Indones. J. Chem., 2025, 25 (4), 1179 - 1192

Synthesis and Characterization of New Conjugated Polymers Based on Furan Ring from D-fructose and Their Photoluminescence and Thermal Properties

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Received: February 17, 2025
Accepted: April 20, 2025

DOI: 10.22146/ijc.104800

Abstract: *Conjugated polymers are one of the most essential branches of polymer science. Most conjugated polymers have a small band gap energy between the ground state and excited state, making them fluorescent materials useful for use as light emitting diodes (LED), sensors, digital screens, and others. We synthesized dialdehyde compound (F1) with good yield and high quality from a natural source (D-fructose) and characterized by proton nuclear magnetic resonance (^{1}H-NMR), carbon-13 nuclear magnetic resonance (^{13}C-NMR), electron impact (EI) mass spectra, and Fourier-transform infrared spectroscopy (FTIR). We synthesized two salts of disubstituted benzene triphenylphosphonium chloride (W1, W2) and characterized them by ^{1}H-NMR and FTIR. We synthesized two polymers by Wittig polycondensation from the reaction of F1 with salts (W1, W2) and characterized by ^{1}H-NMR, FTIR spectroscopy and gel permeation chromatography (GPC). Their photoluminescence properties were studied which giving light emission with λ_{PL} max at 502 and 472 nm for A1 and A2, respectively. We synthesized three polymers (P1, P2, P3) from reacting F1 with ketone by aldol condensation using KOH to give insoluble polymers and characterized them by FTIR spectroscopy. All polymers were evaluated by thermal gravimetric analysis (TGA), showing thermal stability with decomposition temperature beginning from 192 °C.*

Keywords: *conjugated polymers; fluorescent polymers; furan; Wittig polycondensation; aldol condensation*

■ INTRODUCTION

Conjugated polymers are polymers with extended alternating double bonds through the backbone of polymers. It is the most important among all classes of polymers because they are successfully used in polymer light-emitting diodes (PLEDs) especially poly arylene vinylene (PAV), which is a copolymer consist from aromatic units joined together by vinylene linkers [1]. A LED is a light source that emits radiation due to an electric current [2]. The mechanism of emitting light is done by bombarding the substance with energy from any source like an electric current and kicks an electron of an atom out of its ground state (bonding orbital) into an excited state (antibonding orbital) and the energy will be released in the form of light in the visible region as a result of return electron to the ground state [3]. PLEDs have attracted researchers, scientists, and industrialists and bring light to our lives because of their unique properties, such as low cost, wide viewing angle, flexibility, lightweight, low power consumption, and thin panel thickness [4]. Since the first report by the Cambridge group of PLEDs based on poly(*p*-phenylenevinylene) (PPV), a huge range of conjugated polymers with different color emissions was synthesized [5]. The structure of conjugated polymers is diverse, allowing for synthesis with interesting and useful optical properties [6]. Many different conjugated polymer backbones, including PAV, poly(pyrrole), polyfluorene, polythiophene, and polycarbazole, have been prepared and investigated [7] with many different ways to synthesize aromatic conjugated polymers like Gilch polycondensation [8], Knoevengel polycondensation [9], Heck coupling polymerization [10], and Wittig polycondensation [11]. Conjugated polymers acquired their semiconducting and optical properties by having delocalized π-electron bonding in the backbones of the main skeleton. So, the charge carriers will be moving along the polymer chain through a conjugated system [12]. In our study, we prepare dialdehyde [5,5'-oxybis(5-methylene-2-furaldehyde)] from a natural source which is D-fructose which is described mechanism in Scheme 1 [13], and react with a variety of triphenylphosphorous ylide by Wittig reaction to synthesis two conjugated polymers (A1, A2) and another series of conjugated polymers by reacting with ketone compounds through aldol condensation (P1, P2, P3). We studied thermogravimetric analysis (TGA) for all polymers and photoluminescence for polymers that are synthesized by Wittig polycondensation.

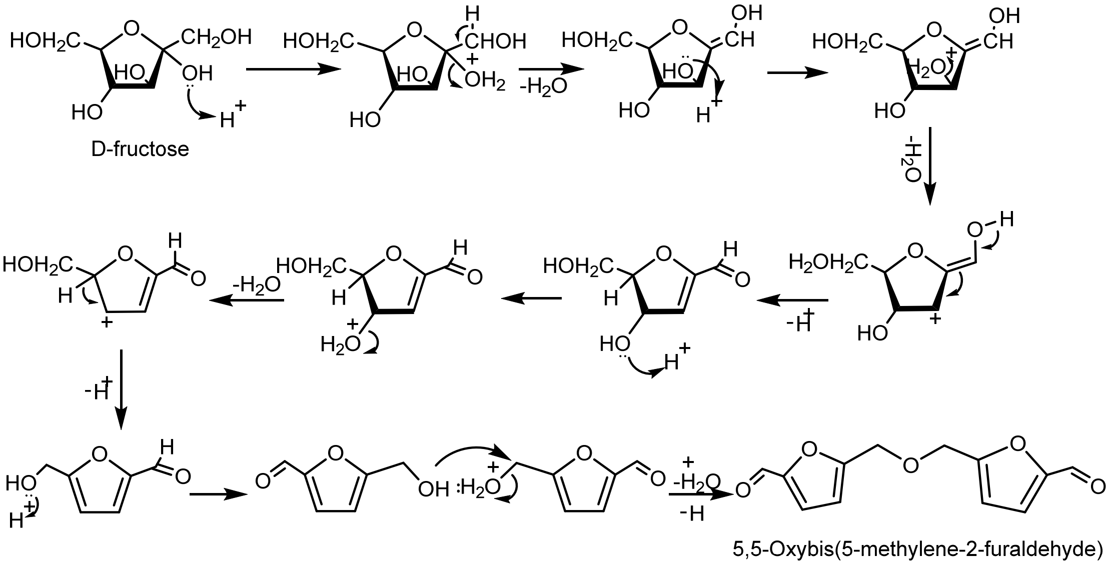
■ EXPERIMENTAL SECTION

Materials

D-fructose (99% purity, HIMEDIA, India), Dowex resin 50 W 8X (Aldrich, American), dimethylsulfoxide (99% purity, HIMEDIA, India), *tert*-butyl methyl ether (99% purity Aldrich, American), *n*-hexane (95% purity, BAKER, American), ethyl acetate (99% purity Merck, Germany), chloroform (99% purity, Merck, Germany), formaldehyde (37% purity, HIMEDIA, India), xylene (95% purity Aldrich, American), *p*-xylene (99% purity, Aldrich, American), *m*-xylene (99% purity Aldrich, American), sodium metal (99% purity, Aldrich, American), triphenylphosphine (95% purity, Aldrich, American), acetone (99% purity, Merck, Germany), cyclohexanone (99% purity, Merck, Germany), and cyclopentanone (99% purity, Aldrich, American) were used in this work.

