



Microwave Synthesis and Characterization of Some Azo-monomers and Their Azo-Polyimides Polymers

Azad S. Sadraddin*, Dler D. Ghafoor



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Chemistry Department, College of Education, Salahaddin University-Arbil, Arbil, Iraq

Abstract

Several azo-monomers were prepared from the diazotation of m-phenylene diamine using different aromatic amines. Side chain azo-polyimides were prepared by the reaction of stoichiometric mole ratio of the prepared azo-monomers with four different dianhydride monomers to produce the corresponding polyamic acids then changed to the appropriate azo-polyimides by dehydration using acetic anhydride and pyridine in (4:1) ratio, then allowed to irradiate under microwave to ensure completely imidation. Structures of the prepared compounds were characterized using IR, H-NMR and ¹³C-NMR spectrometer and LC-Mass. In addition, solubility, inherent viscosity and thermal properties were studied for the prepared azo-polymers.

Keywords: Azo-monomers; Azo-polyimides; Microwave; Synthesis; Thermal.

1. Introduction

Aromatic azo functionalized polymers have been widely used as dyestuffs, pigments, and pH indicators for a long time [1]. This type of polymers has received much attention because of their potential applications of these polymers in different optical applications, liquid crystal [2-5] and holographic surface gratings among others [6,7].

The side-chain polymer has two advantages for the isomerization of an arene group in comparison with its main-chain counterpart. First, the side-chain polymer has little steric hindrance for the azoarene group to be oriented by the polarized light because only one end of it is bound to the polymer backbone and the other is free to move. Secondly, it has good photochemical orientability because the dipole moment of azoarene group is relatively unconnected with respect to the polymer backbone [8,9].

Polyimides are among the most heat resistant polymers with a widely applications in adhesives, dielectrics, optical materials, photo resistant membrane for separation techniques, and Langmuir Blodgett (LB) type films and many other industrial applications. Besides, polyimides have essential applications in the fields of aerospace and military applications, and optoelectronics field. These

polymers are used in the field of liquid crystal alignments, electroluminescent devices, electrolyte fuel type of cells, polymeric memories, electro and photo chromic materials and fiber optics [10].

High temperature plastics, polyimides are a class of thermally stable polymers. The thermal stability is usually attributed to their stiff aromatic backbones. In addition, the chemistry of polyimides is itself a vast field as it includes a large variety of available monomers wide range of industrial applications and different synthetic methodologies. [11-13]

There are some researches about the preparation of polyimides bearing side chain azo groups. Jungho et al. synthesize polyimides have side chain azo group starting from 3-(2-chloroethoxy)-4-((4-nitrophenyl) diazenyl)-N, N-diphenylaniline [14]. Likewise, various polyimides were prepared from a post azo-coupling reactions also, from the polycondensation of N,N-bis[(3,4-dicarboxyphenyl anhydride)-1-carboxyethyl] aniline and 4,4'-diamino-4"-hexadecyl phenylmethane [15-17].

Currently, microwave (MW) irradiation has become a well-established technique in chemical synthesis which is due to the dielectric heating. The main advantages of Microwave-assisted (MW-assisted) chemistry are shorter reaction times, higher

*Corresponding author e-mail: azad.sadraddin@su.edu.krd ; (Azad S. Sadraddin).

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yields, and a reduction of side reactions compared with syntheses performed under conventional heating.

Khoei and Zamani [18], presented the MW-assisted method of synthesis. Simply, domestic MW oven was used in the synthesis of a photoactive poly (amideimide) with fused aromatic rings like anthracene as a side group. The produced polymer was obtained from the reaction of N,N-(4,4-oxy bis(1,4-phenylene))-bis(trimellitic anhydride amide) with N-(4,6-diamino-1,3,5-triazine-2-yl) anthracene-9-carboxamide. The yield of prepared polymer was 80% after 10 min of MW irradiation which shows a potential result. However, the reaction did not proceed under thermal conditions. As a result, the poly (amideimide) polymer was investigated with respect to its thermal stability and fluorescence behavior.

