Article

Ester polymers Synthesized by Azo dye

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Abstract

The current study included the preparation of azo compound (A4) from the aromatic amine reactant (2-aminobenzoate methyl) by the nitrification method and conjugation with pharmaceutical phenolic compounds (pyridoxine hydrochloride, ortho-vanillin, para-vanillin, and kojic acid). Then, the compound (A4) was converted into new ester polymers. By reacting it with succinic acid and apic acid. All compounds and polymers were then characterized by IR, UV-Vis, mass spectrometry and 1H NMR spectroscopy. The effect of pH was studied in the electronic absorption spectra of azo compounds (A_4) in the visible region, in a range of wavelengths (470) nm, using different buffer solutions with different pH values.

Keywords: Azo Compound, ester polymers, IR, UV-Vis, mass spectrometry and 1H NMR spectroscopy.

Introduction

A vast class of industrial organic dyes having nitrogen in the form of azo (N=N) groups inside their molecular structure, with the generic formula RN=NR, are referred to as azo compounds or dyes. 3 -Auxochromoe, often known as color-deepening groups, are acidic, basic, or neutral groups that are present in aromatic [1] rings like (-NH_2, -COOH, -OH, -SO_3H). Based on the type of rings bonded to either end of the bridge azo group homogenous ring, azo compounds are categorised: The interlocking azo group in this title is linked between two unified rings without a hybrid atom [2] like (S, N, or O), and these rings are connected to an acid on either one or both of the rings.Auxochromoe, often known as color-deepening groups, are acidic, basic, or neutral groups that are present in aromatic [1] rings like (-NH_2, -COOH, -OH, -SO_3H).

It is categorised as heterocyclic: Because it comprises heterocyclic rings, which frequently contain hybrid atoms like nitrogen, oxygen, or sulphur, as well as other compounds like imidazole, thiazole, pyrimidine, and pyridine, this type of chemical is very important in many domains [3]. These had Researchers working in the domains of analytical chemistry, inorganic chemistry, and biology are particularly interested in the compounds, as mentioned below.

The presence of nitrogen atoms in the heterocyclic ring, which is thought to be the result of isomerization with metal ions and the creation of complexes, distinguishes heterocyclic compounds from other types of compounds. According to the cross-linked azo group, where the nitrogen atom occupies the ortho position, the creation of stable complexes is made possible by non-covalent electron duplexing on the nitrogen atom [4,5]. The presence of nitrogen atoms in the heterocyclic ring, which is thought to be the result of isomerization with metal ions and the creation of complexes, distinguishes heterocyclic compounds from other types of compounds. The creation of stable complexes is facilitated by non-covalent electron duplexing on the nitrogen atom in the cross-linked azo group, where the nitrogen atom occupies the ortho position.

In general, complexes with pentameric or hexagonal rings are thought to be the most stable [6]. The formation of the five- or six-ring chelate, which increases the stability of the produced compound, is facilitated by the presence of certain compensatory aggregates, such as acidic protons, on the aromatic ring.[7]. It is also divided into groups that are attached to the azo group's two ends and the aliphatic group, where two aliphatic groups are joined by two nitrogen atoms (- N = N -) and are utilised with low diffusion and quick stability of nitrogen and hydrocarbons [8]. It is also divided into groups that are attached to the azo group's two ends and the aliphatic group, where two aliphatic groups are joined by two nitrogen atoms (- N = N -) and are utilised with low diffusion and quick stability of nitrogen and hydrocarbons [9]. We are also classified into mono- and binary based on the number of azo groups present, and tri-azo groups: which are compounds containing 3 azo- groups Polyazo: These compounds contain 4 or more [10,11] groups. Azo compounds can be used in many applications, especially in the field of analytical chemistry in the quantitative and qualitative estimation of metal ions (because of their stability and speed of interaction with metal ions [12]. Azo compounds are therapeutic substances in pharmaceutical preparations in addition to being effective bacterial and fungal inhibitors. There are many azo compounds that have biological activity and have been used as important drugs because of their bactericidal inhibitory role [13].

(NR_2 or COOH) are c groupings. Azo compounds were used as acid-base indicators with strong, clear colours that differ depending on their structure, making them more sensitive to acids and bases because they contain oxochrome groups. These groups produce negative ions in the basic medium (ionization) and positive ions in the anaerobic environment. If they contain basic groups (NR_2 or COOH), they are nevertheless referred to as acidic azo compounds because these groups are acidic (OH, SO_3H, or COOH). As these groups produce negative ions in a basic medium (ionisation) and positive ions in an acidic medium (protonation), NRH or NH_2 are referred to as basic azo compounds

The negative, positive, and neutral forms give a specific color and a certain maximum absorbance in the ultraviolet and visible spectra, and this property is benefited from. In determining the end point of the reaction in the tests (acid - basic), and thus the result of the quantitative estimation of the acid or base depends on the choice of evidence [14]. For a variety of uses, functional polymers are produced in large quantities. Azo polymers are among the most significant of these polymers. The polymer structure contains unique chemical, physical, and biological properties due to the presence of azo=N-N functional groups. Azo polymers have gained popularity as materials since the 1960s and have numerous uses.For a variety of uses, functional polymers are produced in large quantities. Azo polymers are among the most significant of these polymers. The polymer structure contains unique chemical, physical, and biological properties due to the presence of Azo=N-N functional groups. Azo polymers have gained popularity as materials since the 1960s and have numerous uses. [15,16].

