Synthesis, Characterization and Biodegradation of Some Polymeric Azo Compound

By Rehab Abdeen

Kinh Khalid university, Saudi Arabia

Abstract- A diazinum salt of Benzidine was coupled with aniline to form 4, 4'-Bis (1'-azo-4'-aminobenzene) biphenyl. The resulted azo dye was polymerized with different diacid chloride to form azopolymers. Monomer azodye and its azopolymer were determined using elemental analysis, Infrared spectroscopy and HNMR. The microbial degradation constant and rat of azopolymer were quantitatively assessed against fungi (Aspergillus flavus, Aspergillus fumigatus, Aspergillus niger, Aspergillus ochraceous and Fusarium oxysporum). Pleurotus ostreatus Hungary (HAR17) And Ganoderma resencium mycelial hyphae, Candida albicans was used as yeast model. However, Escherichia coli was used as bacterial organisms, using different concentration from azopolymers.

Keywords: azo dye, azo polymers, microbial degradation and azo reduction.

GJSFR-C Classification: FOR Code: 279999p

Strictly as per the compliance and regulations of:

© 2015. Rehab Abdeen. This is a research/review paper, distributed under the terms of the Creative Commons Attribution-Noncommercial 3.0 Unported License http://creativecommons.org/licenses/by-nc/3.0/}, permitting all non commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.
Synthesis, Characterization and Biodegradation of Some Polymeric Azo Compound

Rehab Abdeen

Abstract- A diazinum salt of Benzidine was coupled with aniline to form 4, 4'-Bis (1-azo-4'-aminobenzene) biphenyl. The resulted azo dye was polymerized with different diacid chloride to form azopolymers. Monomer azodye and its azopolymer were determined using elemental analysis, infrared spectroscopy and HNMR. The microbial degradation constant and rate of azopolymer were quantitatively assessed against fungi (Aspergillus flavus, Aspergillus fumigatus, Aspergillus niger, Aspergillus ochraceous and Fusarium oxysporum). Pleurotus ostreatus Hungary (HAR17) And Ganoderma resencium mycelial hyphae, Candida albicans was used as yeast model. However, Escherichia coli was used as bacterial organisms, using different concentration from azopolymers.

Keywords: azo dye, azo polymers, microbial degradation and azo reduction.

I. Introduction

Azo dye has received great attention due to its environmental stability, ease of preparation and its optical and electrical properties. Much work has been done on the molecular design, synthesis, and assembly of structures with desired properties [1-5]. The discovery of diazo compounds occurred around the year 1858, which parallels the beginning of what is considered the starting point of modern organic chemistry [6,7].

An area of polymer research that presents great current interest, yet has received insufficient attention, is the development of polymers with antimicrobial activities, generally known as polymeric biocides. In the area of health care and hygienic applications, biocidal polymers may be incorporated into fibers, or possibly extruded into fibers themselves, and used for contact disinfectants in many biomedical applications such as sterile bandages and clothing. For example, antimicrobial surgical gowns and antifungal polymeric coatings on surfaces such as shower walls and many kinds of tubing minimize the problems of biofouling and the release of pathogenic microorganisms into streams of flowing fluids [8].

To overcome problems associated with the low molecular weight antimicrobial agents, antimicrobial functional groups can be introduced into polymer molecules. The use of antimicrobial polymers offers promise for enhancing the efficacy of some existing antimicrobial agents and minimizing the environmental problems accompanying conventional antimicrobial agents by reducing the residual toxicity of the agents, increasing their efficiency and selectivity, and prolonging the lifetime of the antimicrobial agents. Also, polymeric antimicrobial agents have the advantage that they are nonvolatile and chemically stable and do not permeate through skin. Therefore, they can reduce losses associated with volatilization, photolytic decomposition, and transportation. In the field of biomedical polymers, infections associated with biomaterials represent a significant challenge to the more widespread application of medical implants [9-13]. Research concerning the development of antimicrobial polymers represents a great challenge for both the academic world and industry [8]. Significant advances in the past three decades have been made in the synthesis and applications of polymers to prevent microbial attack and degradation for diverse end uses [15].