2. Experimental methods

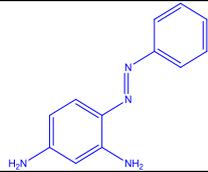
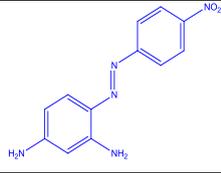
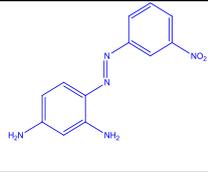
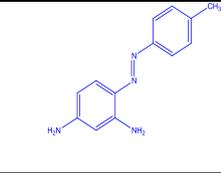
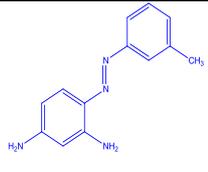
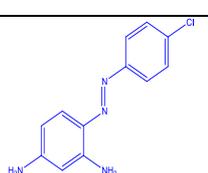
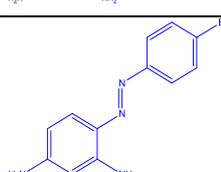
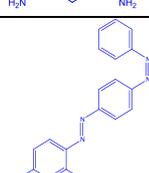
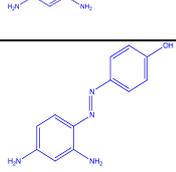
All the chemicals used in this work were either analar or reagent grade used without purification, except aniline derivatives were purified by recrystallization in ethanol. The IR spectra were recorded by Mingde Medicinal Chemistry Center – Wuhan City –China on Bruker Vortex 70 Spectrophotometer, Germany. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were recorded by 400 MHz superconducting NMR spectrometer, Model: Mercury VX-400, Varian, USA spectra. The Mass spectrum of the prepared monomers was taken by Mingde Medicinal Chemistry Center, China using Chromatography – LC-Mass spectrometry, Model: TRACEMS2000, FINNIGAN, USA. The inherent viscosities were measured using Scoot CT 52 viscometer (ubbelohde type-Germany) (measured at concentration of 0.5g/dL in NMP solvent and at 30°C). The Microwave used is domestic from LG-850 Watt made from Korea measured at 180 watt.

2.1. Synthesis of Azo-monomers

The diazonium salt compounds were prepared by using (20 mmol) of different aromatic amines, namely, aniline, 4-nitroaniline, 3- and 4-toluidine, 4-chloro and bormoaniline, 4-aminoazobenzene and 4-aminophenol and then each of these diazonium salts were coupled with 1,3-m-phenylenediamine (20 mmol) to produce (I-IX) azo-monomers listed in Table 1, with their physical properties.

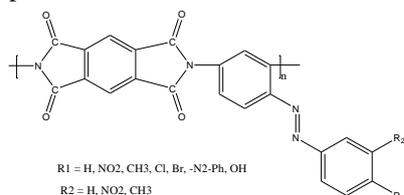
Table 1. :

The physical properties of the azo-monomers (I-IX)

