



Biodegradable Chitosan Dyes for Clean Environment and Their Application as Alternative Green Dyes

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Abstract

This research aimed at preparing derivatives of natural polymer Chitosan (CS) carrying chromophoric chromatic groups, such as amine benzaldehyde groups (I, II, III) and aromatic azo dyes (II-I5), (III-I5), (III1-III4), which are characterized by their stability till the preparation of environment-friendly biodegradable polymers. The study identified polymers resulting from polymer (CS) interaction with three phenolic benzaldehydes and then the interaction of amine derivatives of these polymers with diazonium salts prepared simultaneously by some aniline in the infrared spectrum FT-IR, proton nuclear magnetic resonance, the X-ray spectrum (X-RD) and the change of physical properties.

Keywords: *Chitosan, Schiff Base, Azo Dyes, X-Ray, Chitin.*

Introduction

Chitosan has a certain antibacterial strength and antibacterial spectrum [1] and it is a derivative N-deacetylation of Chitin [2]. Chitosan is insoluble in water but dissolves in aqueous solutions of organic acids, such as acetic, formic and nitric, in addition to inorganic acids such as diluted HCl, resulting in viscous solutions [3]. The solubility in it is controlled by restricting the spread of active groups with Chitosan on the chain length, which contains etheric bonds of Sigma type and six-membered saturated rings [2].

Biopolymers have several applications including pharmaceutical [4], cosmetic [5] and food [6]. The existence of ammine groups in the polymer chain leads to the possibility of many chemical transformations [7], such as the preparation of Schiff bases by interaction with aldehydes and ketones [8] and the formation of amide Chitosans.

In spite of the importance of Chitosan and its various applications, its main source is still Chitin extracted from shrimp and crab. The extraction process includes two phases: acidic and basic [9]. Chitosan is one of the polymers carrying dietary supplements [10] and of the polymers used for slimming [11]. The suspension interaction of the active groups depend on the solubility of Chitosan in acid as well as the activity of the same medium in

the preparation interaction of the Schiff bases successfully [12], where amine derivatives are used in many environmental and analytical applications [13].

Methods and Materials

Preparation of Polymeric Schiff bases (I, II, III) [14]

(0.5) g of Chitosan was dissolved in 20 ml of the absolute ethanol, which was acidified by 2 mL of acetic acid (99.9%), then (0.01) mL of aromatic aldehydes compensators dissolved in 20 ml of absolute ethanol was added in ultrasound bath for 76 hrs. The solution was cooled and left to evaporate the solvent and crystallize the deposit. Then, it was recrystallized by ethanol.

Polymeric Azo Dyes (I1-I5), (II1 -II5), (III1 - III4) [15]

The preparation was done by dissolving (0.2) mL of the amine derivative in a solution consisting of 1:1 hydrochloric acid and water. The mixture was cooled to 0 ° C, then the sodium nitrate solution prepared by dissolving (0.4) g of sodium nitrate in (5) ml of distilled and cooled water to 0 ° C was added drop by drop with continuous stirring and under cooling to complete the process of diazotization.

This solution was added to a 0.2 g solution of the Schiff bases dissolved in 10 ml of NaOH 10% solution and cooled below 0°C. Deposition of the polymeric azo was observed and the mixture interaction was formed after

the completion of the addition process (2 hours). Then, the deposit and solution were left for 24 hrs. After that, the deposit was filtered and recrystallized by water. The results are summarized in Table 1.

Table 1: Physical properties of prepared compounds

No. comp	Color	m.p	solvent	%yield
I	Orange	100	Ethanol	70
II	White	65	Ethanol	73
III	Pale yellow	60	Ethanol	65
I ₁	Red	143	Water	75
I ₂	Red	103	Water	65
I ₃	Red	120	Water	78
I ₄	Red	108	Water	80
I ₅	Yellow	80	Water	81
II ₁	Green	120	Water	77
II ₂	Yellow	105	Water	80
II ₃	Brown	160	Water	82
II ₄	Dark yellow	50	Water	67
II ₅	Orange	165	Water	82
III ₁	Yellow	124	Water	86
III ₂	Yellow	227-229	Water	69
III ₃	Brown	187-189	Water	71
III ₄	Yellow	88-91	Water	66

The working plan is

performed according to the Figure 1.