Basic Requirements for Antimicrobial Polymers. The ideal antimicrobial polymer should possess the following characteristics: (1) easily and inexpensively synthesized, (2) stable in long-term usage and storage at the temperature of its intended application, (3) not soluble in water for a water-disinfection application, (4) does not decompose to and/or emit toxic products, (5) should not be toxic or irritating to those who are handling it, (6) can be regenerated upon loss of activity, and (7) biocidal to a broad spectrum of pathogenic microorganisms in brief times of contact [8]. The elucidation of degradation pathways is of special interest considering health and environmental priorities. Directly on incubation medium have been used for the first time to follow kinetics of sulfonated azo dye Orange II enzymatic degradation. Nine transformation products were identified using these complementary analyses performed ex situ without any prior treatment. Three types of cleavage are proposed for the degradation pathway: (i) a symmetrical splitting of the azo linkage that leads to the formation of 4-aminobenzenesulfonate (and 1-amino-2-naphthol, not detected); (ii) an asymmetrical cleavage on the naphthalene side that generates 1,2-naphthoquinone and 4-Diazoniumbenzenesulfonate as products, with the latter one being transformed into 4-hydroxybenzensulfonate; and (iii) a third degradation pathway that leads to 2-naphthol and 4-hydroxybenzenesulfonate [16].
The goal of this work is to prepare and investigate the production of polyamide containing azogroup, by the reaction of Benzedine with aniline and copolymerization with different diacide chlorideby different methode and discusses the mechanism of degradation of azopolymers.

II. Experimental

a) Materials

(Benzidine, aniline, Terephthaldehyde, PTHFdipropionic acid and Dithiodipropionic acid) was purchased from Aldrich, USA and was used as received without further purification. Succinic acid was purchased from El-Naser pharmaceutical chemicals, Egypt and was used as received. Adipic acid was used as received from El-Gomhouria chemicals Co., Egypt. Azealic acid was purchased from Aldrich and was used as received without further purification.

b) Microorganisms

The following microorganisms were chosen to evaluate its activity towards the reduction or (degradation) of the synthesized polymers Aspergillus flavus, Aspergillus fumigatus, Aspergillus niger, Aspergillus ochraceous and Fusarium oxysporum were isolated from the soil and identified. Pleurotus ostreatus Hungary (HAR17), was obtained from Agricultural research center, Cairo. Egypt. And Ganoderma resencium mycelial hyphae were isolated and purified from their fruiting bodies, Candida albicans was used as yeast model. However, Escherichia coli was used as bacterial organisms.

c) Media

Nutrient agar and Nutrient broth medium were used for growing Escherichia coli as bacterial cultures. However, Sabouraud dextrose agar was used for growing of Candida albicans. Additionally, Malt extract medium was used for growing Pleurotus ostreatus, Ganoderma resencium, Aspergillus fumigatus, Aspergillus niger, Fusarium oxysporum, and Aspergillus ochraceous.

d) Evaluation of the azo polymers microbial biodegradation.

For each tested organism a series of a test tube have been prepared to obtain active vegetative microbial growth before the process of biodegradation. Stock cultures were used to inoculate 5 ml of broth medium specific for organism in number of tested tubes. After incubation for ~24 h at specific temperature for each organism, the cells were harvested by centrifugation (4000 rpm) for 10 min, suspended in 0.5 ml of PBS buffer, pH 7.2 (2mM KH2PO4, 3mM Na2HPO4. H2O, 167 mM NaCl containing 0.125 mM benzylviologen and 6.3 mM (D-glucose monohydrate). A certain volume has been over the proper solid medium, and the colony forming unit has been determined by spread plate technique.

Approximately 10⁷ colony forming unit per ml of tested microorganisms were used to inoculate the proper medium contains 33 µM of tested azo polymers and 0.125 mM benzylviologen in test tube. Then the test tubes were closed with rubber stopper, and incubated at 37°C in a horizontal shaking water bath, set at 100 rpm/min. At regular time intervals, one tube was withdrawn from the water bath, opened and 0.5 ml of 30 % trichloroacetic acid aqueous solution was added to stop the reaction, the absorbance of the clear supernatant was measured at the maximum wavelength of absorbance (λ max=332 &228 for XXI and 320 &230 for XXVII) of the tested azo polymer. A calibration graph for each azo polymer was carried out by measuring the absorbance of PBS buffer solution pH 7.2, solution containing 3% (w/w) of trichloroacetic acid and known concentration of the azo polymer. From the calibration graph, the azo polymer concentration was determined and plotted against the time. The rate of azo polymer degradation (K, the slope of the linear part of the degradation curve) was calculated as micromoles of azo polymer degraded per hour and per ml of inoculum (µ mol/h/ml).