Instrumentation

The melting points of compounds were recorded on a Thermo Fisher thermal point apparatus (England) using an open capillary tube. A 12 UV flashlight model TT-FL001 from the Taotronics company was used to note the emission from polymer solutions. The ^{1}H-NMR and ^{13}C-NMR spectra from the Bruker company were obtained at 400 MHz. Bruker FTIR ALPHA II and Shimadzu FTIR 8400 recorded FTIR spectra. Mass spectra from ABSciex 3200 Q-Trap. UV-visible spectra by the Shimadzu company type UV-1800, fluorescence spectra by Fluo time 300. TGA was recorded by TA Q600(USA). Gel permeation chromatography was recorded using a Knauer system. In thin layer chromatography (TLC) analysis, the plates were coated with silica gel G (suspended in pet ether-ethyl acetate), and UV light was used as a visualizing agent.



Scheme 1. Mechanism of preparation of 5,5'-oxybis(5-methylene-2-furaldehyde) from D-fructose

Procedure

Preparation of 5,5'-oxybis(5-methylene-2-furaldehyde) (F1)

A solution of D-fructose (9.00 g, 50 mmol) in 20 mL of dimethylsulfoxide with Dowex resin 50 W X8 (0.90 g) was put in an open boiling tube and was heated in an oil bath to 110 °C for 24 h. Then, 50 mL of *t*-butyl methyl ether was used to dilute the mixture above after cooling to room temperature, and the ion exchange resin (Dowex) was recovered by filtration. An amount of 5 mL of *t*-butyl methyl ether was used to wash the resin, and this process was repeated three times. The filters were combined and transferred to a separatory funnel and washed with water (3 × 25 mL) to remove DMSO. The *t*-butyl methyl ether layer was separated and concentrated under reduced pressure to give the pale yellow crude product, which was recrystallized from 50% aqueous ethanol to give 5,5'-oxybis(5-methylene-2-furaldehyde) as yellow-white crystals, 8.89 g, 76% yield with melting point 113 °C [13]. TLC by using a mixture of 1:1 of (ethyl acetate:*n*-hexane), Rf = 0.63 as shown in Fig. S1. FTIR showed several bands at 3105, 2931, 1660, 1512, 1189, 1035, and 768 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO) δ 9.59 (s, 2H), 7.51 (d, *J* = 3.5 Hz, 2H), 6.77 (*d*, *J* = 3.5 Hz, 2H), 4.63 (*s*, 4H). ^{13}C-NMR (101 MHz, DMSO) δ 178.87, 157.73, 152.80, 124.24, 112.79, 64.17. MS (*m/z*): 235.4 [M+H] (calc. 234.05).

Preparation of 1,4-bis(chloromethyl)-2,5-dimethylbenzene (M4)

A mixture of *p*-xylene (11.5 mL, 94 mmol), formaldehyde (75.0 mL), and 37% aqueous HCl (105.0 mL, 1.26 mol) in one neck round (250.0 mL) was distilled for 5 h. The mixture was cooled to 0 °C in a refrigerator for 24 h. After that, the mixture was separated into two layers, one of them being the wax layer, which is above, and the aqueous layer. The wax layer will be abstracted and washed with cooled methanol and filtered to produce a crude solid product, and washed several times until the pH of the washing liquid becomes neutral [14]. The white product will be recrystallized with 60% of ethanol to produce white crystals with a yield of 22.6% and a melting point of 134 °C. FTIR (cm^{-1}), 2976, 2920, 1508, 698. ^{1}H-NMR (400 MHz, DMSO) δ 7.24 (*s*, 2H), 4.73 (*s*, 4H), 2.32 (*s*, 6H).

Preparation of 1,3-bis(chloromethyl)-4,6-dimethylbenzene (M5)

Following the procedure above for M4 by using *m*-xylene. The white product was recrystallized with 80% ethanol to produce white crystals, yielding 41.77% and a melting point of 93 °C. FTIR (cm^{-1}), 2970, 2924, 1616, 651. ^{1}HNMR (400 MHz, DMSO) δ 7.39 (*s*, 1H), 7.1 (*s*, 1H), 4.75 (*s*, 4H), 2.34 (*s*, 6H).

Preparation of 2,5-dimethyl-1,4-xylylene)bis(triphenyl phosphonium chloride (W1)

A mixture of 2,5-bis(chloromethyl)-*p*-xylene (2.02 g, 0.01 mol) with triphenylphosphine (7.07 g, 0.027 mol) and 25 mL of xylene in a round-bottom 100 mL flask. The mixture was heated to reflux after 24 h, and the precipitate was filtered out immediately. The sold product was purified by dissolving in minimum amounts of ethanol and reprecipitated by adding 100 mL of ethyl ether and filtered out to produce the white powder of W1 with a yield of 82%, decomposed at 290 °C [15]. FTIR shows several bands at 3008, 2855, 1587, 1436–1111, 1178, 741, 686 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO) δ 7.98–7.68 (*m*, 30H), 6.67–6.62 (*m*, 2H), 4.99 (*d*, *J* = 14.3 Hz, 4H), 1.28 (*s*, 6H).

Preparation of 4,6-dimethyl-1,3-xylylenebis(triphenylphosphonium chloride) (W2)

Following the procedure above for W1 by using 4,6-bis(chloromethyl)-*m*-xylene (2.02 g, 0.01 mol) to produce white powder of W2, yield 74.58% melting point 195 °C. FTIR shows several bands at 3008, 2857, 1583, 1435–1108, 1192, 751, 686 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO) δ 8.04–7.46 (*m*, 30H), 6.72 (*s*, 1H), 6.85 (*s*, 1H), 4.78 (*d*, *J* = 15.0 Hz, 4H), 1.58 (*d*, *J* = 2.6 Hz, 6H).