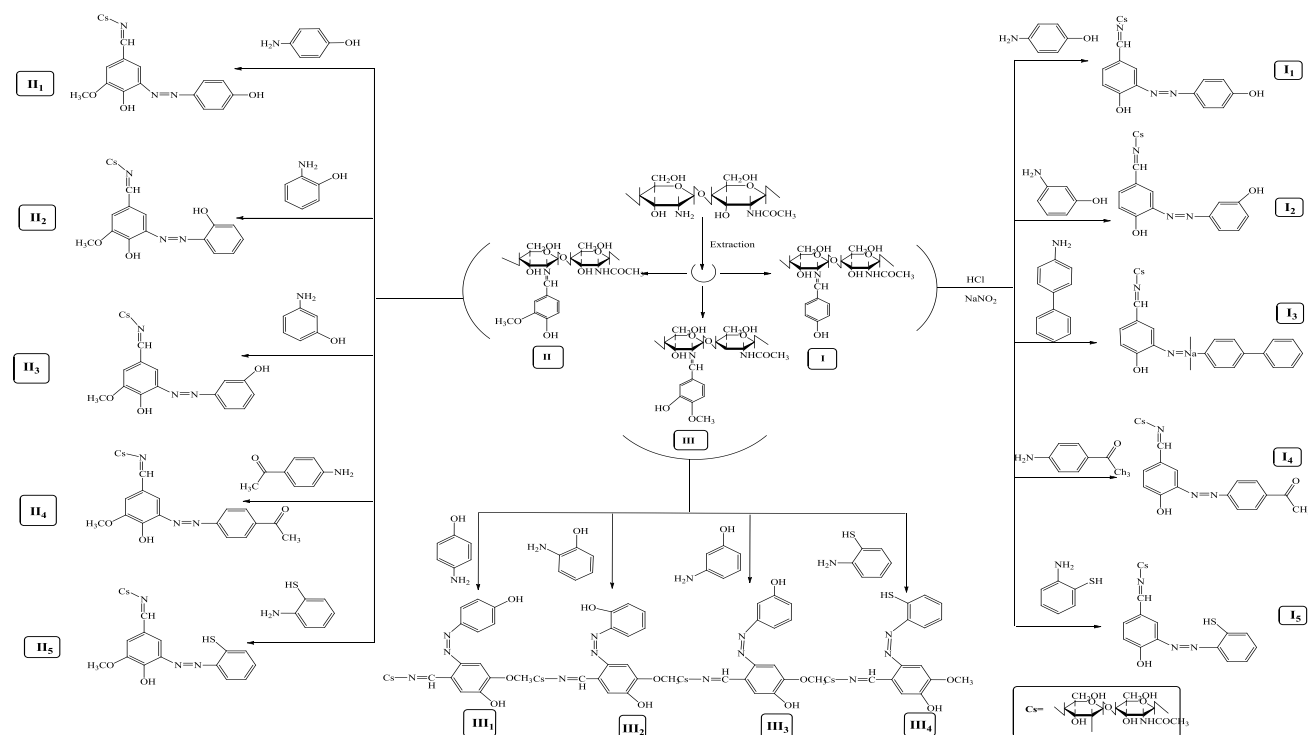
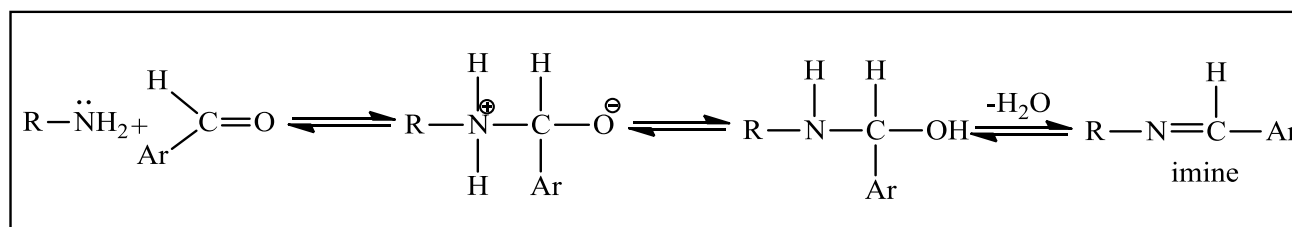


