

SYNTHESIS EXPERIMENTAL OF THE POLYMERIC INDIGOID

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Abstract

This study presents the experimental synthesis of a polymeric indigoid used as a colouring agent for foodstuff. The resulting additive, due to a high molecular mass, will have a low migration tendency and it can safely be used to prepare foodstuff with a much better texture and consistency. The synthesis of the polymeric indigoid was conducted by means of two methods: the first one starting from anthranilic acid and the second one starting from the nitrobenzaldehyde. This is a presentation of the advantages and the disadvantages of the two methods. The alternative synthesis eliminates the disadvantage which the known method presents and which consists of the fact that the product of chlorine- methylation of the ester of the acid o-carboxyl-phenyl- glycyl carboxylic, by reacting with the formic aldehyde, leads to secondary products which end up generating polymers that are different from the synthesized polymeric indigoid.

The spectro-chemical analysis of the two polymeric compounds with indigoid structure shows that their spectro-chemical behaviour is similar. The synthesis method of from o- nitrobenzaldehyde (using the Bayer-Drewsen method as an alternative of generating the chromophore), presents the advantage of obtaining the indigoid polymer under a pure form, without any secondary compounds which might alter its colour. The Baeyer – Drewsen synthesis is superior to the other variant studied due to its small number of technological phases, convenient handling, high conversion level (85-90%), resulting products that are free from mechanical ions, etc. The sulphonation of the polymers has proved to be an alternative for obtaining coloring agents with a high molecular mass, low migration capacity, presumably of interest for the food industry.

Keywords: synthese, polymeric indigo, spectroscopic characterisation

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1. INTRODUCTION

1. It is known that one way of reducing the diffusion of food coloring agents into the products containing them is that of increasing the molecular mass of the respective coloring agents. The study aims at the obtainment of an indigoid polymer which, upon being sulphonated, might result in an analogue of the indigo- carmine foodstuff coloring agent (the 5.5' bisulphonic indigo acid) with a significantly higher molecular mass and a low tendency to migrate.

The sulphonation of the polymers (which contain chromophore sequences analogous to the indigo-carmine foodstuff colorant) has proved to be an alternative for obtaining coloring agents with a high molecular mass, low migration capacity, presumably of interest for the food industry (Tarabasanu et al, 1997; Zollinger, 1991).

2. MATERIALS AND METHODS

Two methods for the synthesis of the polymeric indigoid were used: the first one starting from anthranilic acid and the second one starting from nitrobenzaldehyde (Bratu, 2004).

A. The synthesis of the polymeric indigo starting from the antranilic acid

1. Obtaining the Methyl Antranilate.
50g (0.36 moles) of antranilic acid, 175 ml of methylic acid and 9 ml of 98% H₂SO₄ are poured into a balloon provided with a shaker and an ascending refrigerant. The mix is heated under reflux for 8 hours, the excess methanol is distilled, and then the remaining mix is cooled down to 00 C and it is poured over ice. After a sodium bicarbonate- based neutralization, the ester is extracted by means of ethyl acetate. The extract is dried on anhydrous sodium sulfate,

the ethyl acetate and the methyl antranilate are distilled and the 1350C/15mmHg fraction thereof is then separated. There result 33g of methyl antranilate, with a 69% yield.

2. Obtaining the Methyl Ester of the O-Carboxyl Phenyl Glycine Acid

50 ml of water, 4 ml of 40% NaOH solution and then 5 g (0.053 moles) of monochloroacetic acid are poured into a glass. 7 g (0.05 moles) of methyl antranilate are then added to the cold solution (200C). The solution is stirred for two hours and the resulting product is then separated by 35% HCl- based acidulation and when it precipitates it is filtered and dried. There result 7 g of product, with a 71% yield.

3. Condensing the Methyl Ester of the O-Carboxyl Phenyl Glycine Acid with Formic Aldehyde

7 g (0.03 moles) of ester methylic of the fenilglicin -o-carboxylic acid and 200 ml of 3% water- based formaldehyde are poured into a balloon provided with an ascending refrigerant. The mix is heated up to 800C for 6 hours. Upon reaction completion, the mix is poured over 200 g of ice so that it precipitates, followed by filtering and drying. There result 7 g of product, with a 58% yield.

