



SYNTHESIS OF NAPHTHANILIDE-TYPE POLYMERIC AZO PIGMENTS

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ABSTRACT

Polymeric azo pigments have been prepared by standard diazotization and coupling followed by reduction of the monoazo pigments were reacted with acryloyl chloride to produce bis-functional acryloylamido monomers. These were reacted by free radical polymerization of bis-functional acryloylamido monomers under anaerobic conditions by bubbling nitrogen through the reaction vessel immersed in an oil bath. The intermediate compounds were subjected to mass spectroscopy and elemental microanalyses. The compounds reported had high colour value and improved resistance to common solvents used in surface coatings applications.

Keywords: Naphtharylide, azo, bis-functional, pigments, polymerisation.

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INTRODUCTION

A pigment is commonly defined as a finely divided solid colouring material that is essentially insoluble in its application medium. Thus pigments are considered to have weak affinity for their application media and only at a surface where the pigment particles are in contact with the medium [1].

Azo pigments, both numerically and in terms of tonnage produced, dominate the yellow, orange and red shade areas in the organic pigments. They are generally structurally described as compounds having one or more azo (-N=N-) groups linked to two carbon atoms which are usually, though not always, part of aromatic systems [2]. Simple azo pigments, e.g. Toluidine Red (C.I. Pigment Red 3) have the drawbacks of being susceptible to high processing temperatures, migrate (i.e. they may bleed in and/or bloom) and have poor resistance in plasticizers and solvents [3]. The low light fastness of azo pigments has been anomalously ascribed to the proximity of an electron-rich atom of a function (e.g. negative charge on the oxygen atom of a nitro function) to the azo group preventing electron delocalization, ultimately lowering the order of the alpha nitrogen – carbon link, and therefore increasing susceptibility to photolytic cleavage [4]. Several attempts have been made to improve the properties of simple azo pigments. Most products of these attempts are based on heterocyclic amines and derivatives of aniline, anthraquinone, naphthanilides, etc. and are limited due to their mono-functionality [5]. The method of synthesis of simple azo pigments can, however be designed to meet the adequate dispersion characteristics and improve their fastness properties [6].

The Naphthol AS or naphtharylamide yellows, oranges and reds constitute a range of structurally related pigments. These pigments show rather better solvent resistance than the simple azo naphthols as a result of their increased molecular size, and the presence of the amide (-NHCO-) functionality whose presence frequently enhances

fastness to solvents, light and heat [2]. This may be attributed to the ability of the amide group to participate in strong dipolar interactions and in hydrogen bonding, both intramolecular and intermolecular. They are useful in a wider range of paints and plastics applications, as well as in printing inks.

As reported earlier [7], naphthanilide-type azo pigments, which form the basic monomeric compounds of the present work, possess good durability, average thermal and soap stability, with better light fastness properties compared to simple azo naphthol pigments. The present work is an attempt to use benzoyl peroxide (BPO) as a free radical polymerization initiator in place of azobisisobutyronitrile (AIBN) in the production of polymeric azo pigments with the general formula described as Intermediate Compound I (Fig. 1) reported in our earlier work [8]. R₁ and R₂ were acryloylamidophenyl reactive groups, with the phenyl groups having possible additional methyl and/or methoxy substitution. The percentage yield, colour value and molecular weights of the products from this work are expected to have improved resistance to common solvents encountered in surface coatings applications compared to their conventional counterparts.

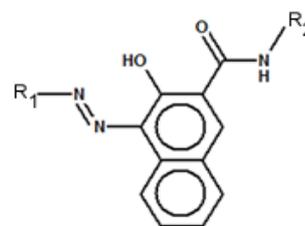


Fig. 1: Structure of intermediate compound I [8].