Figure 1: Working plan

Results and Discussion

Chitosan derivatives of Schiff bases were prepared through interaction with the

appropriate aldehydes in alcoholic acidic medium under the effect of ultrasound at frequency of 240 Hz for 76 hrs according to the following proposed mechanism:



The study identified compounds prepared by the infrared spectrum FT-IR in which the compound [I] showed absorption set at 1597 cm⁻¹ related to amine group ($\nu_{C=N}$). In addition, it showed absorption set at 1670 cm⁻¹ related to ($\nu_{C=O}$) and another one at 3194 cm⁻¹ related to ν_{OH} . It also showed two absorption sets at cm⁻¹ (1452-1514) related to aromatic ($\nu_{C=C}$). The compound [II] showed absorption set at 1593 cm⁻¹ related to $\nu_{C=N}$ and another one at 3174 cm⁻¹ related to ν_{OH} with the appearance of a distinctive set at (1153-1201) cm⁻¹ related to

symmetric and asymmetric ν_{COC} with clear sets at (1429-1512) cm⁻¹ related to aromatic $\nu_{C=C}$. The compound [III] showed absorption set at 1593 cm⁻¹ belongs to $\nu_{C=N}$ and another one at 1668 cm⁻¹ belongs to $\nu_{C=O}$. It also showed a distinctive set at cm⁻¹ (1124-1265) belongs to symmetric and asymmetric ν_{COC} with the appearance of clear sets at (1412-1512) cm⁻¹ belongs to aromatic ν_{COC} as in Table 2. When these compounds interact with amine derivatives, they give polymeric azo dyes, which are identified in the spectrum of IR and ¹H NMR.

Table 2: Infrared spectrum of the prepared polymeric Schiff bases

No. comp	ν_{OH}	$\nu_{C-H_{aleph}}$	$\nu_{C=N}$	$\nu_{C=C_{Ar}}$	δ_{C-H}	ν_{COC}	$\nu_{C=O}$
I	3194	2829	1597	1452,1514	831	-----	1670
II	3174	2738	1593	1429,1512	733	1153,1201	1668
III	3176	2858	1593	1412,1512	733	1124,1265	1668

The compounds [I₁-I₅] showed absorption sets ranging between (1612-1638) cm⁻¹ belong to $\nu_{C=N}$ and other ones ranging between (1471-1603) cm⁻¹ belong to aromatic $\nu_{C=C}$. In addition, the compounds [II₁-II₅] demonstrated absorption sets ranging between (1591-1610) cm⁻¹ related to absorb $\nu_{C=N}$ and other ones ranging between

(1456-1549) cm⁻¹ related to absorb aromatic $\nu_{C=C}$. The compounds [III₁-III₄] demonstrated absorption sets ranging between (1593-1612) cm⁻¹ belong to absorb $\nu_{C=N}$ and other ones ranging between (1470-1583) cm⁻¹ related to $\nu_{C=C}$ as in Table 3.