III. Instrumentation

FTIR spectra were recorded on a Perkin-Elmer 1430 Ratio Recording Infrared Spectrophotometer apparatus from KBr pellets.

UV spectra were taken on a Shimadzu UV-2101 Dc Spectrophotometer.

¹H NMR spectra were recorded using a Varian 300 M, Mercury-Oxford and a Jeol JNM-PM X90 SI NMR spectroscopy.

Tetramethylsilane (TMS) was employed as the internal standard. Melting points were determined on a Gallenkamp apparatus.
IV. Preparation

a) Synthesis of 4, 4’-Bis (1’-azo-4’-aminobenzene) biphenyl (I)

```
H2N—N=N
       |    |
       |    |
       |    |
       |    |
       |    |
       |    |NH2
```

Benzidine, 1.9 g (10 mmol) was dissolved in 8 ml of conc. hydrochloric acid and 90 ml water. The solution was cooled to 2 ºC, and then 5 ml of the sodium nitrite solution (1.5 g of sodium nitrite in 5 ml of water) was added dropwise, below 5 ºC. The reaction mixture was stirred for another 1 h at 5 ºC, and then was filtered. The filtrate was added dropwise to the aniline solution, (1.92 g, 20 mmol) aniline in 5 ml hydrochloric acid and 50 mL water. The solution was stirred for 1 h, and neutralized with a solution of sodium acetate, then kept overnight. The formed yellow azo product was filtered off, washed with water (3x), and then dried under vacuum at room temperature overnight. The product with molecular formula C24H20N6 and molecular weight (392.46) was obtained in 90% yield. It was characterized by 1H NMR, elemental analysis and IR as shown in Tables (1, 2, 3), respectively.

b) Polymerization of 4, 4’-bis (1’-azo-4’-aminobenzene) biphenyl (I) with various diacid chlorides

Polycondensation of 4, 4’-bis (1’-azo-4’-aminobenzene) biphenyl (I) with various diacid chlorides were carried out by two methods as follows:

```
N=N
   |    |
   |    |
   |    |
   |    |
   |    |
H-(HN)
```

Other solution polycondensation were carried out similarly. Scheme (2) shows the outlines of the reaction, and Table (4) show the quantities of the reactants involved. Polymers (III-VIII) were characterized by elemental analysis as shown in Table (2) and IR spectra as shown in Table (3). Polymer (VII) was also characterized by 1H NMR cf. Table (1).

c) Solution Polycondensation Method

Polycondensation of 4, 4’-bis (1’-azo-4’-aminobenzene) biphenyl (I) with various diacid chlorides was achieved by the reaction of the components in dry ethanol free chloroform. The following procedure using succinyl diacid chloride is typical.

For a cooled solution of 1.55 g (10 mmol) of the succinyl diacid chloride in 15 ml of dry ethanol free chloroform, 18 ml of TEA was added in a 100 mL round bottomed flask. The reaction mixture was stirred in an ice bath at -10 ºC for 15 min, then a solution of 3.92 g (10 mmol) of compound (I), in 25 ml dry ethanol free chloroform, was added dropwise with constant stirring. The reaction mixture was further stirred at -10 ºC for 30 min then for 48 h at room temperature .The chloroform layer was extracted with 0.1 M HCl (3X), 0.1 M NaOH (3X) and finally with water. The chloroform layer was dried over anhydrous MgSO4 overnight at room temperature. The MgSO4 was then filtered and the chloroform was evaporated on rotary evaporator and the product (II) was further dried under vacuum at room temperature overnight. The product was characterized by elemental analysis as shown in Table (2) and IR spectra as shown in Table (3). Polymer (VII) was also characterized by 1H NMR cf. Table (1).

d) Interfacial polycondensation method

Interfacial polycondensation of 4, 4’-bis (1’-azo-4’-aminobenzene) biphenyl (I) with various diacid chlorides was achieved by the reaction of the components in methylene chloride. The following procedure using succinyl diacid chloride is typical:

A solution of 3.92 g (10 mmol) of (I) in 45 mL water, 2 drops of pyridine and 13 mL dichloromethane was vigorously stirred. Then a solution of 2.31 g (10 mmol) of succinyl diacid chloride in 27 mL of dichloromethane was added with constant stirring for 10 min. Product (II) was collected by filtration using G4 sintered glass funnel, washed (3x) with dichloromethane, and dried under vacuum at room temperature overnight. Product (II) was characterized by elemental analysis as shown in Table (2) and IR spectra as shown in Table (3).