Materials and methods

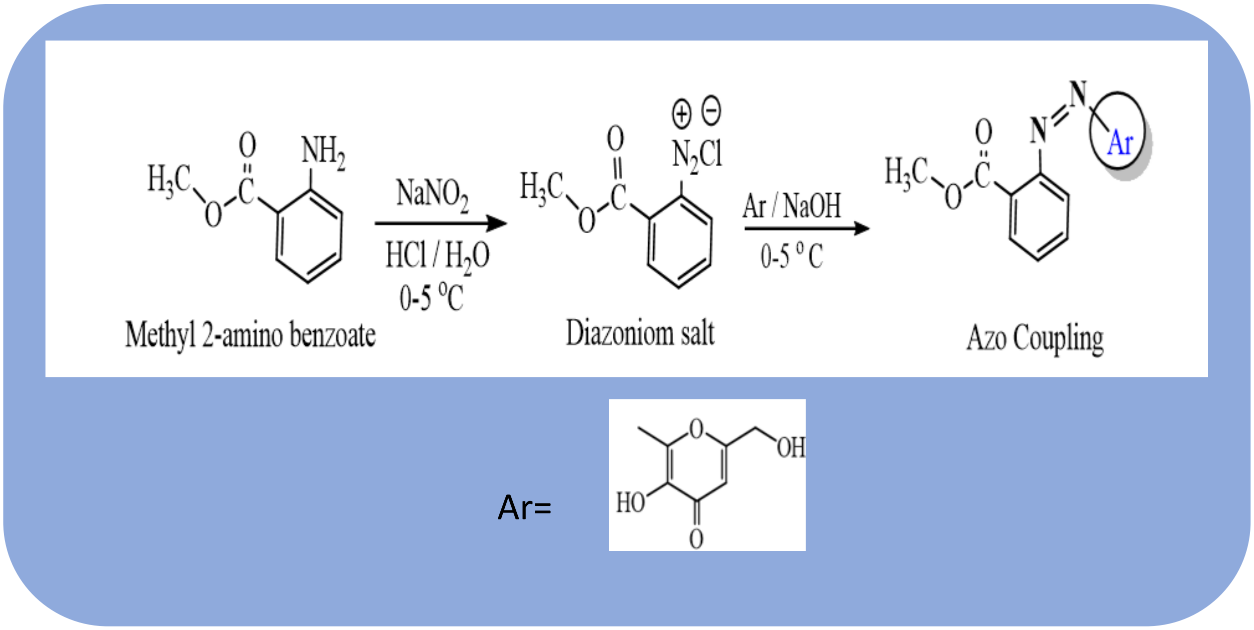
The solvents used of high purity from Aldrich and Merck companies. Infrared spectra were recorded as KBr discs using a SHIMADZU FT-IR-8400S. Melting points of compounds were established by a thermo Scientific (9100). Visible spectra measured by JENWAY 6305 Spectrophotometer. Mass spectra were recorded by EI Technique using Agilent Technologies. The pH measurements were made with pH-Meter (H. Jurgons Co. Bremen,L.Puls Munchen).

Preparation of azo compound

Azo compound derived from the aromatic amine (2-aminobenzoatemethyl) were prepared by the approved method. [17] by taking 0.006 mole of each ethyl-4-amino benzoate and pyridoxine hydrochloride or ventolin in 1.8 % w/v. NaOH.

By the aid of IR and mass spectra, the suggested molecular structures of azo compounds were

shown in Scheme -1.



Scheme -1. Preparation of azo compound

Results and discussion

Infrared spectra of azo compound(A4)

The infrared spectra of azo compound(A4) which is derived from the aromatic amine (2-aminobenzomethyl) showed important absorption bands for this compound, and Figures (1) shows the infrared spectra of (A4) within the range Spectrophotometer (4000-400) cm^{-1}.

The amplitude oscillation band of the alcoholic (O-H) group appears in the spectrum at (3360) cm^{-1},. Either the phenolic (O-H) group appears clearly in all of these spectra within the spectral range (3250) cm^{-1}. It is in the form of a broad band. In the spectrum of compound, it appears in the form of a broad band that overlaps with groups that oscillate within nearby regions, such as the amplitude oscillation band of the alcoholic (O-H) group. The aliphatic C-H band appears in the spectra of this compound within the spectral range (3176-2837) cm^{-1}. We clearly notice the amplitude oscillation band of carbonyl groups (C=O) in spectra of compound(A4) within the spectral range (1747-1687) cm^{-1}[18]. Overlapping with this band are the amplitude oscillation bands of (C=O) groups in the carboxylic acid in the spectra of compound (A4) . The amplitude oscillation bands of the bond (C=C) of the aromatic structure also appear within the spectral range (1622-1585) cm^{-1}.

As for the azo band (N=N), the azo group appeared distinctly within the spectral range (1454-1433) cm^{-1}[19] in the infrared spectra of (A4). Table (1) shows the locations of the most important beam oscillations appearing in these spectra.