No	Molecular formula	Molecular Structure
I	MF: $\text{C}_{12}\text{H}_{12}\text{N}_4$ Nom.: 4-(phenyldiazenyl) benzene-1, 3-diamine Color: Brown Yield: 90% M.P.: 115-118	
II	MF: $\text{C}_{12}\text{H}_{11}\text{N}_5\text{O}_2$ Nom.: 4-[(4-nitrophenyl) Diazenyl]benzene-1,3-diamine Color: Light Brown Yield: 94% M.P.: 242-244	
III	MF: $\text{C}_{12}\text{H}_{11}\text{N}_5\text{O}_2$ Nom.: 4-[(3-nitrophenyl) Diazenyl]benzene-1,3-diamine Color: Brown Yield: 95% M.P.: 257-259	
IV	MF: $\text{C}_{13}\text{H}_{14}\text{N}_4$ Nom.: 4-(p-tolyldiazenyl) benzene-1,3-diamine Color: Brown Yield: 93% M.P.: 193-195	
V	MF: $\text{C}_{13}\text{H}_{14}\text{N}_4$ Nom.: 4-(m-tolyldiazenyl) benzene-1, 3-diamine Color: Yellow Yield: 96% M.P.: 203-204	
VI	MF: $\text{C}_{12}\text{H}_{11}\text{ClN}_4$ Nom.: 4-[(4-chlorophenyl) diazenyl] benzene-1, 3-diamine Color: Brown Yield: 91% M.P.: 248-250	
VII	MF: $\text{C}_{12}\text{H}_{11}\text{BrN}_4$ Nom.: 4-[(4-bromophenyl) diazenyl] benzene-1, 3-diamine Color: Red Yield: 94% M.P.: 262-263	
VIII	MF: $\text{C}_{18}\text{H}_{16}\text{N}_6$ Nom.: 4, 4'-[(-phenyldiazenyl) phenyl] diazenyl]benzene-1, 3-diamine Color: Maroon Yield: 87% M.P.: 223-225	
IX	MF: $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}$ Nom.: 4-[(2, 4-diaminophenyl) diazenyl] phenol Color: Brown Yield: 85% M.P.: 233-235	

2.2. Synthesis of azo-polyimides

1 mmole (0.218 gm) of each of the azo-monomers listed in Table 1, (I-IX), was dissolved in 5 ml NMP at room temperature followed by the addition of the pyromellitic dianhydride (PMDA) (1mmol) at once. The solution was stirred at room temperature for about 12 hours under nitrogen atmosphere. The mixture of acetic anhydride and pyridine (8 ml/4 ml, 2:1) was added to the viscous amic acid solution at room temperature, this mixture was stirred for 12 hours under nitrogen atmosphere then irradiated to microwave at 180 watt in 2 minutes. The polymer was precipitated into equal volume (1:1) methanol and water 10 ml, then collected by filtration. The solid was further purified by dissolving in NMP then precipitated by methanol, then washed with hot methanol. The resulting polyimide was dried under vacuum at 60 °C for 24 hours, Scheme 1. The physical properties are listed in Table 2.



Scheme 1. The structure of the prepared azo-polyimides

Table 2. :The physical properties of the azo-polyimides (I-IX)

Poly mers	Color	Yield %	η_{inh} (dL/g)*	Time** Irr./ min
I	Brown	95	0.525	2.5
II	Brown	98	0.258	1.5
III	Light Brown	95	0.162	2.0
IV	Dark Brown	93	0.185	2.5
V	Brown	92	0.583	2.0
VI	Dark Brown	91	0.232	2.5
VII	Brown	93	0.432	2.0
VIII	Dark Brown	90	0.444	2.0
IX	Dark Brown	89	0.499	3.0

* = Viscosity measured at concentration of 0.5g/dl in NMP solvent at 30°C.

** = Microwave irradiation in minute at 180 watt.

3. Results and Discussion

3.1. Infrared spectra of the azo-monomers

The molecular structure of the azo-monomers was confirmed using IR spectra. The IR frequencies of these azo-monomers are shown in Table 3.

The medium absorption bands (1501-1597) cm⁻¹ attributed to the (N=N) stretching vibrations, and the characteristic strong absorption bands (1599-1635) cm⁻¹ belonged to (C=C) stretching vibrations, and the

medium absorption bands (1235-1328) cm⁻¹ existed to (C=N) stretching vibrations. The (N-H) stretching vibrations are shown two absorption bands in medium intensities between (3250-3478) cm⁻¹.

Table 3.