Other interfacial polycondensation were carried out similarly. Scheme (2) shows the outlines of the reaction and Table (4) shows the quantities of reactants involved. Polymers (III-VIII) were characterized by elemental analysis as shown in Table (2) and IR spectra as shown in Table (3).
Table 4: Reactant quantities of 4, 4-bis (1’-azo-4’-aminobenzene) biphenyl with various diacid chlorides melting point

<table>
<thead>
<tr>
<th>Monomer (mmol, g)</th>
<th>Diacid chloride</th>
<th>Diamine (mmol, g)</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Code</td>
</tr>
<tr>
<td>4, 4-bis (1’-azo-4’-aminobenzene) biphenyl (10 mmol, 3.29 g)</td>
<td>ClCO—(CH₂)₃—COCl</td>
<td>Sucinyl dichloride</td>
<td>(10 mmol, 1.55 g)</td>
</tr>
<tr>
<td></td>
<td>ClCO—(CH₂)₄—COCl</td>
<td>Adipyl dichloride</td>
<td>(10 mmol, 4.26 g)</td>
</tr>
<tr>
<td></td>
<td>ClCO(CH₂)₈COCl</td>
<td>Azel dichloride</td>
<td>(10 mmol, 1.8 g)</td>
</tr>
<tr>
<td></td>
<td>ClCO—(CH₂)₃—S—S—(CH₂)₃COCl</td>
<td>Dithiodipropyl dichloride</td>
<td>(10 mmol, 2.1 g)</td>
</tr>
<tr>
<td></td>
<td>ClOCC—(CH₂)₅—O—(CH₂CH₂CH₂CH₂O)n—(CH₂)₅—COCl</td>
<td>PTHF dipropyl dichloride</td>
<td>(10 mmol, 8.14 g)</td>
</tr>
<tr>
<td></td>
<td>ClOCC—(CH₂)₅—COCl</td>
<td>Terephthaloyl dichloride</td>
<td>(10 mmol, 2.1 g)</td>
</tr>
<tr>
<td></td>
<td>ClOCC—N=N—COCl</td>
<td>ABAC</td>
<td>(10 mmol, 3.71 g)</td>
</tr>
</tbody>
</table>
V. RESULTS AND DISCUSSION

a) Synthesis of 4, 4’-bis (1”-azo-4”-aminobenzene) biphenyl (I)

A procedure using sodium nitrite and sulphuric acid, and coupling of the diazoniun salt with aniline was done in moderately acidic medium at 0-5ºC, to give a yellow dye of 4, 4’-bis (1”-azo-4”-aminobenzene) biphenyl (I) as shown in Scheme (1). The azo dye (I) was in yield (90%), and its structure was confirmed by elemental analysis. The data as given in Table (2), it was in good agreement with the calculated values. IR spectrum of the dye (I) as in Table (3) showed the appearance of peak at 1517 cm⁻¹, 1453 cm⁻¹ for (-N=N-), at 1614 cm⁻¹ for (-NH₂) which confirmed the formation of the azo dye.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} = \text{N} \quad \text{N} = \text{N} \quad \text{N} = \text{N} \\ \text{H}_2\text{N} & \quad \text{N} = \text{N} \quad \text{N} = \text{N} \quad \text{N} = \text{N}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} = \text{N} \quad \text{N} = \text{N} \quad \text{N} = \text{N} \\ \text{H}_2\text{N} & \quad \text{N} = \text{N} \quad \text{N} = \text{N} \quad \text{N} = \text{N}
\end{align*}
\]

Scheme (1) : Synthetic route of 4, 4’-bis (1”-azo-4”-aminobenzene) biphenyl

b) Polymerization of 4, 4’-bis (1”-azo-4”-aminobenzene) biphenyl with various diacid chlorides

The polymerization 4, 4’-bis (1”-azo-4”-aminobenzene) biphenyl was carried out by two methods, the first is solution polycondensation in ethanol free chloroform, with the use of triethylamine (TEA) as an acid acceptor, and the second is the interfacial polycondensation in dichloromethane with the use of pyridine as an acid acceptor.

i. Solution polycondensation

Biodegradable azo-containing polyamides were prepared by solution polycondensation of azo monomer, 4, 4’-bis (1”-azo-4”-aminobenzene) biphenyl (I) with various diacid chlorides.