Table 3: Infrared spectrum of polymeric azo dyes

No. comp	ν_{OH}	$\nu_{C-H_{aleph}}$	$\nu_{C=N}$	$\nu_{C=C}$	δ_{C-H}	$\nu_{N=N}$	athores
I ₁	3246	2877	1618	1537,1564	845	1487	
I ₂	3167	2877	1638	1597,1514	833	1454	
I ₃	3168	2879	1630	1516,1603	833	1452	
I ₄	3170	2852	1632	1506,1597	841	1431	($\nu_{C=O}$)1682
I ₅	3377	2868	1612	1471,1585	752	1442	(ν_{SH})2615
II ₁	3200	2893	1593	1465,1508	873	1427	(ν_{COC}) 1227-1149
II ₂	3203	2841	1591	1512,1543	752	1460	(ν_{COC}) 1273-1153
II ₃	3215	2854	1610	1547,1585	746	1460	(ν_{COC}) 1119-1271
II ₄	3242	2862	1608	1549,1585	755	1437	($\nu_{C=O}$)1689 (ν_{COC}) 1122-1261
II ₅	3408	2839	1606	1549,1437	726	1433	(ν_{SH})2625 (ν_{COC}) 1159-1290
III ₁	3375	2983	1593	1470,1516	837	1456	(ν_{COC}) 1174-1263
III ₂	3059	2839	1597	1491,1510	754	1464	(ν_{COC}) 1151-1271
III ₃	3059	2843	1612	1490,1581	754	1469	(ν_{COC}) 1149-1269
III ₄	3377	2901	1612	1471,1583	752	1442	(ν_{SH})2620 (ν_{COC}) 1155-1246

Some compounds prepared by ¹H NMR spectrum were identified. Hence, the compound [I₃] demonstrated a mono signal at 1.23 ppm related to CH₃ protons. It also showed a multiple signal within the range of (6.95-7.77 ppm) related to the aromatic ring

protons. Measurement of x-ray diffraction of compound (I) exhibited a set at the corner $2\theta = 7.92$ with an interval of $d = 27.93$ nm. The measurement showed another set at the corner $2\theta = 13.35$ with an interval $d = 16.09$ nm.

The measurement also exposed a third set at the corner $2\theta = 13.03$ with an interval $d =$

18.20 nm. The average size of minutes was 20.74 nm, as in Figure2.

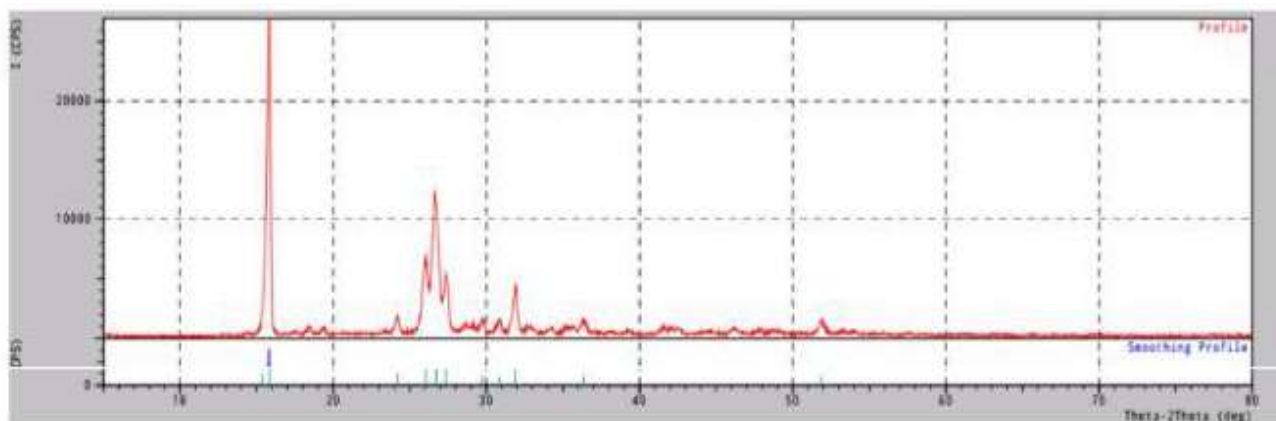


Figure2: Spectrum of X-ray diffraction (XRD) of compound (I)

Measurement of x-ray diffraction of compound (II) demonstrated a set at the corner $2\theta = 6.55$ with an interval $d = 35.29$ nm. The measurement showed another set at the corner $2\theta = 13.44$ with an interval $d =$

30.59 nm. The measurement also exposed a third set at the corner $2\theta = 13.35$ with an interval $d = 16.29$ nm. The average size of minutes was 27.39 nm, as in Figure3.