Synthesis of poly[oxymethylene-2,5-dihydrofuran-1,2-ethylene-2,5-dimethyl-1,4-phenylene-1,2-ethylene-2,5-dihydrfuran-methylene] (A1)

A solution of dialdehyde (1.17 g, 0.005 mol) and (2,5-dimethyl-1,4-xylylene)bis(triphenyl phosphonium chloride) (3.640 g, 0.005 mol) in 100 mL of anhydrous ethanol and chloroform (1/3 v/v) was added to it a dropwise of NaOH solution (0.280 g, 0.012 mol) in 16 mL of anhydrous ethanol at ambient temperature and stirred for 24 h after that added 6 mL of 2% HCl and stirred for 1 h. The mixture was washed with 30 mL of a solution of ethanol and distilled water (1/3). The mixture will be separated into an aqueous layer and an organic layer, and the latter will be extracted and washed again two times with 30 mL of distilled water and evaporated organic layer under reduced pressure [16-17]. Brown powder solid was obtained with a melting point of 130 °C. FTIR spectra show several bands at 3065, 2925, 1720, 1681, 1596, 1515, 1118, 971, 712 cm^{-1}. ^{1}H-NMR shows several bands at 2.27–2.33, 4.35–4.51, 6.47–7.63 ppm. GPC analysis shows the molecular weight (M_w) for A1 is 2182 Dalton, with a polydispersity index (M_w/M_n) of 1.19.

Synthesis of poly[oxymethylene-2,5-dihydrofuran-1,2-ethylene-4,6-dimethyl-1,3-phenylene-1,2-ethylene-2,5-dihydrfuran-methylene] (A2)

Following the procedure above for A1 by using F1 as dialdehyde to react with (4,6-dimethyl-1,3-xylylene)bis(triphenylphosphonium chloride) (3.64 g, 0.005 mol) to produce a brown powder with melting point 126 °C. FTIR spectra shows several bands at 2954, 2871, 1712, 1689, 1600, 1515, 1162, 974, 807 cm^{-1}. ^{1}H-NMR shows several bands at 2.21, 4.46, 6.52–7.63 ppm. GPC analysis shows the molecular weight (M_w) for A2 is 1334 Dalton, with a polydispersity index (M_w/M_n) of 1.05.

Synthesis of poly[5-oxymethylene-1,5-bis(furan-2-yl)-1,4-pentandiene-3-one-methane] (P1)

A mixture of compound F1 (0.702 g, 0.003 mol) with acetone (0.22 mL, 0.003 mol) in 50 mL of absolute ethanol was stirred at room temperature until the reactant was completely dissolved then aqueous solution of KOH (0.006 mol in 10 mL of distilled water) was added dropwise to mixture above with continuous stirred at room temp. For 1 d, the color of the reaction turned yellow after 10 min. The precipitate was formed, and the mixture was poured into 400 mL of water with 20 mL of acetic acid to neutralize. The precipitate was filtered out and washed with methanol and distilled water, then dried overnight to produce a yellowish powder with a melting point > 360 °C (decomposed). The product does not dissolve in common organic solvents [18]. FTIR shows several bands at 2916, 2859, 1714, 1671, 1611, 1516, 1018, 967, 796 cm^{-1}.

Synthesis of poly[5-oxymethylene-2,5-bis(furfurylidene)-cyclopentanone-methane] (P2)

Following the procedure above for P1 by using compound F1 (0.702 g, 0.003 mol) with cyclopentanone (0.26 mL, 0.003 mol) to produce a yellowish powder with a melting point > 360 °C (decomposed). The product does not dissolve in common organic solvents. FTIR shows several bands at 2915, 2858, 1679, 1609, 1518, 1049, 956, 794 cm^{-1}.

Synthesis of poly[5-oxymethylene-2,6-bis(furfurylidene)-cyclohexanone-methane] (P3)

Following the procedure above for P1 by using compound F1 (0.702 g, 0.003 mol) with cyclohexanone (0.310 mL, 0.003 mol) to produce a yellowish powder with a melting point > 360 °C (decomposed). The product does not dissolve in common organic solvents. FTIR shows several bands at 2924, 2860, 1715, 1659, 1601, 1564, 1064, 926, 787 cm^{-1}.

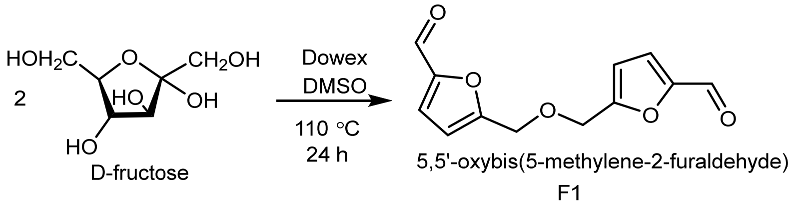
Absorbance and fluorescence measurements

The optical properties of polymer solutions (A1, A2) in chloroform were studied by absorbance and emission spectra. The Tauc plot method was used to calculate the direct band gap energy based on data from the absorption spectrum of polymer solution (A1, A2) in chloroform.