The solution polycondensation of the diacid chlorides was carried out using the quantities listed in Table (4). The amount of the diacid chloride was added to OH terminated azo monomer, 4, 4’-bis (1”-azo-4”-aminobenzene) biphenyl (I) in the presence of dry TEA as an acid acceptor to form the corresponding azopolyester. The reactions were conducted at low temperature then at room temperature under anhydrous condition as outlined in Scheme (3). Both polymer products were obtained in high yields.

The elemental analyses of the synthesized azopolyamides are in a good agreement with the calculated values as shown in Table (2), The IR spectra of the azopolymers as in Table (3) showed appearance of peaks at 1520-1526 cm⁻¹ and 1630-1774 cm⁻¹ for (C=O) in (CONH), at 3028-3052 cm⁻¹ and 3314-3426 cm⁻¹ for (N-H) in (CONH), and disappearance of peak at 701 cm⁻¹ for (C-Cl). The appearance of peak at 2924-2935 cm⁻¹ for (CH) αβ in samples (I-II-VII) confirmed the formation of azopolyamides.

The \(^1\)H NMR spectra for azopolyamide (VIII) was recorded in (\(d_6\)-DMSO) : δ = 7.0-8.0 ppm (m, 12 H, ArH), and δ = 6.5 ppm (s, H, NH₂) and δ = 10.1 ppm (s, H, NH₂) cf. Table (1).
**Scheme (2)**: Synthetic route of copolymer of 4, 4′-bis (1′-azo-4′-aminobenzene) biphenyl with various diacid chlorides

<table>
<thead>
<tr>
<th>Azo polymer</th>
<th>Diacid chloride</th>
<th>(-R-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>Succinyl dichloride</td>
<td>(-(CH_2)_2-)</td>
</tr>
<tr>
<td>III</td>
<td>Adipyl dichloride</td>
<td>(-(CH_2)_4-)</td>
</tr>
<tr>
<td>IV</td>
<td>Azeil dichloride</td>
<td>(-(CH_2)_8-)</td>
</tr>
<tr>
<td>V</td>
<td>Dithiodipropyl dichloride</td>
<td>((CH_2)_3-S-S-(CH_3)_3-)</td>
</tr>
<tr>
<td>VI</td>
<td>PTHF dipropyl dichloride</td>
<td>((CH_2)_3-O-(CH_2CH_2CH_2CH_2O)_n-(CH_2)_3-)</td>
</tr>
<tr>
<td>VII</td>
<td>Terephthaloyl chloride</td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>ABAC</td>
<td></td>
</tr>
</tbody>
</table>

**ii. Interfacial polycondensation**

Interfacial polycondensation of 4′-bis (1′-azo-4′-aminobenzene) biphenyl (I) with various diamines were carried out by a solution of the diacid chloride in dry methylene chloride according to the quantities of the reactants used listed in Table (4) was added to 4′-bis (1′-azo-4′-aminobenzene) biphenyl (I) in (water-methylene chloride) mixture in the presence of pyridine as acid acceptor as shown in Scheme (2). This method is faster than solution polycondensation, but with low yield as a result of hydrolysis apart of azobenzene diacid chloride. The quantities of the reactants used are as listed in Table (4) and the reaction scheme is as outlined in Scheme (3).

The elemental analysis and the IR spectra of the synthesized azopolyamides from interfacial polycondensation were similar to the azopolyamides synthesized from solution polycondensation.

