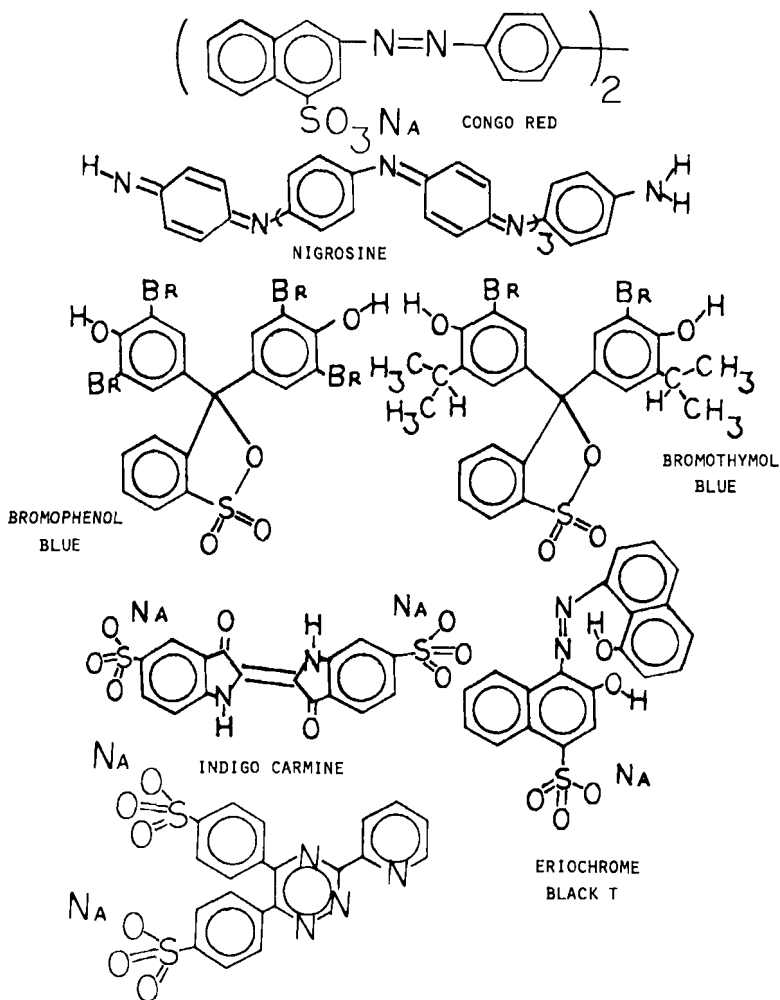


FIGURE 1. STRUCTURES OF UTILIZED DYES

from 1060 cm^{-1} for the dye to 1080 cm^{-1} for the polydye [8]. Spectra of the polydyes exhibit no bands about $3100\text{ to }3500\text{ cm}^{-1}$ consistent with an absence of the alcohol moiety. The polydye products do exhibit a band about 1600 cm^{-1} characteristic of a ketone carbonyl conjugated with alkenes [8]. A shoulder

was present at 1580 cm^{-1} characteristic of alkene stretching vibrations in conjugated systems [8,9]. Elemental analyses were also consistent with a structure of form VII. For instance the percentage titanium found for the product derived from Bromophenol Blue was 5.9, calculated was 5.7.

Further control reactions are consistent with the precipitated material being derived from both the dye and Cp_2TiCl_2 . Reactions were attempted excluding either monomer (dye or Cp_2TiCl_2). No precipitation occurred.

Thus spectral, elemental analyses and control reaction results are consistent with a structure of form VII as the repeating unit for the polydyes derived from PSP, etc.

The polymeric nature of the polydye products is indicated by both viscometry and light scattering photometry results. For instance the Bromophenol Blue product which gave an LVN of 7 ml/g exhibited a dn/dc of 0.24 and a weight average molecular weight of 5.3×10^5 .

Table 1 contains a list of polydyes synthesized and reaction conditions. Generally polydyes are formed utilizing only the interfacial technique though analogous titanium polyamines, polyethers and polyesters are formed using both the interfacial and aqueous solution techniques. None of the aqueous solution systems were extensively studied so polydye formation might occur under other sets of reaction conditions employing the aqueous solution systems.

Product yield and molecular weight are sensitive to both stirring time and amount of added base. Results given in Table 2 illustrate such dependencies. Thus product yield decreases with stirring time. The decrease in product with increase in stirring times beyond 10 seconds is typical for systems employing more than an exact equivalence of base and for many systems such a decrease is typical even when only an equiva-

TABLE 1
Results as a function of dye.