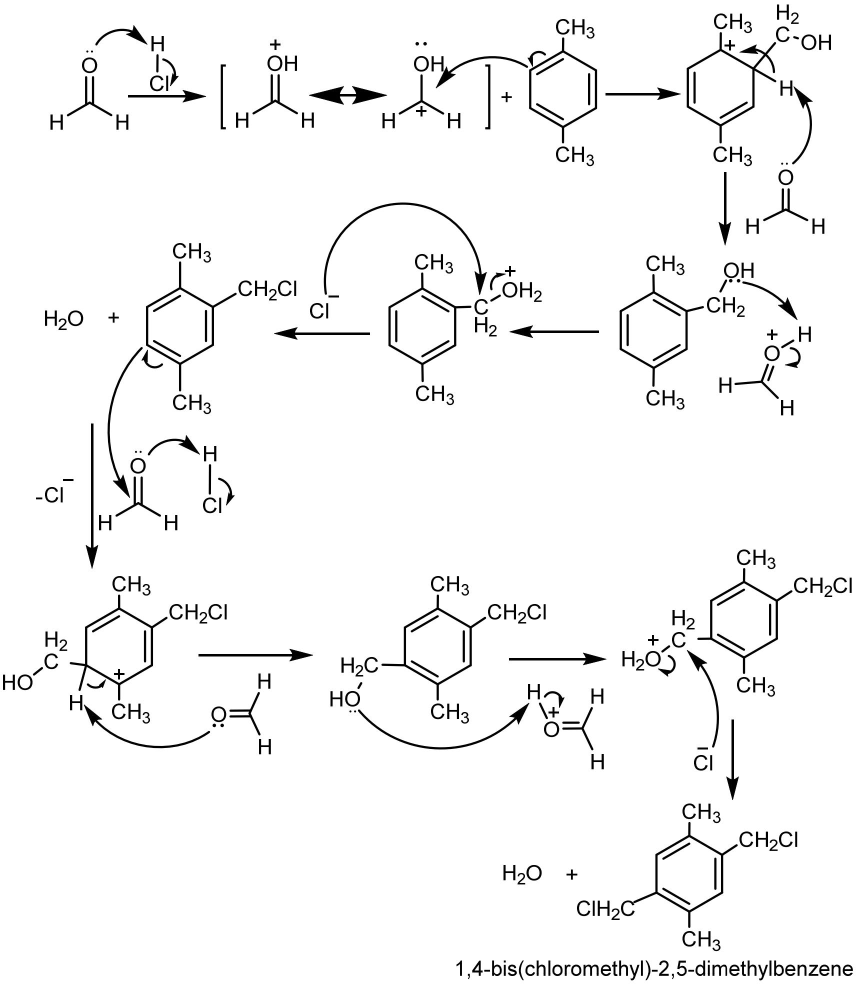
■ RESULTS AND DISCUSSION

Synthesis

Dialdehyde (F1) was synthesized using D-fructose dissolved in dimethylsulfoxide and Dowex resin and stirred at 110 °C for 24 h, as described in Scheme 2, and the mechanism was described previously in Scheme 1. Aromatic chloromethylation products (M4, M5) were synthesized by reaction of para-or meta-xylene (X1, X2) with formalin and HCl at distillation temperature for 5 h, which is described mechanism as shown in Scheme 3 [19]. After that, triphenylphosphonium salts (W1, W2) were prepared by distillation of M4 and M5 compounds with triphenylphosphine in xylene solvent for 24 h as described in Scheme 4. Two different conjugated polymers were synthesized by the Wittig reaction (Scheme 5) from reacting F1 monomers with W1 and W2



Scheme 2. Reaction synthesis of 5,5'-oxybis(5-methylene-2-furaldehyde)

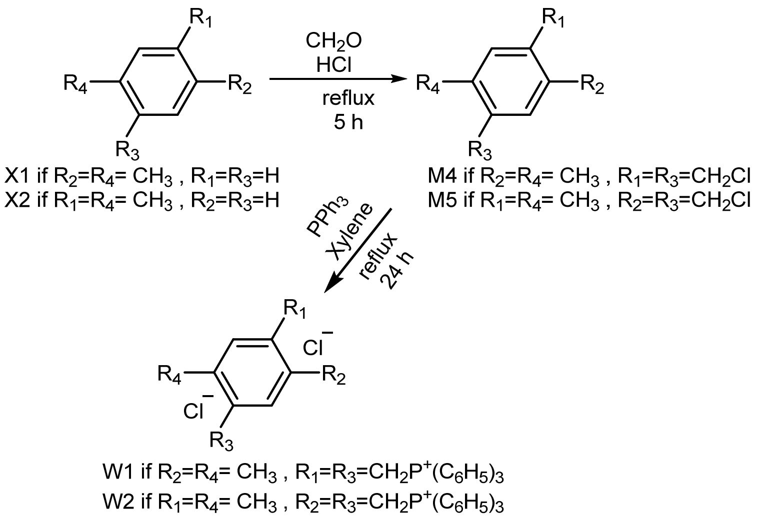


Scheme 3. Mechanism of chloromethylation of 1,4-bis(chloromethyl)-2,5-dimethylbenzene from *p*-xylene

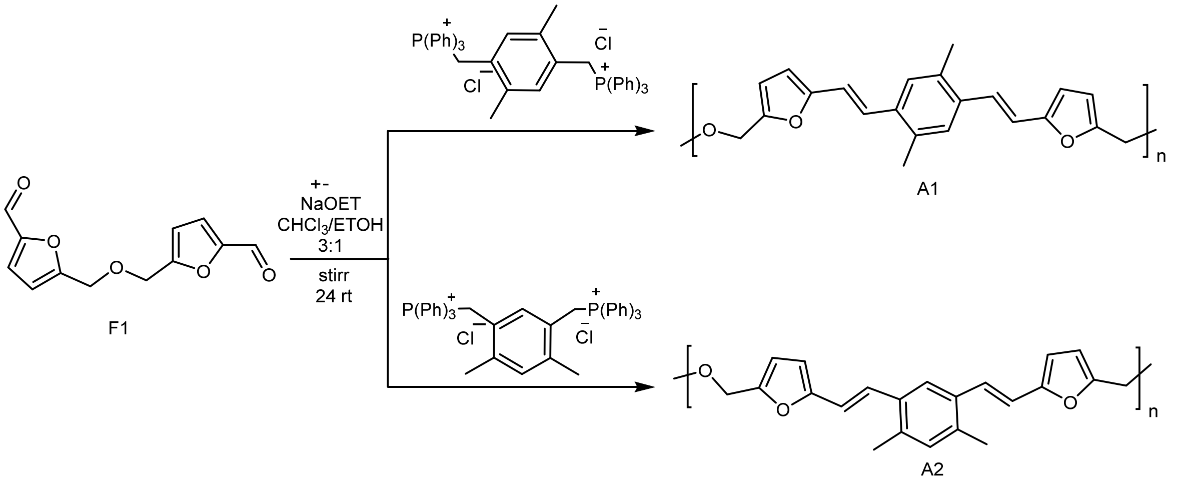
in 1:1 ratio using sodium ethoxide solution as a base catalyst. Three different conjugated polymers were synthesized by aldol condensation from reacting an equivalent ratio of compound F1 as dialdehyde and ketones (acetone, cyclopentanone, cyclohexanone) using KOH solution as a base catalyst (Scheme 6).

Absorbance and Fluorescence Analysis

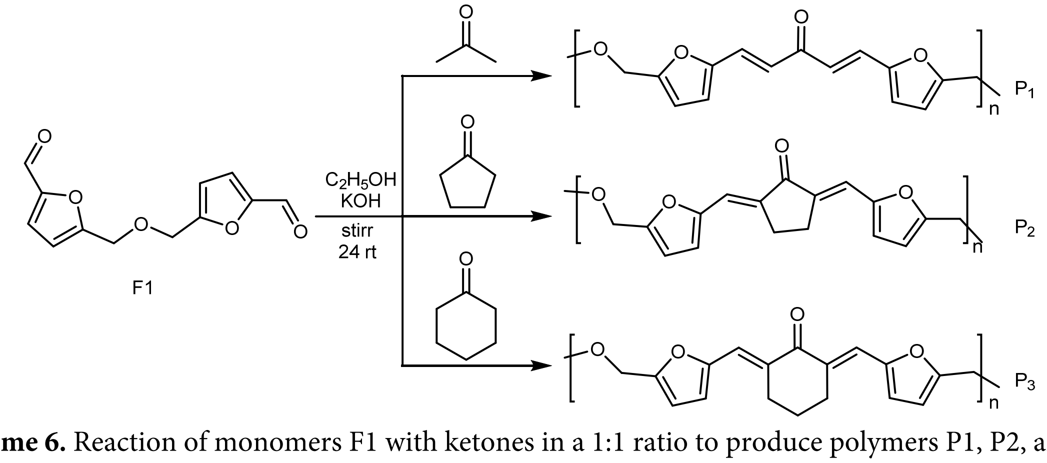
Furan is a five-member heterocyclic ring with four carbon atoms and an oxygen atom with sp^2 hybridization for all atoms. Its aromatic ring is because of the participation of the lone pair of oxygen with the π-electron system of carbon atoms [20]. We synthesized polymers consisting of substitution phenylene with a furan ring in the backbone of the polymers. The solutions of polymers emitted green light when exposed to a UV flashlight as a practical improvement to the synthesis of fluorescent polymers, as shown in Fig. 1.