**Table 1**: \(^1\text{H NMR. shifts in ppm for azo dye (I) and polymers (VIII)}\)

<table>
<thead>
<tr>
<th>Groups</th>
<th>Compound</th>
<th>NH</th>
<th>NH2</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6.5-8 (m)</td>
<td>6.2 (s)</td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>7-8 (m)</td>
<td>10.1 (s)</td>
<td>6.5 (s)</td>
</tr>
</tbody>
</table>

* s. singlet  m: multiplet  
* Appearance of two peaks at \(\delta=2.4\) for DMSO and \(\delta=3.5\) for water

**Table 2**: Elemental analyses of azodyes and its copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Calc.</td>
<td>73.46</td>
<td>Found</td>
</tr>
<tr>
<td>II</td>
<td>66.01</td>
<td>5.10</td>
<td>4.45</td>
</tr>
<tr>
<td>III</td>
<td>71.70</td>
<td>63.74</td>
<td>5.20</td>
</tr>
<tr>
<td>IV</td>
<td>72.66</td>
<td>67.92</td>
<td>6.05</td>
</tr>
</tbody>
</table>
iii. Microbial degradation of the azo polymers

The degradation of azopolyamide by tested fungal species as Aspergillus, Candida albicans, Escherichia coli, Pleurotus ostreatus and Ganoderma resencium vs the incubation time was study. It can be seen that, after an initial latency phase, the concentration of azo compounds decreases linearly as a function of the incubation time, indicating that the azo reduction is a zero-order phenomenon [16].

Moreover, the linearity of the degradation was confirmed by studying the influence of the dye concentration on the degradation rate (data not shown). No change of the degradation rate could be observed when the initial concentration of azo polymer was doubled.

To our knowledge, almost little or no work has been done concerning the biodegradation of azo dyes by fungi. Present study revealed that all tested microorganisms could degrade poly azo benzene diamino-Azelic dichloride as indicated by measuring the absorbance at wave length 332 nm. The maximum biodegradation percentage was obtained by A. fumigatus (97%), and the minimum was achieved with E. coli (91%) at wave length 328 nm. However, A. flavus was degraded 89% of used poly azo benzene diamino-Azelic dichloride as indicated with measuring absorption at 230 nm. Furthermore, A. flavus was also performed the highest degradation percentage for poly azo benzene diamino-co-Azelic dichloride (96%) at both measured wave length (332 and 228 nm). E. coli didn’t produced any absorbance change at either at 332 nm in case of poly azo benzene diamino-co-PTHF dipropyl dichloride or at 228 nm in case of poly azo benzene diamino-co-Azelic dichloride indicating that the degradation of these polymers might with a mechanism different from that of fungi. Actually, the process of azo polymers degradation isn’t easy. Bacteria or fungi are unable to oxidized azo dyes readily due to the azo linkage which doesn’t occur in nature [17]. On the other hand, it has been found that aerobic bacteria can degrade aromatic amines. Therefore, non-enzymatic reduction of azo dyes to amines could facilitate further degradation by bacteria. It has been demonstrated that two pseudomonas strains completely degrade 6-aminonaphthalene-2-sulfonic acid [18].

Degradation of poly azo benzene diamino-co-PTHF dipropyl dichloride and poly azo benzene diamino-co-Azelic dichloride as azopolymer by microorganisms has demonstrated that Aspergillus fungi have produced the highest value, followed with yeast (C. albicans.), and then E. coli as bacterial organism. However, G. resencium and P. ostreatus as a model organism of basidiomycete fungi came in the last rank.

There is extensive informations available on biodegradation of polymers by hydrolysis; although little is known about azo polymers. There is no reliable

---

**Table 3**: I. R. analysis of azodyes and its copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>-NH₂</th>
<th>1,4 Disubstitued benzene</th>
<th>O=N=N-O=N=C-NH</th>
<th>(CH)alpe</th>
<th>N=CH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C=O</td>
<td>-N-H</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>1614</td>
<td>697</td>
<td>1453, 1517</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>II</td>
<td>—</td>
<td>821</td>
<td>1443, 1553</td>
<td>1630, 1520</td>
<td>3052, 3423</td>
</tr>
<tr>
<td>III</td>
<td>—</td>
<td>759</td>
<td>1452, 1592</td>
<td>1664, 1520</td>
<td>3088, 3402</td>
</tr>
<tr>
<td>IV</td>
<td>—</td>
<td>758</td>
<td>1406, 1595</td>
<td>1664, 1526</td>
<td>3040, 3314</td>
</tr>
<tr>
<td>*V</td>
<td>—</td>
<td>808</td>
<td>1434, 1565</td>
<td>1727, 1520</td>
<td>3424</td>
</tr>
<tr>
<td>*VI</td>
<td>—</td>
<td>756</td>
<td>1408, 1486</td>
<td>1732, 1519</td>
<td>3023, 3444</td>
</tr>
<tr>
<td>VII</td>
<td>—</td>
<td>759</td>
<td>1441, 1596</td>
<td>1774, 1520</td>
<td>3421</td>
</tr>
<tr>
<td>VIII</td>
<td>—</td>
<td>761</td>
<td>1489, 1599</td>
<td>1677, 1520</td>
<td>3037, 3426</td>
</tr>
</tbody>
</table>