MATERIALS AND METHODS

The synthesis of Intermediate compound I (Fig 1) reported in earlier work [8] was adopted, for example, sample number 1 in Table 1 was obtained by substituting R_1

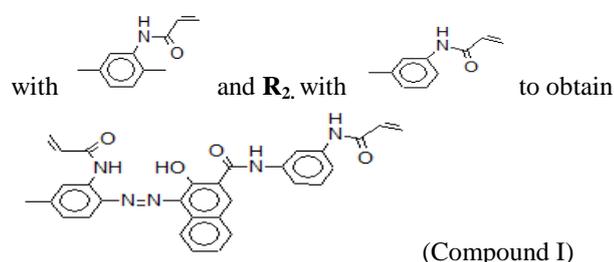


Fig. 2: Structure of compound I

The synthesis involved the following steps:

Synthesis of intermediate compound I

0.05 moles of 2,3-hydroxynaphthoic acid was dissolved in 100 mL distilled water and 1.2 moles NaOH added at the boil. The solution was buffered by adding 5g sodium acetate and coupled with the diazonium salt of 4-methyl-2-nitroaniline at $10 \pm 5^\circ\text{C}$ and pH 6-7 [9].

The dye carboxylic acid was converted to the acid chloride by treatment with thionyl chloride in chlorobenzene and a catalytic amount of 2, 2-dimethylformamide (DMF). 6.3 g of the acid chloride were stirred into 70 mL of o-dichlorobenzene and heated to 80°C . A warm solution of 2.8 g of 2-nitro-p-benzamide in 20 mL o-dichlorobenzene was added and the mixture heated at $140\text{-}145^\circ\text{C}$ for 12hrs. The recrystallized soft red powder had a melting point of $281\text{-}282^\circ\text{C}$ from xylene. Analysis of this product gave 66.18% C, 4.20% H and 14.44% N which agreed with theoretical values of 66.22% C, 4.19% H and 14.45% N.

Reduction of nitro groups in the bis-nitroazo compounds was achieved using approximately 3 moles of sodium sulphide per mole of pigment at $75\text{-}95^\circ\text{C}$ in 2-ethoxyethanol; with careful temperature and concentration control to avoid simultaneous reduction of the azo link and hydrolysis of the amide linkages in the compound.

Addition polymerizable monomers (Intermediate Compound I) were produced by condensing the products of reduction reactions with acryloyl chloride (which had been prepared by reacting acryloyl chloride with benzoyl chloride in 2:3 molar ratio) with the bis-aminoazo compounds obtained in the last reaction.

Polymerization of intermediate compound I

Benzoyl peroxide (BPO) was used as the initiator. Polymerization was achieved under anaerobic conditions by bubbling nitrogen through the reaction vessel which was immersed in an oil bath. A mixture of 2.0 g of monomer, 20.0 mL of 0.2% stock solution of benzoyl peroxide in chloroform and 100.0 mL of dioxane was added to the

vessel and stirred at 90°C for 12 hr. The polymer was collected from an excess of petroleum ether and filtered off, washed with ethanol and dried at 40°C .

Molecular weight analysis using Rast's Camphor method

The high freezing depression point of camphor, $\text{C}_{10}\text{H}_{16}\text{O}$ [10] allows an ordinary melting point apparatus to be used to determine the melting point of an additive. The sample under investigation together with sublimed camphor were placed into a loosely stoppered test tube and melted by carefully heating over a small flame for 30 s while stirring with a platinum wire. (Care was taken not to heat the mixture above 1min to avoid sublimation of camphor from the solution).

The difference between the melting point of the pure camphor and that of the mixture gave the melting point depression of camphor caused by the addition of the sample. Molecular weight (M) was calculated from the equation:

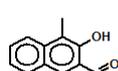
$$M = \frac{1000kw}{\Delta T W}$$

where k is the molecular depression constant of camphor (49.7), w is the weight of the sample, W is the weight of camphor (usually 5-10 times the value of w), and ΔT is the depression of the melting point of camphor.