Scheme 4. Reaction synthesis of triphenylphosphonium salt (W1, W2)



Scheme 5. Reaction of monomers F1 with W1 and W2 in a 1:1 ratio to produce polymers A1 and A2



Scheme 6. Reaction of monomers F1 with ketones in a 1:1 ratio to produce polymers P1, P2, and P3

UV-vis spectra of polymers (A1, A2) have λ_{max} at 286 and 272 nm, which is attributed to the π-π* electronic transition as described in Fig. 2 and emission spectra have λ_{max} at 502 and 472 nm as described in Fig. 3

absorbance and emission spectra. Polymer A1 has a longer maximum wavelength for both absorbance and emission processes than polymer A2 because of the *p*-linkage in the backbone of A1, which increases crystallinity, stability, and delocalization through the main chain than the m-linkage in polymer A2. Stoke shift is a very important feature for fluorescent compounds, which is defined as the difference between the maximum wavelength of absorbance and emission. As a result, the values of Stokes shift for the polymers A1 and A2 are 216 and 200 nm, respectively.

Energy Band Gap

Fluorescent compounds have a characteristic feature which is a small energy gap known as an energy band gap (E_g) defined as the difference between the energy level of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), more precisely between the energy of the excited state and the ground state [21]. One of the most common ways to decrease the E_g is the extension of π-conjugated through the main skeleton of compounds. For example, energy band gaps for ethene, butadiene, and octatetraene are 6.7, 5.8, and 3.1 eV, respectively, as shown in Fig. 4 [22].

The Tauc plot method is a mathematical method to measure E_g, and Eq. (1) is the principle of this method [23];

$$(\alpha \cdot h\nu)^2 = B(h\nu - E_g) \quad (1)$$

where h is the Plank constant, ν is photon frequency, B is a constant, and α is the absorption coefficient. The

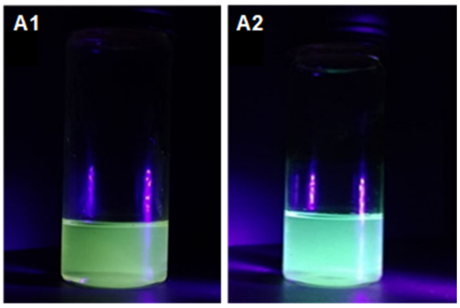


Fig 1. Emission of light from polymer solutions (A1, A2) in chloroform after exposure to a UV flashlight

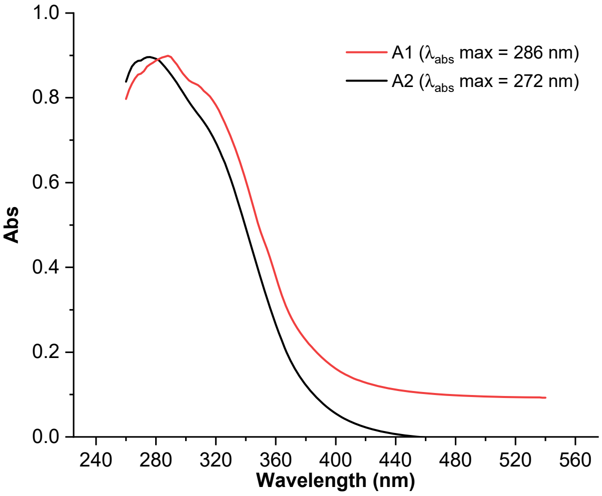


Fig 2. Absorbance spectrum of polymer solutions (A1, A2) in chloroform

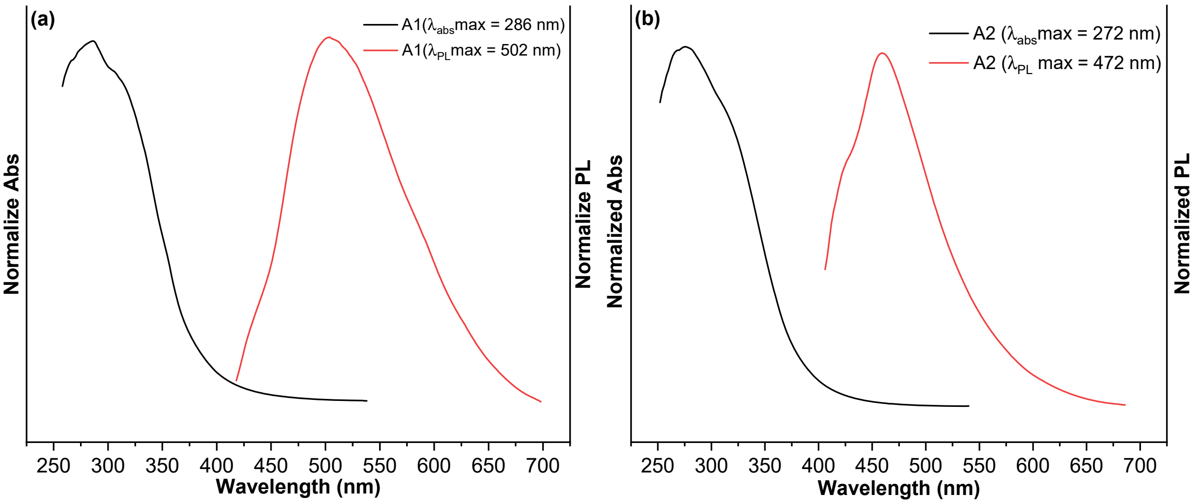


Fig 3. Absorbance and emission spectrum for the solution of polymers: (a) A1 and (b) A2 in chloroform