ID	IR frequencies of the prepared azo-monomers (I-IX)					
	N=N str.	C=C str.	C-N str.	N-H str.	O-N-O str.	O-H str.
I	1577	1620	1333	3435, 3380	-	-
II	1568	1635	1287	3453, 3382	1498, 1313	-
III	1586	1631	1265	3437, 3358	1507, 1348	-
IV	1572	1618	1330	3400, 3320	-	-
V	1570	1623	1328	3427, 3307	-	-
VI	1580	1603	1236	3390, 3288	-	-
VII	1575	1600	1239	3293, 3201	-	-
VIII	1502	1599	1302	3478, 3382	-	-
IX	1597	1626	1249	3396, 3321	-	3473

3.2. ¹H-NMR spectra of the azo-monomers

The molecular structure of the azo-monomers was also confirmed using ¹H-NMR spectrum. There are different aromatic protons detected between δ (6.8-8.3) and eight types of protons located within the region (5.9-7.7) ppm. For example, the azo-monomer (I) has shown a doublet signals at 7.68 ppm for proton (H8) due to the neighbor carbon atom attached to -N=N- group and other protons attached to the benzene rings for (H7), (H6), (H5), (H3) and (H1) are shown bands; triplet (7.42 ppm), doublet (7.36 ppm), triplet (7.27 ppm), doublet (6.00 ppm), singlet (5.86 ppm) respectively. As well as there are two characteristic bands one is broad; singlet signal (H2) at 7.06 ppm and other is also singlet signal (H4) belong to the protons of -NH₂ groups, Figure 1. Similarly, the ¹H-NMR data of the rest of monomers are tabulated in Table 4.

Figure 1. :¹H-NMR spectrum of azo-monomer (I)

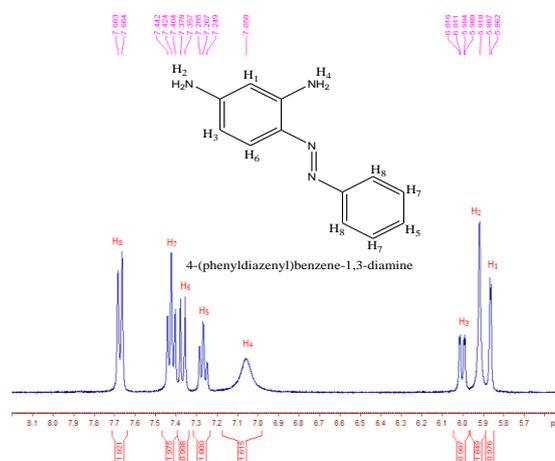
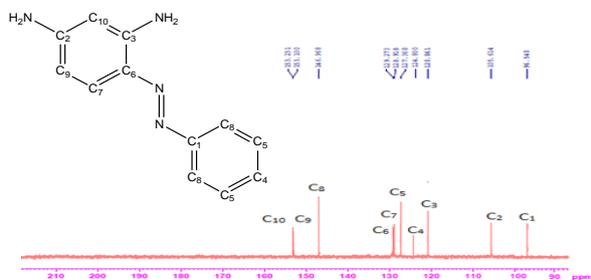


Table 4. ¹H-NMR data for azo-monomers (I-IX).