RESULTS AND DISCUSSION

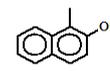
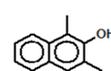
Mass spectra of intermediate compound I

The mass spectra of these compounds showed a cluster of fragments at $m/e = 170$ corresponding to naphthoyl group for bis-functional compounds, and for the hydroxynaphthyl groups at 142 and 143. This justified the use of excess acryloyl chloride during the polymerization reactions to ensure good yield owing to the higher reactivity experienced with amino groups and acryloyl chloride than with hydroxyl groups – an indication that little reaction of the hydroxyl groups occurred. The other principal peaks were for the molecular ion peaks, e.g. for the pigment moiety for sample 5 (Table 1), the peak for the molecular ion ($\text{C}_{10}\text{H}_{25}\text{O}_4\text{N}_5$)⁺ appeared at $m/e = 517$.



Naphthoyl group Hydroxynaphthyl group

$m/e = 170$



$m/e = 142$
 $m/e = 143$

Infra-red spectra of intermediate compound I

The infra-red spectra of the acryloylamido compounds (Intermediate Compound I) reported before [8] were very similar to the parent compounds. However, an absorption band of great interest present was the CH₂-CHO absorption at about 3040-3010 cm⁻¹ and 3095-3075 cm⁻¹, respectively. These absorption peaks differ from -OH absorption, which also appears in this region, by their sharpness.

Polymeric pigments The results in Table 1 show that polymeric pigments were produced using benzoyl peroxide (BPO) as initiator to polymerize bis-acryloylamido monomers I having molecular weights in the range 18,000-42,000 and average yield of 73.0±4.4%. This spread of molecular weights and the yield is smaller than the 78.3±6.7% and 12,000 to 55,000, respectively reported [8] for azobisisobutyronitrile (AIBN) initiated polymerization reactions. Under conventional conditions, as in this work, concerning bulk polymerization with BPO, propagation is the main reaction [7]. The high molecular weights of the polymers (Table 1) are confirmation of high ratio of polymerization to termination. The results in this Table also show that due to the amide group, which gives the molecule more flexibility and increased intercrystalline bonding, it was possible to select moieties with appropriate functionality to produce pigments with varying molecular weights and improved resistance to solvents.

It was observed that a change in the concentration of the free radical initiator (BPO) affected the colour, molecular weight and yield of the polymer as clearly shown in sample numbers 8 and 9 in Table 1. This suggests that higher concentration of the initiator favored transfer of the kinetic chain from the growing polymer to another molecule, resulting to formation of lower molecular weight polymer (sample 8). A change in solvent type gave similar results (sample numbers 2 & 3). Halogenated solvents gave lower yields but relatively higher molecular weight polymers (sample 3). Increases in molecular size and/or polarity will tend to reduce the rate of diffusion out of the substrate and the vapour pressure of the pigment and, thus, increase (sublimation and wash) fastness [11]. In the pigments of this work, variation in the terminal amino groups provides an important means of increasing light fastness due to the electron-withdrawing effect exerted by the amide group [7, 12].

It is universally useful to produce polymers with high colour value as homopolymers but co-polymers could also be produced with other monomers such as acrylamide, acrylonitrile, and methylmethacrylate with careful control of the polymerization procedure to still give products of high colour values.

The methods reported here can also be used for the mass coloration of plastics in any shade from very weak to very strong. Such a method might be used where pigmentation leads to blooming, e.g. in the coloration of polypropylene with block insertion.

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Table 1: Pigments produced showing substituents **R₁** and **R₂** and properties.

Sample No.	R ₁	R ₂	Pigment Moiety	Solvent	% Yield	Colour	Average M.W.
1				Dioxane	72.7	Purple	29,173
2				Dioxane	79.0	Purple	29,967
3				Chlorobenzene	66.8	Violet	32,546
4				Dioxane	69.0	Purple	30,953
5				Dioxane	74.8	Violet	36,751
6				Dioxane	76.3	Violet	17,784
7				Dioxane	72.3	Purple	42,289
8				Dioxane	78.5	Violet	20,005
9				Dioxane	68.5	Purple	33,225