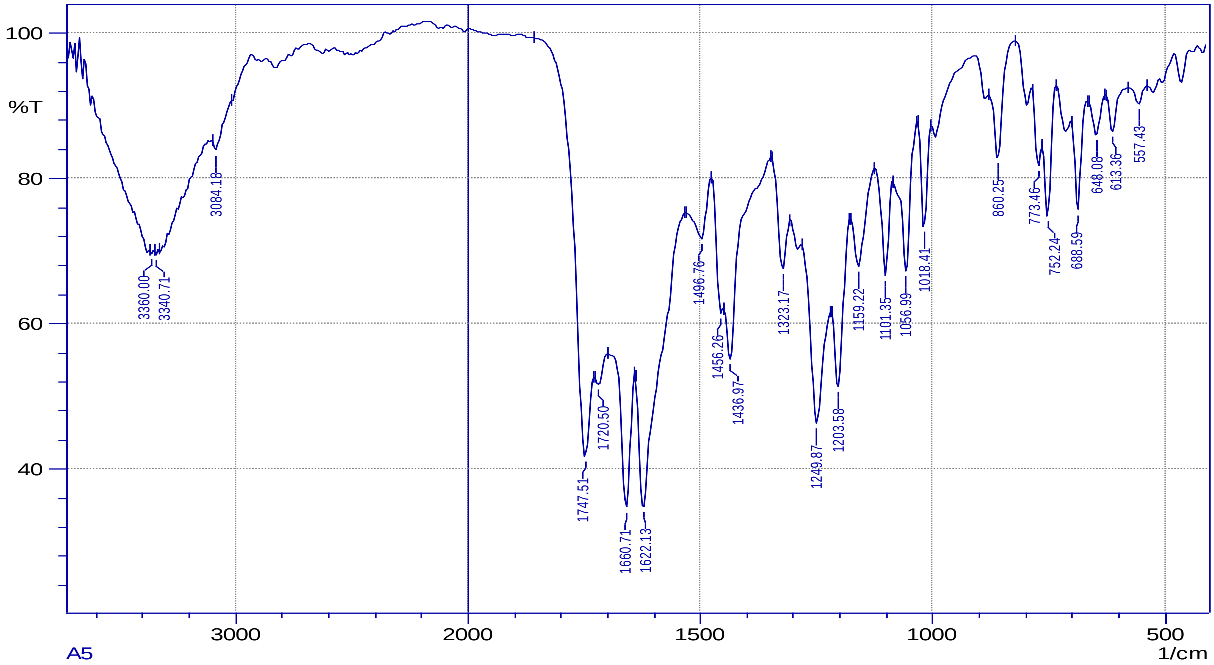


Figure. 1: IR spectrum of Azo compound(A4)

Table1. 1: IR spectrum of Azo compound(A4)

1101	1203	1249	1448	1622	1747	3360	
M	M	m	M	m	M	br	
w = weak , m = medium , s = strong , br = broad							

Mass spectra of azo compound(A4)

The mass spectra of the azo compound (A4) were characterized by the appearance of the molecular ion peak [M^+] at (m/z) consistent with the molecular weight and their proposed formulas, as in Figures (2).

It is noted in mass spectra of azo compound (A4) that the ion appears at m/z = 136) and is due to the amine part in these compounds, which is the result of fragmentation from breaking the bond between the nitrogen belonging to the azo group (N=N) and the aromatic ring containing the azo group. (CO-O). It is also noted in the mass spectrum of the compound (A4) that the base ion peak appears at locations at m/z = 77. Figure(2) shows the most important fragment ions, molecular ions, and basic ions in the mass spectra of azo compound (A4) .

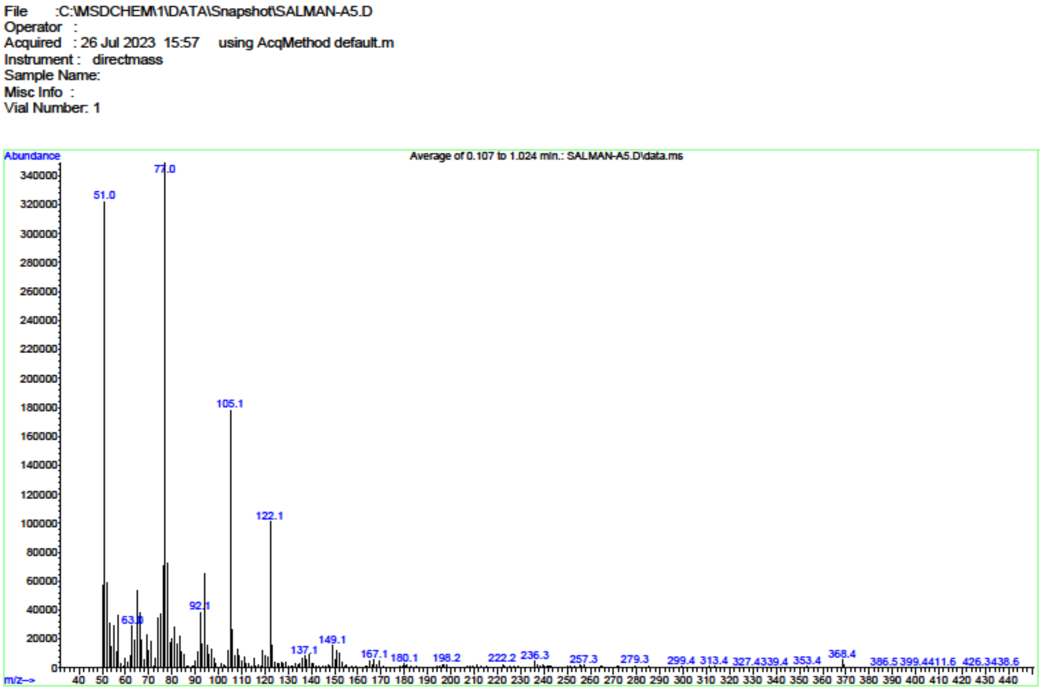


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Figure. 2 : Mass spectra of azo compound.

The effect of pH on the visible absorption spectra of azo compound(A4)

The absorption spectra of the visible region of the azo compound (A4) was measured using a range of wavelengths (320-570) nm with a range of acid functions (12-2) through the combined buffer solution. Figure (3) is shown the absorption spectra of azo compound in buffer solutions with different pH levels. The spectra of this compound were characterized by the presence of two absorption peaks. The first peak was due to the transformation of the compound molecule into the positive form (acid form), which is sulfonated and expected to be present in acidic solutions, and the second peak was due to the absorption of the ionized compound and was expected to be present in basic solutions [20].