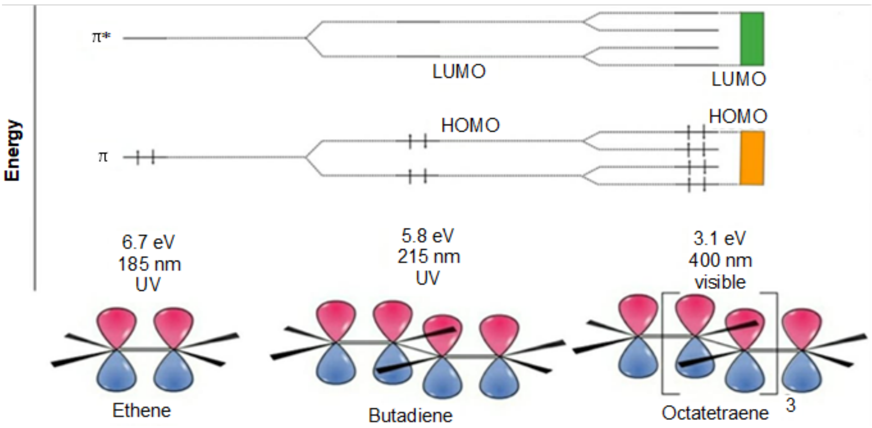


Fig 4. Effect of the π-conjugated system on energy band gaps

absorbance coefficient is calculated by Eq. (2);

$$\alpha = \ln(10)\cdot A/L \qquad (2)$$

where A is absorbance, and L is the path length of the quartz cuvette (1 cm), so the absorption coefficient will be calculated according to Eq. (3).

$$\alpha = 2.302A \qquad (3)$$

The estimation of E_g according to the Tauc plot can be done from the plot of $(\alpha h\nu)^2$ y-axis versus hν (energy) x-axis by extrapolating the straight line over the slope of the main peak to the energy axis [24-25]. As a result, the E_g value of polymers is 3.42 and 3.46 eV for A1 and A2, respectively (Fig. 5).

FTIR Analysis

FTIR spectrum of F1 is described in Fig. S2. The reference, is provided in the supplementary file, showed several peaks at 3015 $\mathrm{cm^{-1}}$ for the stretching vibration of the aromatic protons, 1660 $\mathrm{cm^{-1}}$ for the stretching vibration of the C=O group, 1512 $\mathrm{cm^{-1}}$ for the stretching vibration of the C=C aromatic, and 1035 $\mathrm{cm^{-1}}$ for the asymmetric stretching vibration of the C–O–C bond [9,26]. FTIR spectra for compounds M4 and M5 described in Fig. S3 and S4 have a distinguished peak at 698 and 651 $\mathrm{cm^{-1}}$, respectively, for stretching vibration of the CH_2–Cl bond [27]. FTIR spectra for compounds W1 and W2, described in Fig. S5 and S6, have a sharp peak at 686 $\mathrm{cm^{-1}}$ for stretching vibration of the aliphatic P–C bond for both compounds. Two peaks at 1436 and 1111 $\mathrm{cm^{-1}}$ for aromatic stretching vibration for P–C of compound W1; two at 1435 and 1108 $\mathrm{cm^{-1}}$ for aromatic stretching vibration for P–C of compound W2 [15]. FTIR spectra for almost all polymers have a peak at the

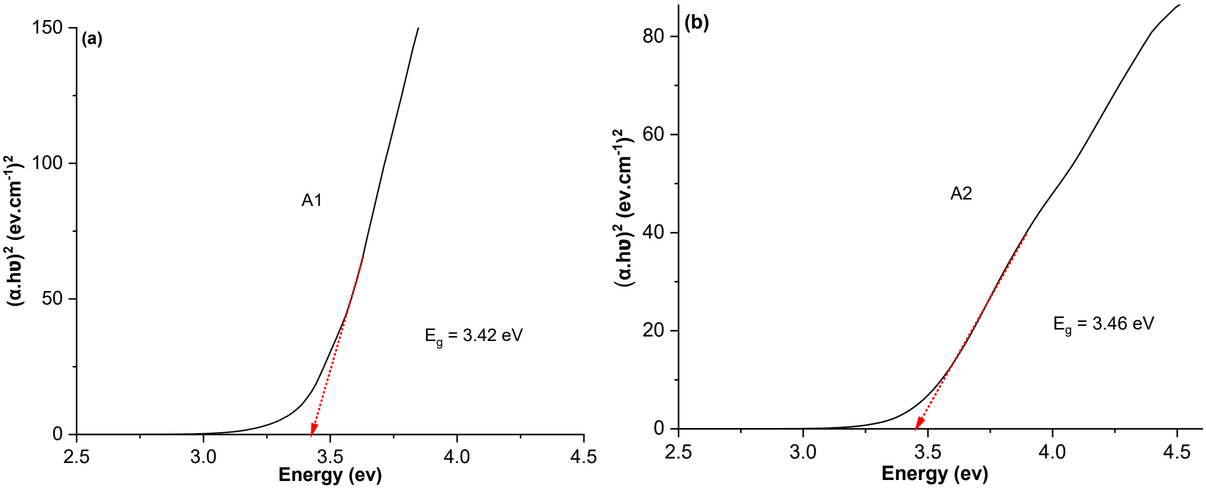


Fig 5. Tauc plot for polymer (a) A1 and (b) A2

range 1700 cm^{-1} attributed to terminal aldehyde. FTIR spectra for polymers A1 and A2 described in Fig. S7 and 8 show several peaks at 1681 and 1689 cm^{-1} for stretching vibration of vinylene bond (linker between monomers), as well as at 971 and 974 cm^{-1} attributed to bending vibration out-of-plan for trans vinylene of C–H bonding respectively [28]. FTIR spectra of polymers P1, P2, and P3 described in Fig. S9–S11 show several peaks at 1671, 1679, and 1659 cm^{-1} for the stretching vibration of the carbonyl group, as well as at 1611, 1609, and 1601 cm^{-1} for the stretching vibration of vinylene bond (linker between monomers), respectively [29].