Code	δppm(Mult., Int.,Assign.)
I	5.86(s,1H,H1); 7.27(b,2H,H2); 6.00(d,1H,H3); 7.06(s,2H,H4); 7.27(t,1H,H5); 7.36(d,1H,H6); 7.42(t,2H,H7); 7.68(s,2H,H8)
	5.85(s,1H,H9); 6.08(d,1H,H10); 6.44(s,2H,H11); 7.11(b,2H,H12); 7.39(d,1H,H13); 7.82(d,2H,H14); 8.24(d,2H,H15)
	5.82(s,1H,H16); 6.10(d,1H,H17); 6.38(s,1H,H18); 7.00(b,2H,H19); 7.34(d,1H,H20); 7.38(t,1H,H21); 7.64(d,1H,H22); 7.88(d,1H,H23); 7.99(s,1H,H24).
	2.40(s,3H,H25); 5.85(s,2H,H26); 5.86(s,1H,H27); 5.98(d,1H,H28); 6.97(b,2H,H29); 7.23(d,2H,H30); 7.34(d,1H,H31); 7.58(d,2H,H32).
V	2.40(s,3H,H33); 5.87(s,1H,H34); 5.90(s,2H,H35); 6.00(d,1H,H36); 7.08(b,2H,H37); 7.10(d,1H,H38); 7.30(t,1H,H39); 7.37(d,1H,H40); 7.47(d,1H,H41); 7.50(s,1H,H42).
	5.85(s,1H,H43); 5.87(s,2H,H44); 6.08(s,1H,H45); 7.00(b,2H,H46); 7.35(d,1H,H47); 7.54(d,2H,H48); 7.69(d,2H,H49)
	5.86(s,1H,H50); 6.01(d,1H,H51); 6.05(s,2H,H52); 7.15(b,2H,H53); 7.36(d,1H,H54); 7.60(d,2H,H55); 7.63(d,2H,H56)
VIII	5.71(s,1H,H57); 6.05(s,2H,H58); 6.67(d,1H,H59); 7.15(b,2H,H60); 7.43(t,1H,H61); 7.51(t,2H,H62); 7.68(d,1H,H63); 7.74(d,4H,H64); 7.93(d,2H,H65).
	5.70(s,2H,H66); 5.87(d,1H,H67); 5.95(d,1H,H68); 6.76(b,2H,H69); 6.81(d,2H,H70); 7.31(d,1H,H71); 7.56(d,2H,H72); 9.76(s,1H,H73).
IX	

3.3. ¹³C-NMR spectra of the azo-monomers

¹³C-NMR was used to verify the molecular structure of the azo monomers. For example, azo-monomer (I) has shown 10 signals for 12 carbons with different environments in the molecule. The signals are appeared between (96.54-153.23) for carbons (C1-C10) which was illustrated in Figure 2 and Table 5.

Figure 2.:¹³C-NMR spectrum of azo-monomer (I)Table 5. ¹³C-NMR data of azo-monomer (I) using DMSO-d₆ solvent

δ ppm	Assign.	δ ppm	Assign.
96.54	C1	128.91	C6
105.61	C2	129.27	C7
120.86	C3	146.97	C8
124.80	C4	153.10	C9
127.36	C5	153.23	C10

3.4. LC-MASS spectra of the azo-monomers

LC-MASS of the prepared azo-monomers is taken with the purpose of indicating their molecular weights. Azo-monomer (I) has shown 100% peak area 0.704 mAU and the base line of molecular weight is 213.2, even as the exact molecular weight of the monomer is 212.25, Figure 3.

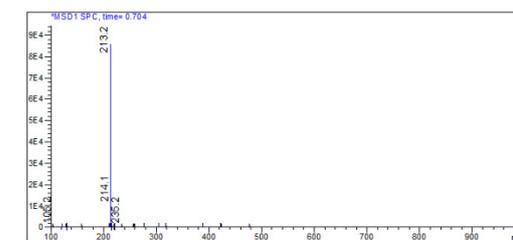
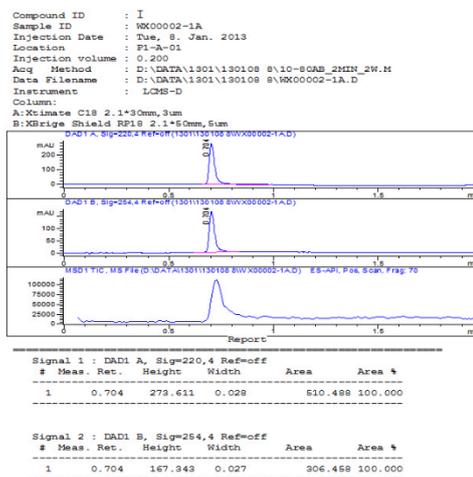


Figure 3.:LC-Mass spectrum of azo-monomer (I)

3.5. Synthesis of azo-polyimides

Polyimides with aromatic side chains, are generally prepared through a two-step procedure. These two steps include the ring-opening polyaddition of aromatic diamines to aromatic tetracarboxylic dianhydrides in solvents like NMP, DMF (or DMAc). This step gives soluble polyamic acids that will be followed by thermal cyclodehydration. Polyimides are condensation polymers derived from aliphatic or

aromatic dianhydrides and diamines, or their derivatives. They may contain a heterocyclic imide linkage in the repeat unit.