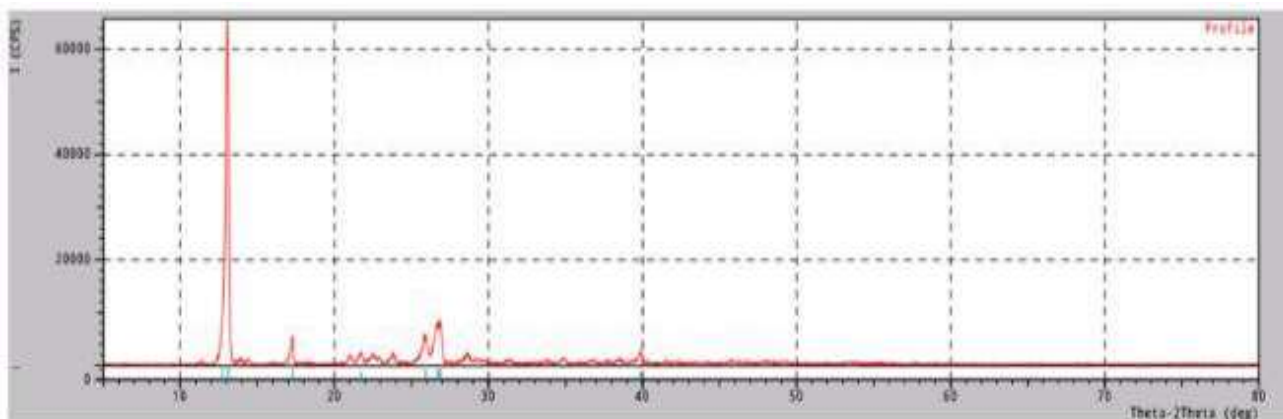


Figure3: Spectrum of X-ray diffraction (XRD) of compound (II)

Measurement of x-ray diffraction of compound (III) exhibited a set at the corner $2\theta = 6.57$ with an interval $d = 30.27$ nm. The measurement showed another set at the corner $2\theta = 19.95$ with an interval $d = 52.69$

nm. The measurement also exposed a third set at the corner $2\theta = 13.36$ with an interval $d = 27.80$ nm. The average size of minutes was 36.89 nm, as in Figure4.

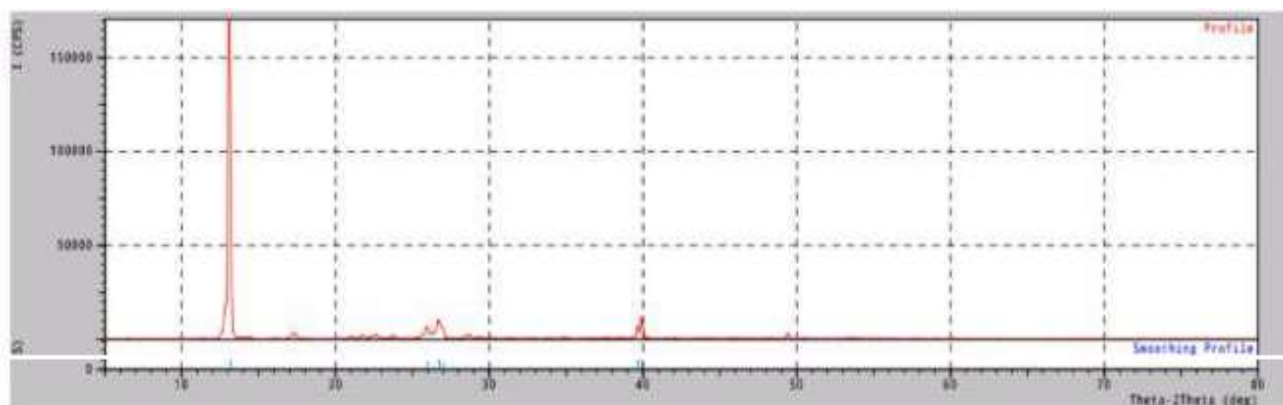


Figure4: Spectrum of X-ray diffraction (XRD) of compound (III)

The compound showed another mono signal at 9.79 ppm belongs to protons of amine group NH_2 with a signal at 10.73 ppm, which

may be related to the protons of the hydroxyl groups OH , as shown in Figure 5.