NMR Analysis

^{1}H-NMR spectrum of F1, described in Fig. S12, shows a singlet signal at 9.59 ppm for aldehydic proton, two doublet signals at 7.51 and 6.77 ppm for aromatic protons, and a singlet signal at 4.63 ppm for protons of ether group. ^{13}C-NMR spectrum of F1, described in Fig. S13, shows several bands which correspond with the number of carbon atoms (having different environments), a band at 178 ppm for the carbon of aldehyde group and 64 ppm for the carbon of ether group [9]. ^{1}H-NMR spectrum of M4, described in Fig. S14, shows a singlet signal at 7.24 ppm for two equivalent aromatic protons, and ^{1}H-NMR spectrum of M5, described in Fig. S15, shows two signals at 7.38 and 7.09 ppm for two aromatic protons [26]. ^{1}H-NMR spectra of W1 and W2 (Fig. S16 and S17) show several bands in the range of 7.46–8.04 ppm for aromatic protons belonging to three aromatic rings that are bonded with phosphorus atoms and one signal at 4.99, and 4.78 ppm for aliphatic protons bonded with phosphorus atoms respectively. ^{1}H-NMR spectra of polymers A1 and A2 (Fig. S18 and S19) show a broad band at 2.2 ppm for aliphatic protons and at 4.4 ppm for protons of the ether group and a multi-band at the range of 6.4–7.6 ppm for aromatic and vinylic protons (cis and trans). Fig. 6 and 7 compare (differences and similarities for the proton NMR spectra of polymers A1 and A2, and their monomers, taking into account some peaks in the spectra of polymers caused by traces of unreacted monomers or terminal aldehyde in polymers [15,30].

EI-Mass and GPC Analysis

The results obtained from the mass spectra for the synthesis dialdehyde (F1) described in Fig. S20 with molecular ion peaks are consistent with the proposed molecular formula of this compound [31].

GPC is an empirical method used to measure molecular weight distribution (MWD) and average molar mass of polymers. The term size-exclusion chromatography (SEC) is sometimes used [32]. So, in this study, the number average molecular weight (M_n)

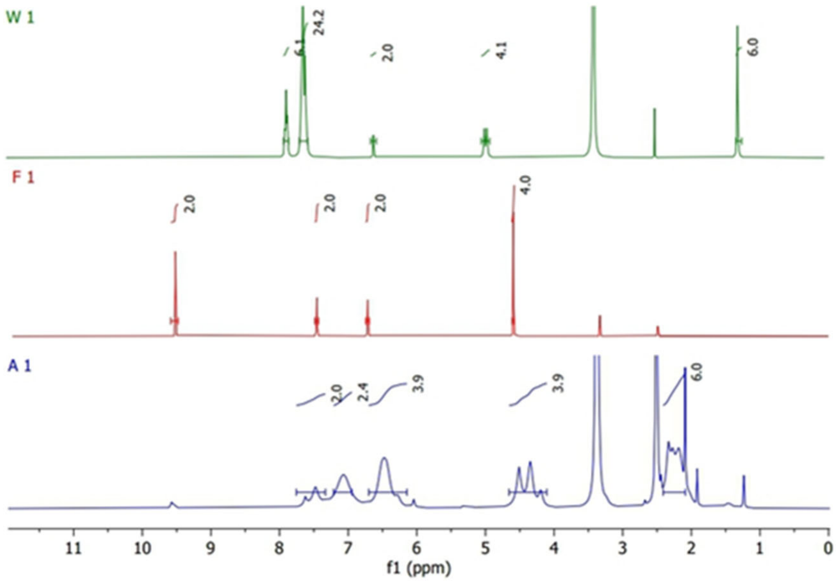


Fig 6. ^{1}H-NMR spectra of polymer A1 with their monomers (F1 and W1) in DMSO

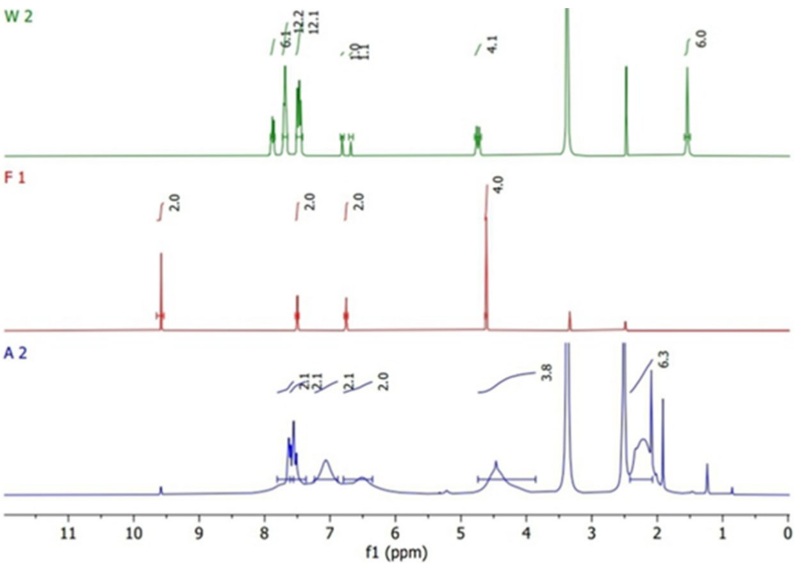


Fig 7. ^{1}H-NMR spectra of polymer A2 with their monomers (F1 and W2) in DMSO

Table 1. GPC analysis results for A1 and A2 polymers

Sample	M_n	M_w	M_v	PD
A1	1828	2182	2121	1.1935
A2	1265	1334	1324	1.0542

and weight average molecular weight (M_w) were determined using the Knauer system in tetrahydrofuran solvent, with a flow rate of 1.00 mL/min and a column set length of 950 nm with 200 mL volume injection. From the results in Table 1 and Fig. S21 and 22, we noted that the order of the different molecular weights of polymers according to their value is as follows: $M_n < M_v < M_w$, here M_v is the viscosity average molecular weight. On the other hand, the polydispersity index (PDI) can be calculated from the Eq. (4) [33].

$$\mathrm{PDI} = \frac{M_w}{M_n} \tag{4}$$

We note that the PDI for the polymers A1 and A2 was 1.1935 and 1.0542. From these values, the polymer chains have some crystallinity in their structure.