4. Hydrolyzing the Ester

4g (0.008 moles) of ester and 40 ml of 20% NaOH solution are poured into a balloon

provided with an ascending refrigerant. The mix is heated under reflux until the solution becomes clear. Such solution is then filtered for impurities, it is acidulated by means of 30% HCl until a positive reaction is obtained on Congo Red paper, at which point the free acid precipitates and it is dried. There result 3g of product (the free acid), with an 87% yield.

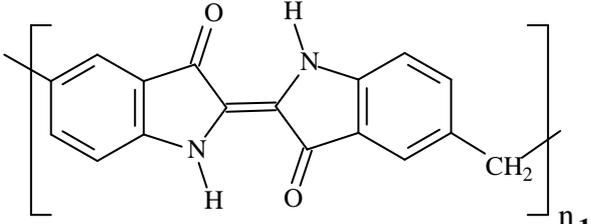
5. Obtaining the Acetilate Monomer

40 ml of acetic anhydride, 2g of anhydrous sodium acetate and the 3g of free acid previously obtained are poured into a balloon provided with a shaker and an ascending refrigerant. The mix is heated for 8 hours at 140 0C, then it is cooled and the precipitate obtained is separated by filtration and then it is dried. There result 2g of product (acetylate monomer) with an 83% yield.

6. Obtaining the Polymeric Indigoid

50 ml of 1% NaOH solution and 2 g of the previously obtained precursor are poured into a balloon provided with an ascending refrigerant and an air bubbler. There follows a 10 hour reflux with permanent air bubbling. At reaction completion, the indigo polymer is precipitated in the reaction mass and it is separated through filtering. There result 1,9g of product ($\eta=95\%$). The product is characterized by means of IR and UV-VIZ spectroscopy, the resulting information being presented in table no. 1

Table 1. Experimental Data Regarding the Characteristics of the Indigo Polymer(1) obtained from the Anthranilic Acid

Compound	Spectrum IR (KBr) cm ⁻¹	Spectrum UV-VIZ (DMF)	
		λ_{\max}	$\lg\epsilon_{\max}$
	$\nu_{\text{CO}} = 1605$ $\nu_{\text{NH}} = 3236$ other bands: 539, 671, 740, 860, 1052, 1148, 1189, 1280, 1292, 1368, 1434, 1467	595.1	0.756

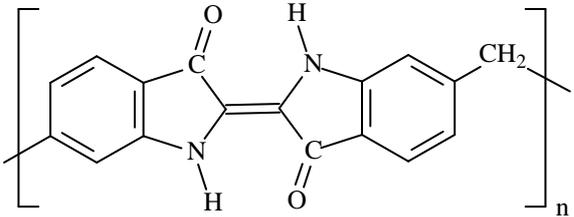
B. Synthesizing the Polymeric Indigo Starting from a O-Nitro-Benzaldehyde**1. Condensing an O-Nitro-Benzaldehyde with Formic Aldehyde**

10 g (0.065 moles) of o-nitrobenzaldehyde and 200 ml of 3% water- based formaldehyde are poured into a balloon provided with an ascending refrigerant. The mix is heated up to 80°C for 6 hours. Upon reaction completion, the mix is poured on 200 g of ice, followed by filtration and drying. There result 9 g of product, with a 90% yield.

2. Obtaining the Polymeric Indigoid

40 ml of acetone and the previously obtained 9 g of monomer are poured into a glass. Then, a solution of 13 ml of 50% NaOH and 100ml of water are dripped into the mix, with the temperature being maintained at 40°C. The mix is then left at room temperature for 12 hours, then it is filtered, washed with acetone, then with water and finally dried. There result 10g of product, ($\eta=95\%$). The product is characterized by IR and UV-VIZ spectroscopy, and the resulting data is presented in table no. 2.