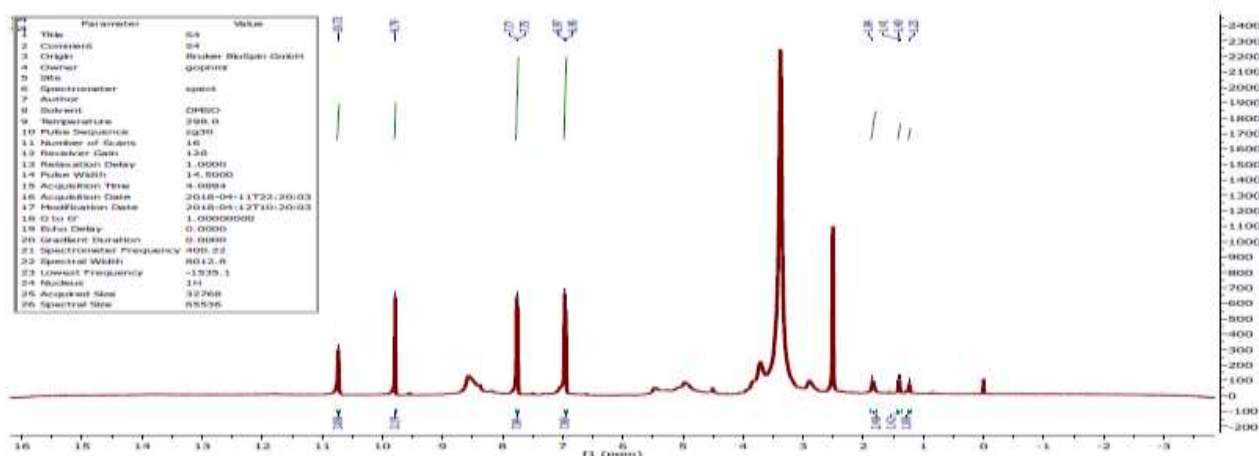


Figure5: NMR spectrum of compound I3

The compound [I₄] revealed a multiple signal at (6.93-7.87 ppm) belongs to the aromatic ring protons, a mono signal at 9.95 ppm belongs to the amine group protons NH and a

mono signal at 11.70 ppm related to the hydroxyl group protons OH, as shown in Figure 6.

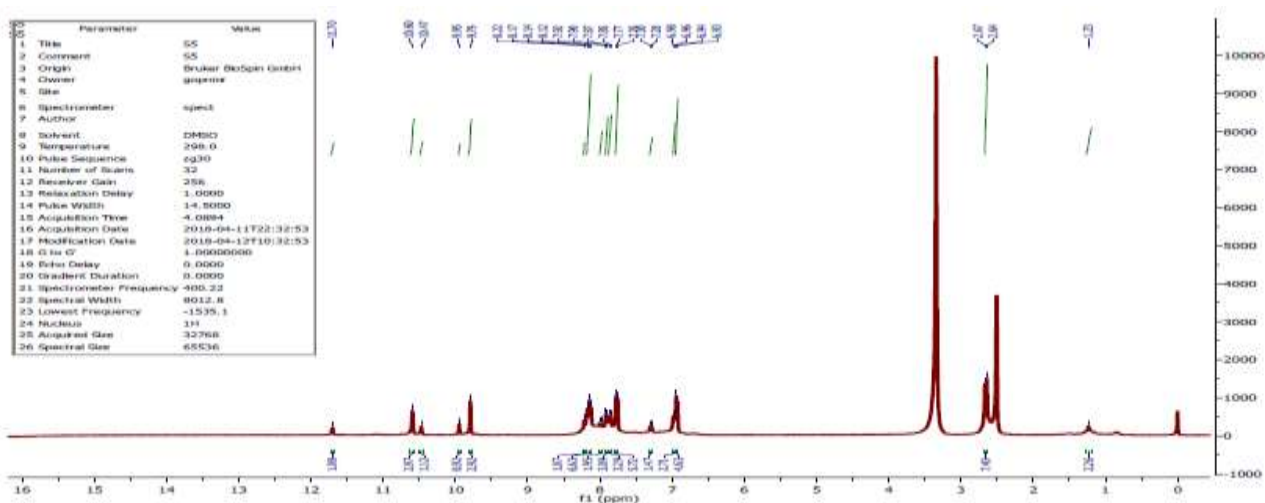


Figure6: NMR spectrum of compound I4

The compound [II₁] exposed a mono signal at 1.23 ppm belongs to protons CH₃, a mono signal at 9.61 ppm belongs to the amine group protons NH and a multiple signal