TGA Analysis

Polymers have attracted large interest due to their potential as active materials and electronic optical and optoelectronic applications such as LEDs, photodiodes, and photovoltaic cells. Many tests have been conducted on them to evaluate the final properties of polymers to identify the major specifications and, thus, the possibility of determining the final use or application. TGA is a technique used to characterize a wide variety of polymers. TGA measures the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The measurement is used primarily to determine the thermal and oxidative stability of materials as well as their compositional properties. This technique is especially useful for the study of polymeric materials, including thermoplastic, thermosets, elastomers, composites, films, fibers, coatings, and paints [34]. Differential thermogravimetric analysis (DTG) is the first derivative of the rate of weight loss of a substance concerning time or temperature and provides valuable thermal information like optimum degradation temperature [35]. So, in this study, to evaluate the thermal behavior of the prepared polymeric LED (A1, A2, P1, P2, P3) the results of this study were shown in Fig. 8(a–e) and listed in Table 2. Polymer A1 decomposes at temperatures greater than A2 (196 °C, 192 °C), respectively. This may be due to *p*-linkage in polymer A1 compared to *m*-linkage in polymer A2, and this leads to polymer A1 having a lower rate of decomposition (3.31%/min) than A2 (3.82%/min) on the other hand (P1, P2, P3) which differ from each other by the spacer. These polymers have 25, 50, and 75% weight loss temperatures, more than A1 and A2. Also, the rate of decomposition of P3 is

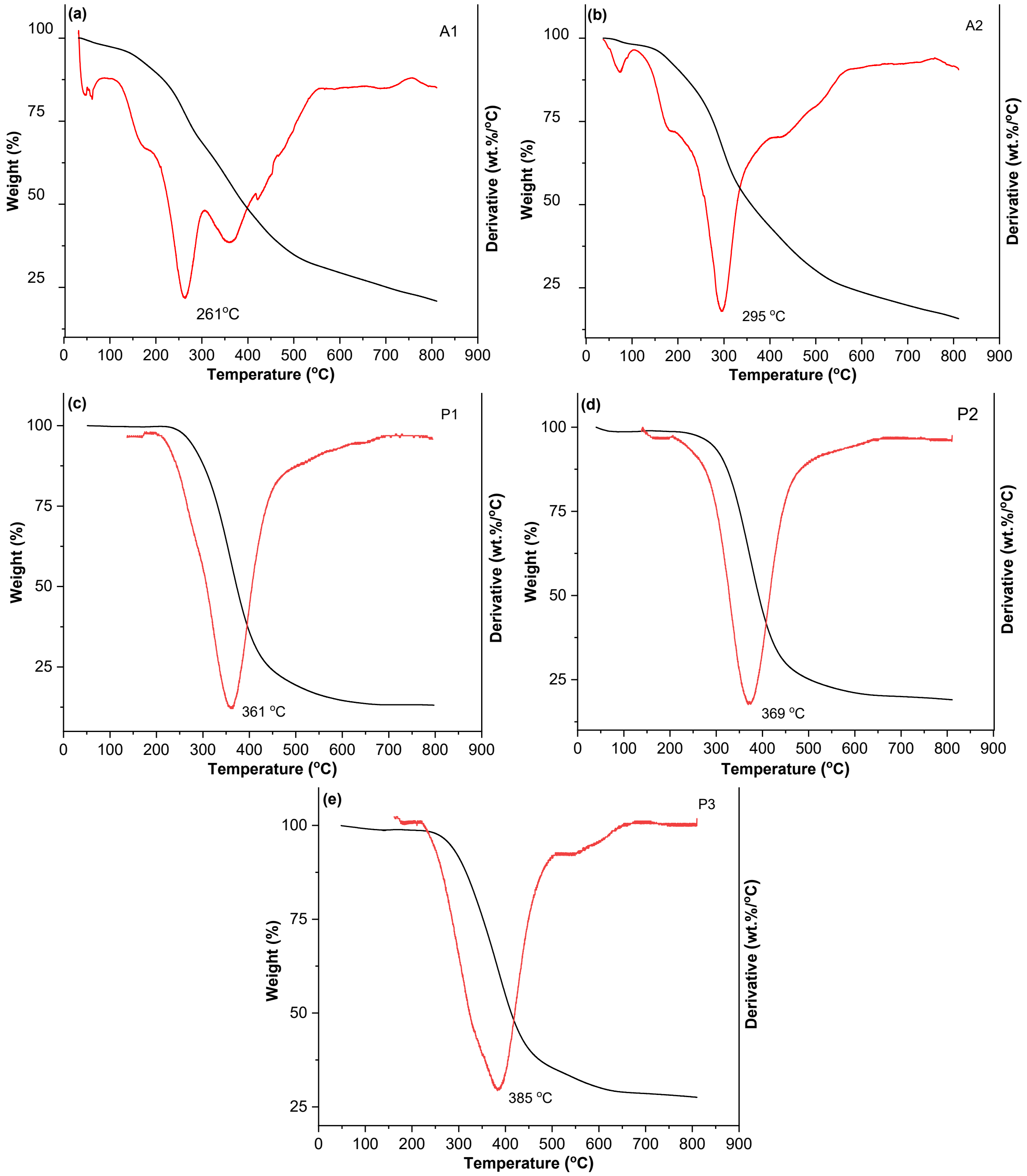


Fig 8. TGA and DTG thermogram 0–800 °C for polymer (a) A1, (b) A2, (c) P1, (d) P2, and (e) P3

Table 2. Results of TGA and DTG analyses (0–800 °C) for polymers A1, A2, P1, P2, P3

Sample	Decomposition temp. (°C)	Optimum degradation temp. (°C)	Temp. of 25% weight loss (°C)	Temp. of 50% weight loss (°C)	Temp. of 75% weight loss (°C)	Char residue (%)	Rate of decomposition (%°C/min)
A1	196	261	271	393	709	21.00	3.31
A2	192	295	276	358	574	16.21	3.82
P1	274	361	332	372	442	12.74	3.19
P2	299	369	347	388	505	22.98	3.48
P3	281	385	351	410	>800	38.91	2.52

lower than that of other polymers, which is due to a more stable cyclohexyl ring structure. Generally, by observing Fig. 8, we note that the dissociation of the prepared polymers begins at 192 °C, which indicates the great thermal stability of the prepared polymers. This is attributed to their containing aromatic structures along the polymeric chain [36].

■ CONCLUSION

We successfully synthesized and analyzed dialdehyde (F1), which features a difuran ring structure. This was done using D-fructose and dewaxed resin at 110 °C, resulting in a good yield and high quality. Two triphenylphosphine salt compounds (W1 and W2) were also synthesized and characterized. Polymers A1 and A2 were obtained through Wittig polycondensation using sodium ethoxide as a base catalyst, followed by characterization via ^{1}H-NMR, FTIR, and GPC. Thermal properties and photoluminescence behavior were evaluated through TGA analysis. Moreover, three polymers (P1, P2, P3) were synthesized via aldol condensation using KOH as a base catalyst, and characterized by FTIR and TGA analyses.

■ ACKNOWLEDGMENTS

We thank the University of Basrah College for all the facilities provided

■ CONFLICT OF INTEREST

The authors declare no conflicts of interest.

■ AUTHOR CONTRIBUTIONS

Widad Salih Hanoosh and Raed Kadim Zaidan were involved in supervision, funding provision, conceiving the experimental design of the study. Wael Sadiq Hanoon was involved in conducting the experiment, data collection, analysis, and writing the manuscript.

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