Polyimides are essential polymers in both scientifically and commercially applications. Their importance is due to their excellent thermal stability and high mechanical strength. Innovative polyimide design has brought these materials to the field of aerospace, packaging industries, automotive and microelectronics [19,20].

Polymers with azo-benzene make the polymer to defeat good stability and usually show high glass transition temperature (T_g) and obviously, improving thermal stability and allow a wide range of applications as engineering.

The process involves polycondensation of the prepared azo-monomers (I-IX) in stoichiometric mole ratio with PMDA dianhydride in NMP solvent, to afford polyamic acids then followed by imidation using acetic anhydride and pyridine (3:1) under nitrogen. Finally, the product was irradiated to the microwave to produce the appropriate polyimide which was precipitated using equimolar amount of water and methanol.

Obviously, the polyamic acid is a combination of difunctional amine and a difunctional anhydride in a polar aprotic solvent. This usually followed by a reversible nucleophilic substitution reaction through the attack of amine group to one of the carbonyl carbons in the anhydride moiety and displaces carboxylate functionality and ended by proton transfer process.

The formation of polyimides from the corresponding polyamic acids were accomplished using chemical imidization using good dehydration agents like acetic anhydride; in addition, using pyridine to capture the water from the reaction media; nevertheless, to ensure ring closure of the proper polyimide we use domestic microwave, which was the solution irradiated to microwave at 180 watt which improve the yield as well as reduces the reaction time from 24 hours to the minutes, all the prepared polymers were pre tested by measuring melting points, thus, their melting point is over 300°C.

An almost exponential increase of the number of publications in this field reflects the steadily growing interest in the use of microwave irradiation for polymerizations. It offers a number of advantages over conventional heating, such as noncontact heating, instantaneous and rapid heating and highly specific heating.

3.6. Infrared spectra of the prepared azo-polyimide

The structures of the synthesized polymers were established on the basis of IR spectra as shown in Table 6 and Figure 4. The formation of polyimides was confirmed by the appearance of absorption modes at approximately (1787-1771) cm^{-1} , (1728-1711) cm^{-1} due to symmetric C=O, asymmetric C=O stretching respectively. (1384-1344) cm^{-1} (C-N stretching vibration); (1171-1063) cm^{-1} and (798-703) cm^{-1} (imide ring deformation).

Table 5. The IR data in cm^{-1} of azo-polyimides (I-IX).

Code No.	C=O str. sym.	C=O str. assy.	C-N str.	Imide ring def.
I	1780	1728	1384	1107,724
II	1780	1728	1338	1103,731
III	1780	1728	1384	1107,724
IV	1775	1714	1366	1122,723
V	1774	1711	1371	1132,735
VI	1780	1728	1368	1086,728
VII	1780	1728	1345	1096,722
VIII	1779	1726	1369	1114,743
IX	1776	1722	1365	1142,754

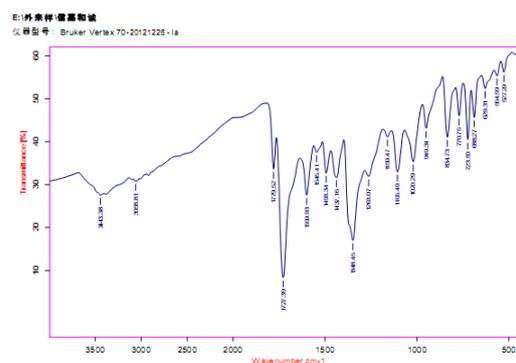


Figure 4. IR spectrum of azo-polyimide (I)