within the range of (7.03-7.27 ppm) belongs to the aromatic ring protons, as shown in Figure7.

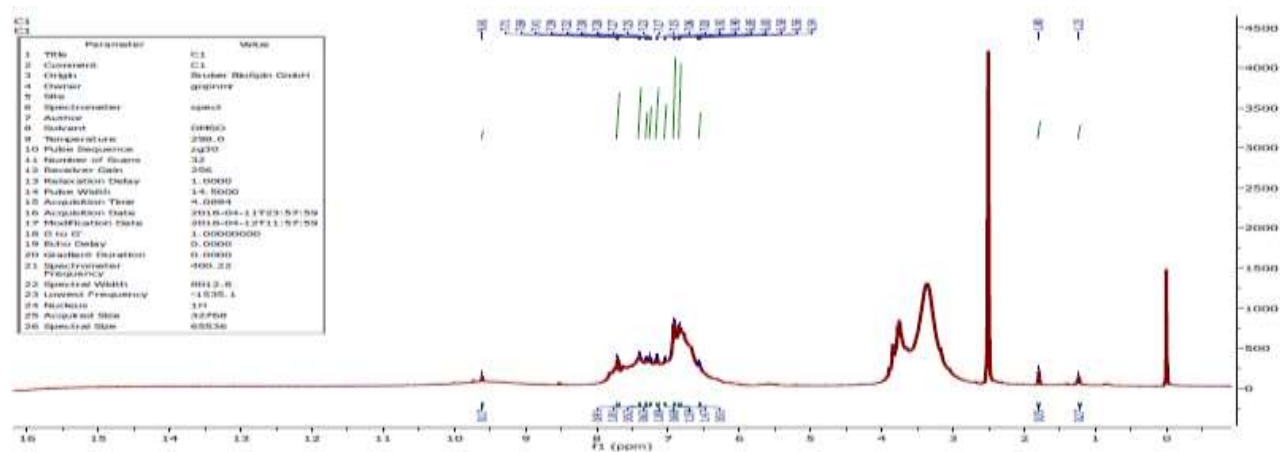


Figure7: NMR spectrum of compound II₁

The compound [II₂] demonstrated a multiple signal within the range of (7.17-7.64 ppm)

related to the aromatic ring protons, as well as a signal at 10.26 ppm belongs to the amine

group protons NH₂ and a mono signal at 10.77 ppm related to the hydroxyl group protons OH, as shown in Figure8.