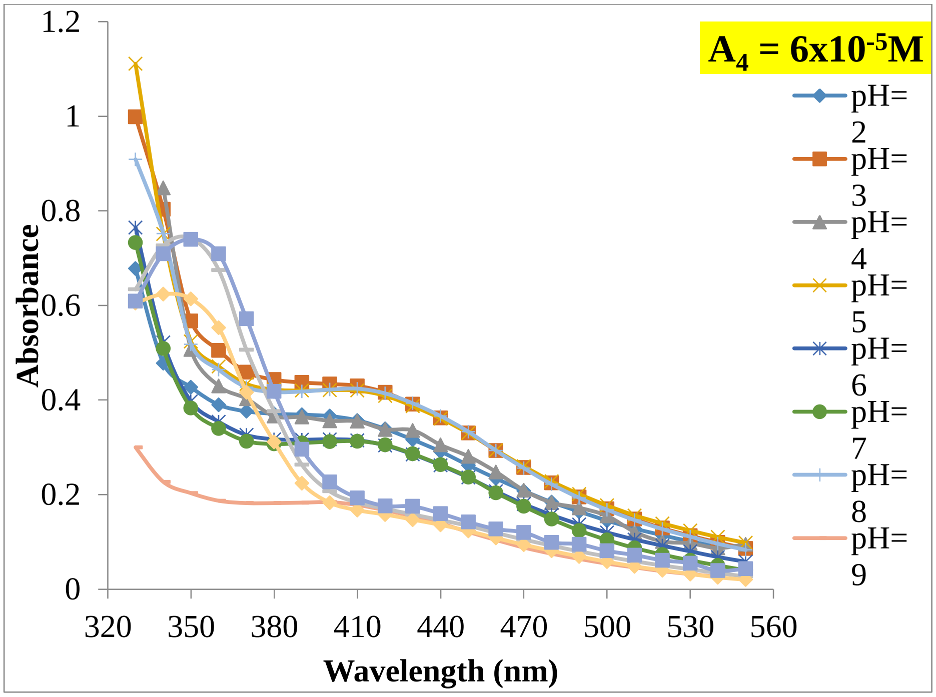


Figure. 3: Absorption spectra of azo compound at different pH values

Calculating ionization and protonation constants

Data gathered by examining the impact of acid function on visible absorption spectra was used to calculate the ionisation and protonation constants for azo compounds. In this case, the mid-height curve approach was applied. A line was then drawn connecting the values of the acid function with the associated absorption at the selected wavelength, which was the wavelength at which the divergence between the spectra became apparent. scheme (2) depicts the curve of the acid function (pH) vs absorption for the substances.

We determine the value of the lowest absorption (Amin), A1/2 (the function of the average absorption), and the highest absorption (AL), which represents the complete conversion of one form of the azo compound to the other [21,22]. At this pH level, both forms of the azo compound are present in equal amounts.

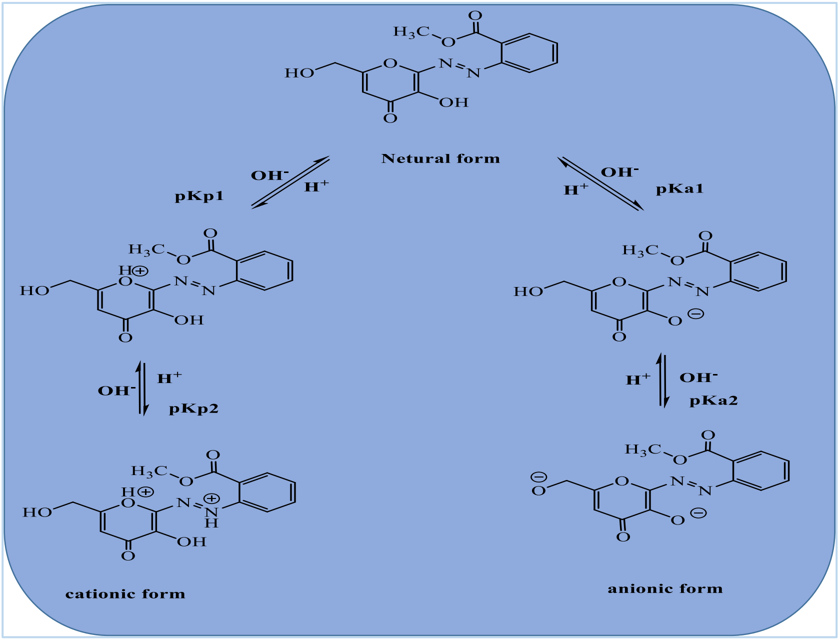
$$\mathbf{A_{1/2} = (A_L + A_{min})/2}$$

From the pH value corresponding to A1/2, the pK values are determined as in the following equation

$$\mathbf{pK=pH\ (at\ A_{1/2})}$$

Table 2: Values of ionization and protonation constants for azo compound (A4)

pK_{a2}	$A_{1/2}$	pK_{a1}	$A_{1/2}$	pk_{P2}	$A_{1/2}$	pk_{P1}	$A_{1/2}$	Λnm	Azo compound
11<	----	7.5	0.36	4.5	0.37	2.5	0.39	420	A_4



Scheme -2: Suggested mechanism of protonation and ionization of azo compound

Applications of the prepared Azo compound (A4)

Polymers derived from the azo compound(A4). The prepared polymers (p1 and p2) derived from the azo compound were characterized by the approved spectroscopic methods, which are: -

Infrared spectra of polymers

The polymers were characterized by infrared spectroscopy in the range (4000-400) cm^{-1}. Figures (4) and (5) show the infrared absorption spectrum of polymers (p1 and p2), respectively. In the infrared spectrum of polymers, we notice the disappearance of the amplitude vibration bands of the alcoholic and phenolic (O-H) bonds, which indicates the participation of these groups in the binding and formation of the studied polymers.