* measured in solution state in chloroform.
Synthesis, Characterization and Biodegradation of Some Polymeric Azo Compound

evidence to suggest that the insoluble azopolymers degradable through azo reduction by biological systems. In spite of the ability of many bacteria and mammalian cells to cleave the azo bonds in low molecular weight azo compound and water soluble high-molecular weight polymeric derivatives of certain azo dyes has been demonstrated.[19]

Current data indicated that the degradation of poly azo benzene diamino-PTHF dipropyl dichloride and poly azo benzene diamino-Azelic dichloride, with different tested microorganisms produced different values of degradation rate constant (Azo Reductase Activity), which varied from organism to other. The highest rate constant of poly azo benzene diamino-Azelic dichloride degradation was obtained by A. niger which produced 5.5±0.115 µmol/ml/h at 230 nm, however A. ochraceous performed 0.84±0.12 µmol/ml/h. degradation constant increase of poly azo benzene diamino-PTHF dipropyl dichloride at 328 nm. The highest poly azo benzene diamino-Azelic dichloride degradation rate constant (µmol/ml/h) was obtained by A. fumigatus which preformed 5.71±0.23 µmol/ml/h at 228 nm; however A. ochraceous produced the lowest poly azo benzene diamino-Azelic dichloride degradation rate constant of 0.94±0.72 µmol/ml/h at 332 nm.

We anticipate that the azo polymers degradation process occurs exactly if the azo reductase was able to distinguish between the azodyes present concurrently in the medium according to their redox potential as also listed by [19]. Surprisingly, P. ostreatus and G. resencium have preformed the highest rate constant for degradation of poly azo benzene diamino-Azelic dichloride which produced 10.43±0.21 and 8.55±0.16 µmol/ml/h at 330 nm and Pleurotus ostreatus (edible mushroom) was preformed a high rate of degradation constant more than Ganoderma resencium with two synthesized polymers as shown.

Since the discovery of the activation mechanism of sulphasalazin into 5-amino salicylic acid by the intestinal microflora. Until now, there is insufficient understanding of azo reduction mechanism and the difficulty in obtaining successful colonic delivery system to protect a drug from mouth to caecum and to afford its site- specificity are obstacles[19]. From results it appears that no relationship could be established between the structure of azopolymers and degradation rate constant value (K). The degradation process occurs exactly as if the azo reductase were able to distinguish between the azopolymers present in the medium.

We believe that adding one of the safe microorganisms used in this study to the drug coated or supplied or supplied with the azopolymer will performed hydrolysis or degradation to the polymer and hence liberate the drug.

Figure 1: Degradation percent for poly azo benzene diamino-PTHF dipropyl dichloride (VI) against different microorganisms

Figure 2: Degradation percent for poly azo benzene diamino-Azelic chloride (IV) against different microorganisms
Synthesis, Characterization and Biodegradation of Some Polymeric Azo Compound

VI. Conclusion

Azo dye polymer compounds have been synthesized from 4, 4'-Bis (1'-azo-4'-aminobenzene) biphenyl with diacid chloride. The azo dyes were investigated by elemental analysis, infrared spectroscopic, H¹NMR spectroscopic and absorption spectrum are used to prove the structure of azodye and its polymers. The UV-visible spectroscopic studies shows that the novel azo dye polymer compound has high degradation rate by treatment with different organisms.

REFERENCES Références Referencias

5. Towns A D , Dyes pigments,1999, 42.3.
Synthesis, Characterization and Biodegradation of Some Polymeric Azo Compound