Table 2 Experimental Data regarding the Spectroscopic Characterisation of the Indigoid Polymer(1') obtained from O-Nitro-Benzaldehyde

Compound	Spectrum IR (KBr) cm ⁻¹	Spectrum UV-VIZ (DMF)	
		λ_{\max}	$\lg\epsilon_{\max}$
 <p style="text-align: center;">1'</p>	$\nu_{\text{CO}} = 1606$ $\nu_{\text{NH}} = 3227$ other bands: 539, 671, 740, 860, 1052, 1105, 1148, 1189, 1280, 1293, 1368, 1434, 1467	595.7	0.774

3. Sulphonating the Polymeric Indigoid

50ml of 96% sulphuric acid and 10 g of indigoid polymer are poured into a balloon provided with a thermometer, shaker and an ascending refrigerant. The mix is heated up to 40°C for two hours. Upon reaction completion the mix is cooled and poured over 300g of ice. The resulting mix is filtered for impurities, salified with 40g of NaCl, shaken for another 30 minutes, then left to rest for 4 hours. The resulting precipitate is filtered, washed in 20% NaCl solution and dried. There result 11.5g of the sodium salt of the sulphonated acid of the polymer. The salt- free product can be obtained

by ethyl alcohol based extraction when the sulphonated polymer dissolves, the salt being eliminated as a precipitate (sediment). The sulphonated polymer is isolated from the ethanolic solution by concentration, followed by filtering and drying in void at 40-600 C[4].

3. RESULTS AND DISCUSSION

The spectro-chemical analysis of the two polymeric compounds with an indigoid structure shows that their spectro-chemical behaviour is similar. There can be noticed a distortion of the frequency of the C=O group towards values inferior to that of the indigo ($\nu_{\text{C=O}}$ indigo = 1626cm⁻¹), as well as a decrease in the ν_{NH} (ν_{NH} indigo = 3246 cm⁻¹) frequency.

This confirms a linear polymeric structure, the drop in the frequencies being due to the formation of hydrogen bonds between the macromolecules of the polymers. The corresponding vNH band is much wider than that of the indigo, especially for the compound obtained from o- nitrobenzaldehyde, due to the imposed linear structure.

For the compounds obtained from antranilic acid, the band is sharper, which indicates the presence of some irregular macromolecular fragments.

The alternative to the proposed synthesis eliminates the disadvantage which the known method presents and which consists of the fact that the product of chlorine- methylation of the ester of the acid o-carboxyl-phenyl- glycin carboxylic, by reacting with the formic aldehyde, leads to secondary products which end up generating polymers that are different from the synthesized polymeric indigoid.

The synthesis method starting from o-nitrobenzaldehyde (using the Bayer-Drewsen method as a chromophore generation alternative), presents the advantage of obtaining the indigoid polymer under a pure form, thus eliminating the disadvantage presented previously.

This variant was chosen both on the basis of a study in the existing specialised literature and on the running of a series of experimental tests concerning the synthesis of the indigoid system.

4. CONCLUSIONS

The synthesised compounds were characterised by IR and UV-VIS spectroscopy. The spectrum obtained attested the synthesised structures.

An analysis of the indigo synthesis methods referred to in the specialised literature indicates that most of them use aromatic amines ortho-substituted by carboxy, cyan, amide, etc. groups as raw materials, the preparation means consisting of a grafting of carboxy or cyano-methylene traces onto the amino group and the alkaline melting of the intermediary resultants. The examination of the various synthesis methods suggests that none of them is

appropriate for the preparation of the foodstuff type of indigo as the alkaline melting is based on sodium hydroxide resulting from electrolytic procedures (therefore containing Mercury ions impurities).

The Baeyer – Drewsen synthesis is superior to the other variant studied due to its small number of technological phases, convenient handling, high conversion level (85-90%), resulting products that are free from mechanical ions, etc.

To conclude, we consider that this method is the most appropriate for the preparation of indigoid colorants for foodstuff products.

The sulphonation of the polymers (that contain chromophore sequences analogue to the indigo-carmine foodstuff colorant) has proved to be an alternative for obtaining coloring agents with a high molecular mass, low migration capacity, presumably of interest for the food industry.

5. REFERENCES

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