The spectrum of these polymers shows the appearance of the aliphatic (O-H) vibration bands of the carboxylic (O-H) bond in the carboxylic acid part, overlapping with the bands in the nearby regions, such as the aliphatic (C-H) band at (3061 and 3302) cm^{-1} for the polymers (p1 and p2), respectively.

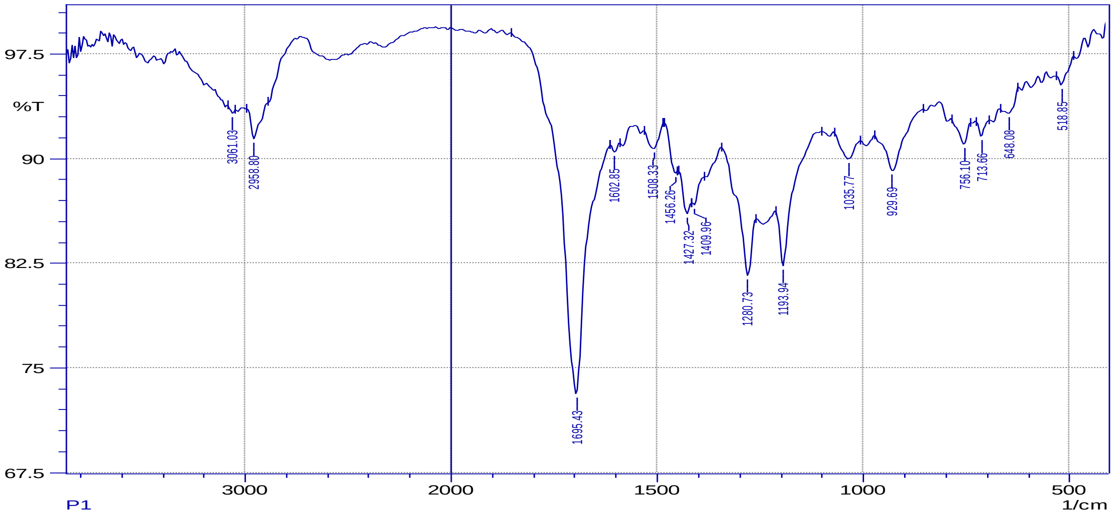


Figure .4: The infrared spectrum of compound p1

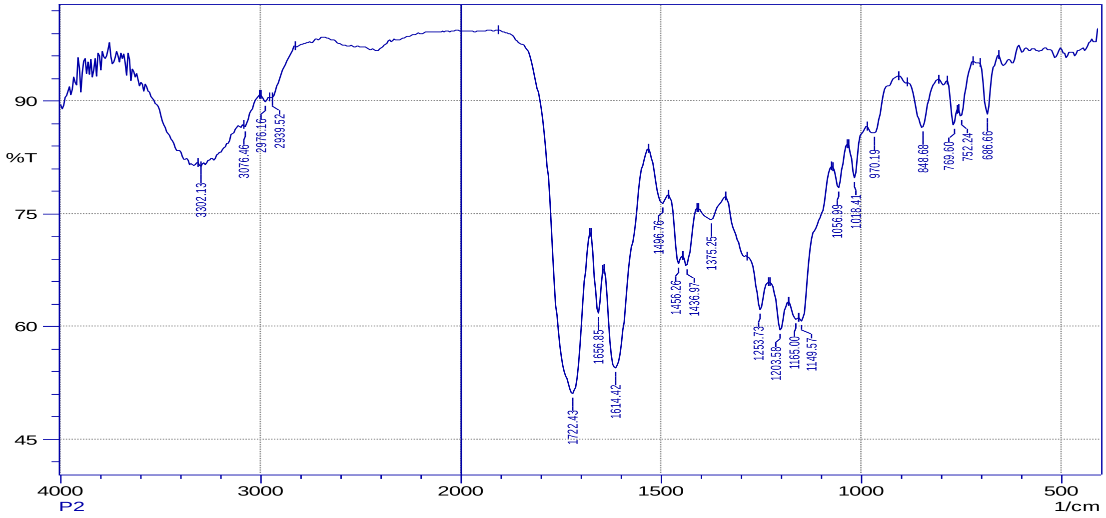


Figure 5: Infrared spectrum of compound p2

^{1}H NMR spectroscopy of polymers

The ^{1}H NMR spectrum of the two compounds (p1 and p2) is characterized by the appearance of a single signal that belongs to the proton of the unreacted phenolic O-H group forming hydrogen bonds, so it appears broad with a chemical shift of 12.5 ppm)δ. Multiple signals appear in the spectrum with a chemical shift in the range of 8.4-6.2 ppm)δ, which belong to the protons of the aromatic rings [9]. We also notice the protons of the (CH_2) group between 4.2-2.3. We notice the protons of the (CH_3) group attached to the aromatic ring (Ar- CH_3) appears as a single signal with a chemical shift ppm(4.2-2.3)δ. Either the single signal due to the protons of the (CH_3) group in the aliphatic chain appears in the form of a single signal with a chemical shift ppm(1.4)δ. As shown in Figures (6) and (7) for the compounds (p1 and p2), respectively, and Table 3.