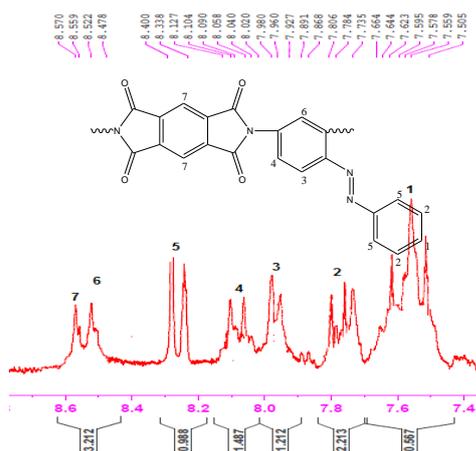
3.7. $^1\text{H-NMR}$ spectra of the prepared azo-polyimide

A representative $^1\text{H-NMR}$ spectra of the prepared azo-polyimides dissolved in DMSO- d_6 is shown in Figure 5 and Table 9. The prepared azo-polyimide (I) was shown different signals for hydrogen 1 to 7 for benzene ring between (7.51-8.57).

Similarly, the rest of the azo-polyimides (II-IX) has shown different signals for protons as shown in Table 7.

3.8. $^{13}\text{C-NMR}$ spectra of the prepared azo-polyimide

An envoy $^{13}\text{C-NMR}$ spectra of azo-polyimide (II) is shown in Figure 6. It has shown 13 signals for 22 carbons between (118.3 to 167.8) ppm as shown in Table 8.

Figure 5. ¹H-NMR spectrum of azo-polyimide (I)Table 7. ¹H-NMR data of azo-polyimides (I-IX) using DMSO-d₆.

Code No.	δppm(Multi.,Int.,Assign.)
I	7.56(t,1H,P1); 7.78(t,2H,P2); 7.96(d,1H,P3); 8.04(d,2H,P4); 8.37(d,1H,P5); 8.52(s,1H,P6); 8.57(s,2H,P7).
II	7.61(d,1H,P35); 7.81(d,2H,P36); 8.06(d,1H,P37); 8.18(s,1H,P38); 8.30(d,2H,P39); 8.40(s,2H,P40).
III	7.36(d,1H,P65); 7.59(d,1H,P66); 7.76(t,1H,P67); 8.00(s,1H,P68); 8.10(d,1H,P69); 8.14(d,1H,P70); 8.37(s,1H,P71); 8.79(s,2H,P72).
IV	2.70(s,3H,P103); 7.81(d,2H,P104); 8.06(d,1H,P105); 8.18(d,1H,P106); 8.30(s,1H,P107); 8.40(s,2H,P108); 8.06(d,2H,P109).
V	2.36(s,3H,P137); 7.23(d,1H,P138); 7.31(t,1H,P139); 7.41(d,1H,P140); 7.47(d,1H,P141); 7.59(s,2H,P142); 7.61(d,1H,P143); 7.78(s,1H,P144); 7.97(s,1H,P145).
VI	7.55(D,3H,P179); 7.61(d,2H,P180); 7.78(D,2H,P181); 7.92(S,1H,P182); 7.97(d,2H,P183); 8.55(S,1H,P184).
VII	7.43(d,1H,P209); 7.61(d,1H,P210); 7.63(d,2H,P211); 7.70(s,1H,P212); 7.78(d,2H,P213); 8.60(s,2H,P214).
VIII	7.02(t,1H,P239); 7.35(d,1H,P240); 7.87(t,2H,P241); 7.96(d,4H,P242); 8.06(d,1H,P243); 8.12(s,1H,P244); 8.19(d,2H,P245); 8.53(s,2H,P246).
IX	5.87(s,1H,P277); 6.81(d,2H,P278); 7.42(d,1H,P279); 7.57(d,2H,P280); 7.80(d,1H,P281); 8.19(s,1H,P282); 8.26(s,2H,P283).