Dye	Reactant Amount(mole) Dye:Ti:NaOH	Reaction Time (Secs)	Yield (%)	Reaction System	Visual of Degradation (°C)	Inception Color (250°)	Final Color (250°)
Indigo Carmine	0.6:0.42:0.12	60	7	IF	80-90	dk brown	dk brown
Nigrosine	0.4:0.42:0.6	60	29	IF	130-150	dk brown	dk brown
	0.3:0.3:0.6	30	29	IF			
	0.5:0.5:1.0	60	0	S			
	1.0:1.0:1.5	60	54	IF			
	0.5:0.7:1.0	300	0	S			
	0.4:0.7	40	66	IF			
Eriochrome Black T	0.5:0.7:1.0	60	0	S			
	0.5:0.7:1.0	60	48	1F	170-180	dk brown	dk brown
	1.0:1.0:2.0	60	65	IF			
Bromothymol Blue	0.5:0.7:1.0	60	0	S			
	0.5:0.7:1.0	60	0	IF			
	0.5:0.7:0.0	60	0	IF			
Bromophenol Blue	0.5:0.5:1.5	13	51	IF	100-120	brown-black	brown-black
	0.5:0.7:1.0	90	0	S			
	0.5:0.7:1.0	40	19	IF			
Congo Red	0.5:0.7	90	8	IF			
PDTD	0.4:0.8	15	5	1F			

Reaction Times: Cp_2TiCl_2 in 30 ml of chloroform added to rapidly stirred (18,600 rpm no load) solution of dye in 30 ml of water containing any added base (sodium hydroxide) at 25°C for the interfacial systems (IF). The aqueous solution (S) systems were identical to those employed for the IF except the Cp_2TiCl_2 is in 30 ml of water. PDTD is 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid, disodium salt.

TABLE 2

Results as a function of reaction variables for the synthesis of polydye products utilizing Bromophenol Blue.

Reaction Amount(mmole)	Reaction Time (secs)	Yield (%)	LVN (ml/g)
Dye: Ti: NaOH			
0.5:0.5:0.0	60	0	--
0.5:0.5:0.50	40	32	
0.5:0.5:1.0	7	43	14
0.5:0.5:1.5	1.3	51	17
0.5:0.5:2.0	50	12	44
0.5:0.5:1.0	60	19	
1.0:1.0:2.0	16	80	
1.0:1.0:2.0	20	65	
1.0:0.7:2.0	40	19	9

Reaction Conditions: Cp_2TiCl_2 in 30 ml of chloroform added to rapidly stirred (18,600 rpm no load) aqueous solution of Bromophenol Blue with any added sodium hydroxide at 25°C.

lence of base is present. Thus 0.085 grams of a polydye product (a titanium polyetherester) was added along with 0.5 mmoles of sodium hydroxide to 30 ml of water and stirred (23,000 rpm no load) for 30 seconds. Only 14% of the polydye product was recovered. This was repeated except omitting the base. A recovery of 65% of the polydye product was made.

Use of excess base also typically reduces product yield, probably through hydrolysis of formed polydye chains.

The use of electrophillic metal containing monomers such as Cp_2TiCl_2 is important in reactions utilizing R-SO_3^- functional groups (such as the PSP dyes) since organic acid chlo-

rides do not condense with the $R-SO_3^-$ moiety under the conditions employed in this study.

The polydyes exhibit thermograms similar to other organo-metallic polymers where stability plateaus (TG) and exothermic (in air, DSC) degradation occur [3]. Most products exhibited poor weight retention with initial degradation beginning below $200^\circ C$. For instance the polydye derived from Eriochrome Black T begins losing weight about $100^\circ C$, losing about 10% to $600^\circ C$ whereupon an additional 60% is lost by $650^\circ C$ in air. The product from Bromophenol Blue begins losing weight about $100^\circ C$ with 5% weight loss to $300^\circ C$, followed by loss of an additional 60% to $550^\circ C$ in air. The final degradation product at 800 to $1000^\circ C$ in air is titanium dioxide.