Table 3: Chemical shifts in the H NMR spectrum for polymers (p1 and p2)

δ(ppm)	Compounds
12.5(s,1H,OH), 8.1-7.52(m,14,H,Ar-H), 4.2-2.3(T,CH_2), 2.2(s,3H, Ar-CH_3), 1.4(s,3H,CH_3)	p_1
8.4-6.2(m,14,H,Ar-H), 4.2-2.3(T,CH_2), 2.2(s,3H, Ar-CH_3), 1.5(s,3H,CH_3)	P_2
s = singlet, d = douplet, t = triplet, q = quartet	

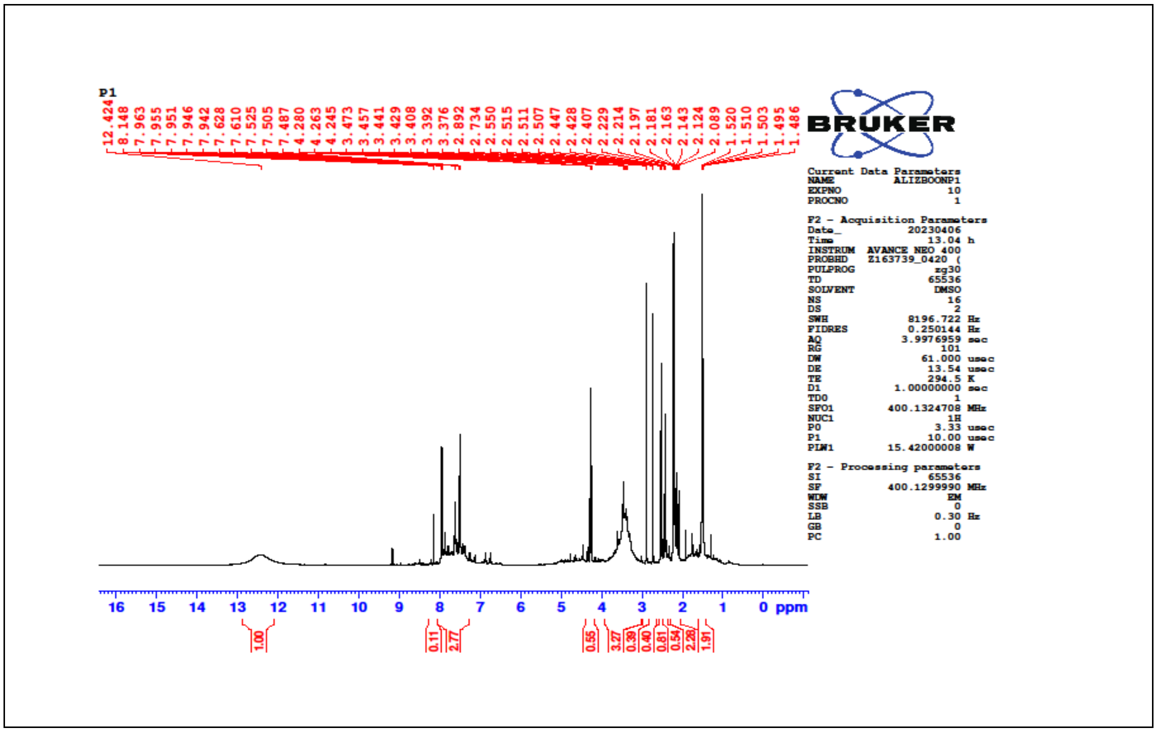


Figure (6): ^{1}H NMR spectrum of compound p1

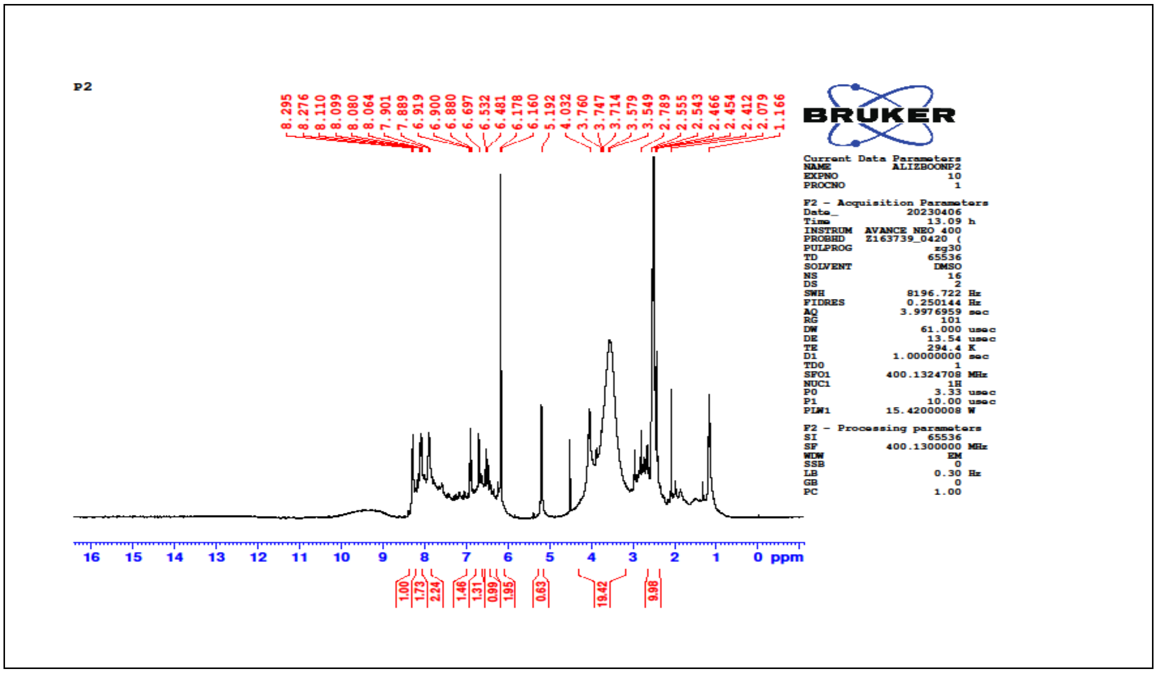


Figure (7): ^{1}H NMR spectrum of compound p2

Thermal analysis of polymers (P1 and P2)