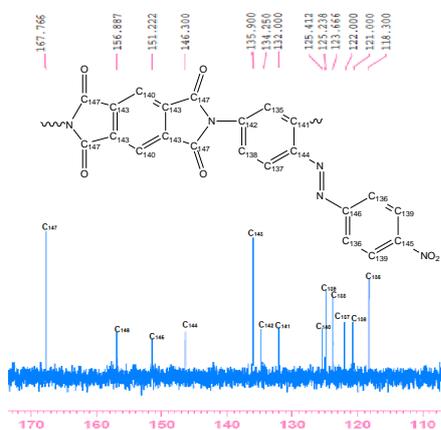
Figure 6. ¹³C-NMR spectrum of azo-polyimide (II)

Table 8.

¹³C-NMR data of azo-polyimide (II) in DMSO-d₆ solvent.

δ ppm	Assign.	δ ppm	Assign.
118.30	C135	134.25	C142
121.00	C136	135.90	C143
122.00	C137	146.30	C144
123.66	C138	151.22	C145
125.23	C139	156.88	C146
125.41	C140	167.76	C147
132.00	C141		

3.9. Inherent viscosity

The inherent viscosity of the prepared polymers was recorded using Ubbelohde capillary viscometer (measured at concentration of 0.5g/dL in NMP solvent and at 30°C). As shown in Table 2, viscosity of a polymer solution depends on concentration and size (i.e., molecular weight) of the dissolved polymer. There are disparities in the values of viscosity ranging from (0.162 – 0.571) dL/gm; the high value of the viscosity meaning the polymer has a high molecular weight.

3.10. Thermal properties

The thermal properties of azo-polyimides (I-IV) and (VIII) were investigated by means of thermo gravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis in a nitrogen atmosphere at a heating rate of 10 °C/min. For example, azo-polymer (I) was appeared different transition temperature at (90°C, 126°C, 475°C and 570°C) respectively. The polymer has Tg at 498°C and the weight loose of polymer is 51.4% at 700°C; i.e. the polymer exhibited good resistance to thermal decomposition, Figure 7. Azo-polymer (II) has shown unusual transition temperature at (180°C, 283°C, 420°C and 545°C) respectively with a Tg at 275°C and weight loose of polymer at 50.4% at 700°C.

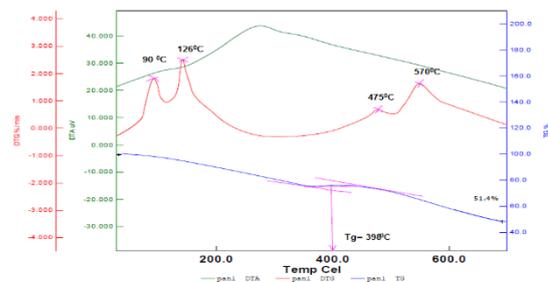


Figure 7. DTG-DTA Diagram of azo-polyimide (I)

3.11. Solubility

The solubility of the azo-polyimides (I-IX) was tested in the solvents, DMF, DMSO, NMP and DMAc. All the polymers have shown good solubility in DMSO and NMP at ambient temperatures while they need some heating to be soluble in DMF and DMAc.

4. Conclusions

A number of azo-polyimides were prepared from the reaction of newly prepared azo-monomers with dianhydride followed by microwave irradiation. The azo-monomers and the corresponding azo-polyimides were characterized using IR, ¹HNMR, ¹³C-NMR, LC-mass, inherent viscosity and thermal analysis. The prepared azo-polyimides have shown good thermal stability and good solubility in different solvents.

5. Conflicts of interest

This work is part of PhD thesis. There are no conflicts to declare.

6. Acknowledgments

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All the spectra and analysis data of all the prepared compounds are available and it can be provided by the corresponding author.

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