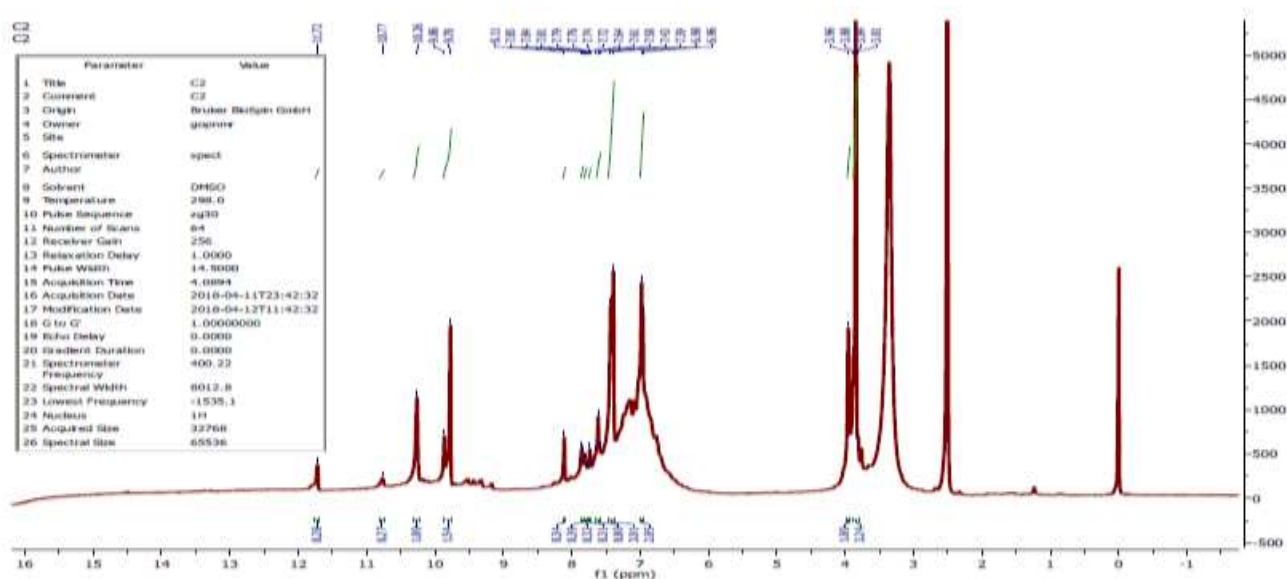


Figure8: NMR spectrum of compound II2

The compound [III₃] exhibited a multiple signal within the range of (7.04-7.18 ppm) belongs to the aromatic ring protons, as shown in Figure9.

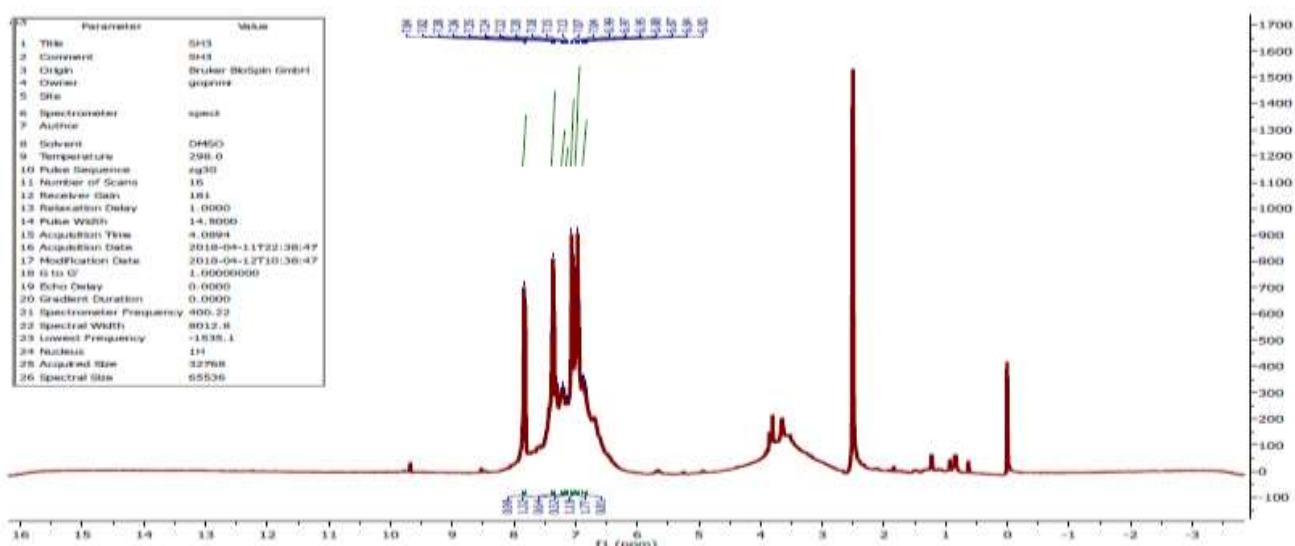


Figure9: NMR spectrum of compound III₃

Conclusion

It is possible to prepare the bases of a polymeric shim with good proportions, and it

is possible to prepare azo-polymer dyes in very good proportions to be used as alternative green dyes.

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