Thermogravimetric analysis is a distinct technique used to study thermal behavior and to verify the proportions of organic and inorganic components in ligands. In order to determine the thermal stability of azo polymers, thermogravimetric analysis (TGA) was performed under a N2 atmosphere in the temperature range (40-550) °C. A general decomposition was obtained, as the azo polymers were in two steps. The TGA curve for compound p1 shows two stages of mass losses at temperatures ranging from 128 to 549 °C. These phases have mass losses of about 56.6% over certain temperature ranges. The first stage occurs with a weight loss of 53.60% in the temperature range (128-412) degrees Celsius. This is likely due to thermal decomposition, eliminating the nitrogen and benzene atoms and breaking the azo bond. The second stage, in the temperature range (467.963-549) °C, was observed with a mass loss of 2.99%, which corresponds to the elimination of organic residues. The remaining 43.4% of the material shows that the polymer has good resistance to thermal decomposition.

The TGA curve for compound p2 shows a stage of mass loss at temperatures ranging from 253 to 454 degrees Celsius. The first stage occurs with a 49.5% weight loss in the temperature range of 235-454°C. This is likely due to thermal decomposition, eliminating the nitrogen and benzene atoms, and breaking the azo bond. The remaining 50.5% of the material shows that the polymer has good resistance to thermal decomposition. As shown in Figures (8) and (9) for components (p1 and .p2), respectively