Visual observations of the physical changes of the polydye products and the dyes were made from $25^\circ C$ to $300^\circ C$ utilizing the Fisher-Johns Melting Point Apparatus. The polydyes generally did not melt in the normal sense for organic compounds. Color changes accompanied the transitions. TGA thermograms of the polydyes showed that weight losses accompanied these physical changes. For compounds such as the Cp_2TiCl_2 condensation products with Bromophenol Blue, the product appeared to melt between 100 and $200^\circ C$. There was an accompanying change in color from a dark red to a brownish color which became dark brown to black by $300^\circ C$. A majority of the compounds did not melt below $300^\circ C$ but did gradually change color. Onset of the color change often was accompanied by an apparent change in the solid structure (i.e. breakup of the larger layered crystals to smaller "crystals" and changes in the texture of the solid) which appeared to correspond within about $50^\circ C$ of the noted initial degradation. The temperature ranges and texture changes were recorded in Table 1 as visual inception of degradation and final color at $250^\circ C$.

APPLICATIONS (POTENTIAL AND ACTUAL)

The advantages of including dyes as part of the backbone of polymer chains is the (potential) permanent, nonleaching nature of such polydyes compared with the monomeric dyes themselves where movement even within apparently solid lattices (such as within plastics) occurs over extended time.

The following miniexperiments were conducted utilizing polydyes derived from Nigrosine and Bromophenol Blue contained to 0.01 to 1.0% weight per volume solutions of DMSO, DMF and HMPA. The polydye solutions readily impregnated paper such as Whatman #1 filter paper and #235 No-Rivl (Fort Howard Paper Co., Green Bay, Wis.) commercial paper towels to give highly colored, fluorescent paper. Thus such polydyes may be of use in the construction of specialty fluorescent posters and other areas requiring permanent, nonleaching coloring agents.

Cotton, Denim and 50%-50% polyester-cotton fabric were impregnated with the dyes. Typically a 3 inch by 3 inch piece of white cloth became highly colored by addition of 1.0 to 0.1 mg. of polydye product. The coloration was not permanently fixed, washing out after two to three machine washings employing typical bleach and fabric soap. A fixing agent or procedure will have to be found to more permanently fix the dye to the fabric before they can be used in the fabric and textile industries as coloring agents.

The following plastics were doped by gently heating about 3 grams of plastic above its T_m and then adding dropwise 3 to 10 drops of 0.1 to 1.0% by weight polydye solution: polyethylene (with 12% vinyl acetate; Union Carbide; Bakelite), polycarbonate (DuPont, Lexan Grade 131, 112 Natural), polypropylene (Hercules, ProFax), high density polyethylene (U.S.I., Petrothene NA-144), nylon (DuPont, Zytel), polyvinyl chloride (B.F. Goodrich, Geon type 102E PF 5), polystyrene (Monsanto,

Lustrax HH-101-2020 Crystal 300) and SAN-styrene copolymer (Monsanto, Lustran A 21-2020 Crystal Run M1527). The plastics accepted the "dope" retaining the polydye product throughout the plastic. The greatest problem was experienced with polyvinyl chloride where the heated polyvinyl chloride often partially decomposed giving HCl which appeared to often change the color of the polydye.

Polydyes that were fluorescent before they were utilized as "doping" agents in the plastics yielded fluorescent plastic plugs. Good fluorescence was noted at the 10 ppm concentration level for most of the doped plugs. (Some of the tested plastic samples were fluorescent so added caution had to be exercised in evaluation of these doped plugs.) The plugs remained fluorescent over the six month test period. Again the polydye products could be employed in plastics to give permanent coloration and/or fluorescence to the plastic.

Impregnation of DuPont white latex paint was carried out by simple addition of about 0.1 to 1.0 ml of 0.01 to 1.0% polydye product contained in DMSO, HMPA, and DMF solutions to 10 ml of latex paint. These doped paints were applied to wood and teflon coated surfaces. The wood applied paints dried to give a typical latex coated surface, while the teflon coated surface yielded flexible, coherent films. The colors were bright and appeared to be commercially acceptable. Of particular interest was the pleasing blue coloration derived from the Bromophenol Blue polydye product because of the difficulty often experienced in obtaining good blue colored coatings. Good coloration was achieved using about 10 to 500 ppm of the polydye product. Again the coatings were fluorescent under both short and long ultraviolet radiation.

The polydyes may not only offer desirable coloring, but desirable ultraviolet "sink" activity due to the presence of

the Cp_2Ti moiety. This may lead to better weatherability for exterior coatings through retardation of ultraviolet-associated coatings failures.

Other potential uses include as laser dyes and as energy exchangers permitting greater depth of penetration of coatings curing.

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