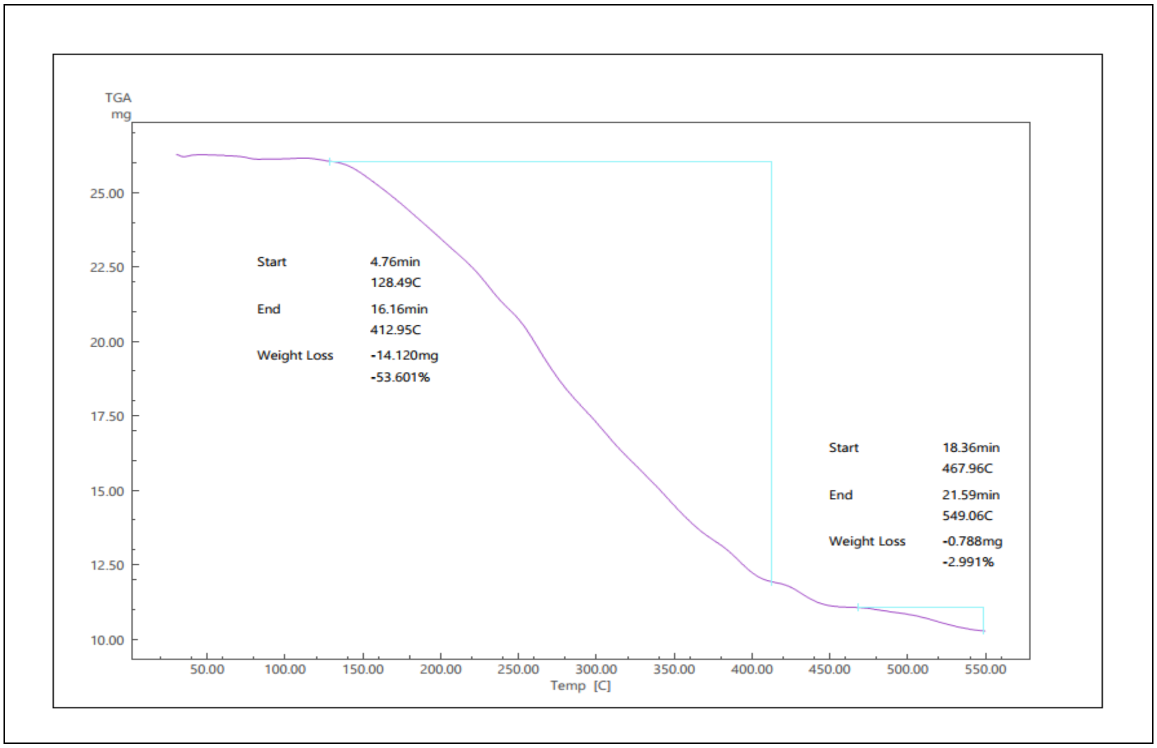


Figure (8): Thermal analysis curve for compound p1

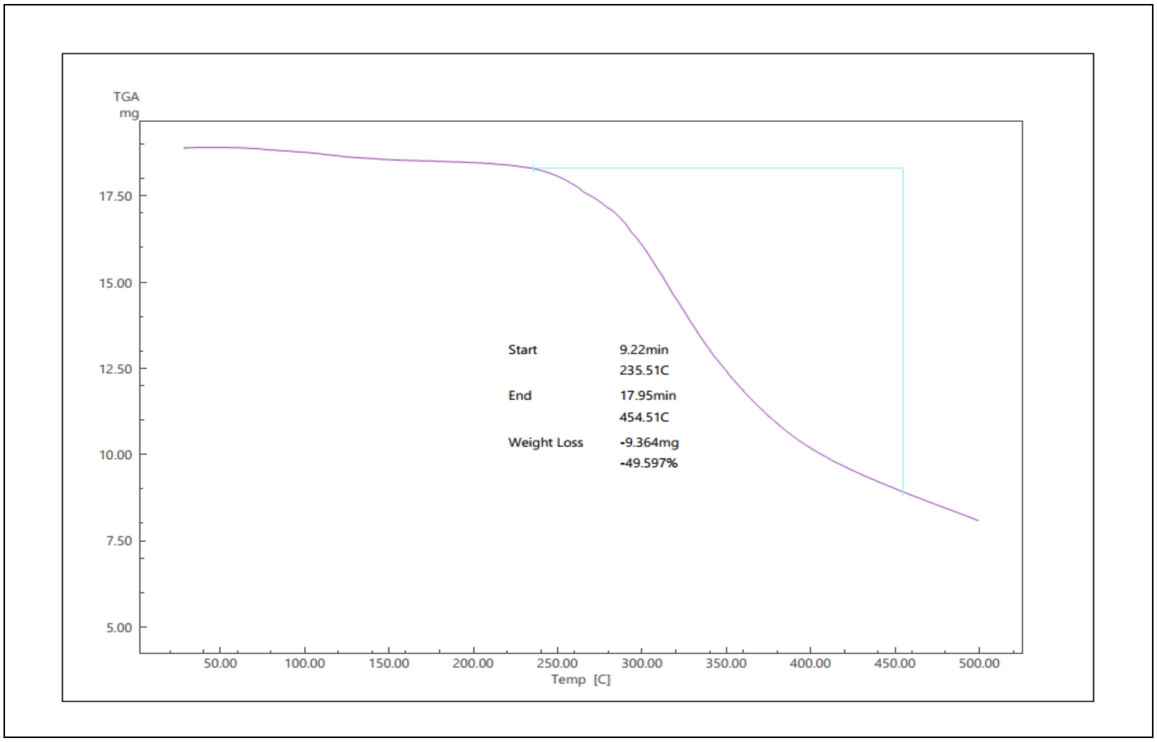


Figure (9): Thermal analysis curve for compound p2

Conclusion

The current study included the preparation of azo compound (A4) from the aromatic amine reactant (2-aminobenzoate methyl) by the nitrification method and conjugation with pharmaceutical phenolic compounds (pyridoxine hydrochloride, ortho-vanillin, para-vanillin, and kojic acid). Then, the compound (A4) was converted into new ester polymers. By reacting it with succinic acid and adipic acid. All compounds and polymers were then characterized by IR, UV-Vis, mass spectrometry and ^{1}H NMR spectroscopy. The results of the study of thermogravimetric analysis of polymers showed the extent to which these polymers are stable and can withstand high temperatures, and this is very important from a usage perspective. The results of the study of thermogravimetric analysis of polymers showed the extent to which these polymers are stable and can withstand high temperatures, and this is very important from a usage perspective.

References

[1] S. Benkhaya, S. M'rabet and A. El Harfi, Classifications, properties, recent synthesis and applications of azo dyes. Heliyon. **6**,1 , (2020).

[2] M. A. Juma, A. G. Sager, *J. Anbar for pure scince.*, **7**, 75, (2013).

[3] H. Alzain etal., International Journal of Research and Review. 10, 6, (2023)

[4] H. K. Ebraheem, M. Sc. These, Basrah University , Iraq, (2010).

[5] B.R. Kirthan etal., Chemical Data Collections, 29, 100506, (2020).

[6] A. S. Abdul-Nabi and E. Q. Jasim, *J. Res. Sci.*, **39**, 3, (2013).

[7] A. S. Abdul-Nabi and A. A. Hussain, *J. Res. Sci.*, **38**, 1.A, (2012).

[8] F.Carey,***"Organic Chemistry"***,Inc. 3rd ed., USA, P.935(1996).

[9] R.T.Morrison and R.N.Boyd**,*"Organic Chemistry"***, 3rd, Allyn and Bacon, Inc, Boston, p.765, 772 and 773(1973).

[10] G.K.R Senadeera andK.J.Jiang ;***Sir Lankan J.Phys***., **6** ,.43 -50 (2005).

[11] H.Valizadeh,M.Amiri,A.Shomali and F.Hossein Zadeh; ***J.Iran. Chem. Soc***., **8**,(2),

[12] E. Bagda, *Emviron Techn* , **35**, 9, p.1164-1174, (2014).

[13] S. Bondock, A. Gaber and A. Tudda, *ARKIVOC*, p.113-156, (2006).

[14] R. S. Sherate and T. Prakash, *Amer. J. Env. Sci.*,**10**, 15, p.489-499, (2014).

[15] Y. Etal, *Inorg. Chem. Act*., **35**, p.3934, (2006).

[16] F. Eltaboni, N. Bader, R. El-Kailany, N. Elsharif and A. Ahmida., J. Chem. Rev., 2022, 4(4), 313-330.

[17] H. A. Abdullmajed, A. A. Ali and R. H. AL-Asadi, *J. of Kufa for Ch. Sc*., **2**, 7, (2021).

[18] O. H. Shehab and A.AL-Ali, *N. Jou. of Chem.*, **28**, p.687-694, (2007).

[19] E. Elemike, H. U. Nwankwo and D. C. Onwudiwe, *J. of Mol. Str.*, p.253-262, (2017).

[20] A. A. Ali and Kh. H. Montha, *J. of Thi-Qar Sci.*, **4**, p.83-89, (2014).

[21] T. A. Fahad, A. A. Ali and A. H. Baty, *World J. of Pharmaceutical Res.*, **8**, 2, p.707-715, (2019).

[22] D Ariyanti and W Saputri, Journal of Physics: Conf. Series1436, 012018,(2020)