Synthesis, Characterization, and Fluorescence Study of New Polyesters Derived from Curcumin Analogs

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ARTICLE INFO **ABSTRACT**

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This work describes the synthesis, characterization, and evaluation of a new series of polyesters. The polyesters were synthesized by condensation polymerization using curcumin analogs as one monomer while the other monomer was of sebacoyl chloride and adipoyl chloride. The chalcones monomers were prepared by aldol condensation reactions. The structure of the prepared polyesters was characterized by FTIR spectra. The thermal stability of the new polymers was measured by thermogravimetric method. The solubility of the polymers in organic solvents was also studied. The prepared polyesters were found to possess fluorescent properties and some of them were found to have good emissive properties.

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1. Introduction

Curcumin, denoted by the chemical formula diferuloylmethane, represents the primary curcuminoid compound present in the roots of turmeric. A perennial herb belonging to the ginger family (Zingiberaceae), the Curcuma plant (Curcuma longa L.) is used to make curry. Turmeric's tuberous rhizome serves as a color, spice (which can take the place of ginger), and medicinal herb. Around 500 BCE, turmeric initially started to play a significant role in Ayurvedic treatment. Three of the most important curcuminoids are curcumin, demethoxycurcumin, and bisdemethoxycurcumin. Curcumin has antioxidant, anti-amyloid, anti-microbial, anti-tumor, immune-modulating, and neuroprotective effects. Curcumin also shown antidepressant qualities via regulating serotonin and dopamine release [1], [2]. Polyesters contain at least one Ester group per repeating unit within the main chain of the polymer. Polyesters can be obtained by the reaction of dicarboxylic acids with dihydroxy compounds or their derivatives, and there are other methods used to prepare this type of polymers [3]. Polyesters are classified as one of the most versatile industrial polymers due to their excellent properties [4]. Polyesters can be characterized as either naturally derived or chemically produced. Natural polyesters are distinguished by their biodegradability, whereas synthetic polyesters are typically not biodegradable in normal environmental conditions, but they decompose readily in specific chemical environments by splitting or dissolving ester bonds in the polymer chain, which, upon complete dissolution, result in the formation of monomers [5], [6]. Polyesters are divided into aromatic and aliphatic categories based on their chemical makeup, with the aromatic or aliphatic classification having an impact on the polyester's mechanical and thermal qualities. Linear polyesters are classified into three groups [7]:

1- aliphatic polyesters

They are semi-crystalline polymers or viscous liquids possessing a low melting point (40-80 ˚C) and have poor mechanical properties.

2- aromatic polyesters

They are either amorphous polymers with a high glass transition degree or semi-crystalline polymers with a high melting point and often exhibit crystalline properties.

3- aliphatic-aromatic polyesters

They are semi-crystalline polymers with a high melting point (150-270 ˚C) containing the aliphatic group in addition to the aromatic group, used in thermoplastic, fiber and film engineering applications.

2. Experimental

2.1. Chemicals

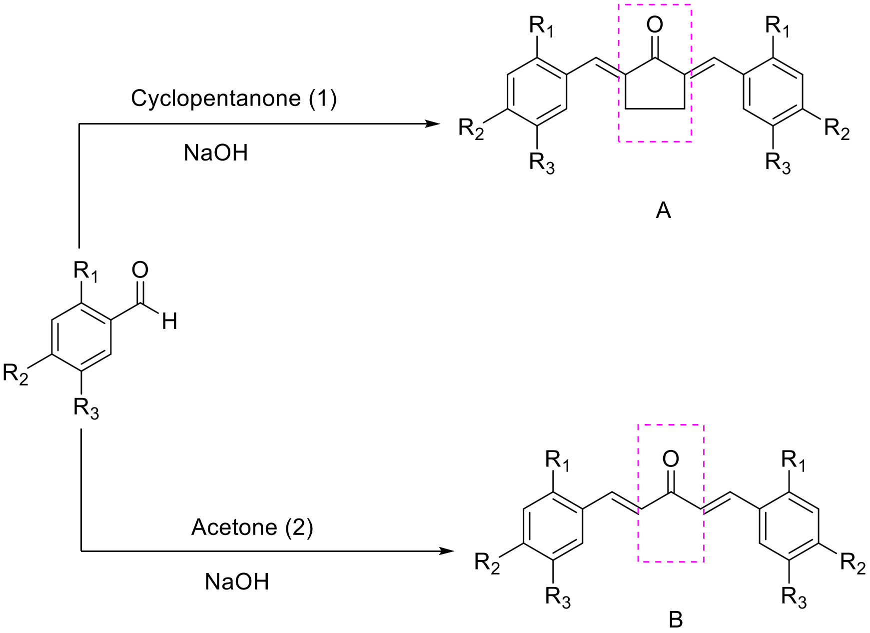
The chemicals p-vanillin and cyclopentanone were supplied from Merck company. Dimethyl sulfoxide and 1,2-Dichloroethane were obtained from HIMEDIA company. methanol, acetone, hydrochloric acid, n-Hexane and ethanol were purchased from Baker company. adipoyl chloride, sebacoyl chloride, salicylaldehyde, sodium hydroxide and triethylamine from Sigma-Aldrich company.

2.2. Methods

IR spectra were recorded on Bruker AlphaII- FT-IR spectrometer within the wavenumber range of 400–4000 cm^{-1}. Thermogravimetric analysis was carried out using a Shimadzu TGA-50 thermogravimetric analyzer, under nitrogen flow (30 mL/ min) at a heating rate of 20 °C/min from 30 to 600 °C. Absorption spectra were run on a Shimadzu-UV-1800 spectrophotometer. Absorption studies were conducted on a SHIMADZU model 1800 UV Visible spectrophotometer between 200–800 nm. The Fluorescence spectra were performed using a Fluo time 300 spectrophotometer.

2.3. Synthesis of Curcumin Analogs

The curcumin analogs (A and G) was synthesized based on the modified steps previously reported [8]. Dissolve (0.02 mol) of suitable aldehyde in 2.5 ml of ethanol the solution was placed in a glass flask with one opening under constant stirring at room temperature. Then (0.01 mol) of the appropriate Ketone was added to the solution and shaken vigorously, NaOH (20% ,50ml) was added to the solution in the form of drops while maintaining the temperature below 40 ˚C and leaving the reaction for 24 hours under constant stirring. where the formation of a solution with a red color was observed and the reaction was followed up by thin layer chromatography technique. After the end of the reaction, 15 ml of cold distilled water was added to the solution and it was equalized (pH=5.5) using HCl (6N), where the formation of a precipitate with a yellow color was observed it was purified by recrystallization using methanol. Scheme 1 shows the synthesis of curcumin analogs based on (Table 1).



Scheme 1. Synthesis of Curcumin Analogs

2,5-bis (4-Hydroxy-3-methoxybenzylidene) cyclopentanone (A)

FTIR (cm^{-1}) 3290, 3030, 2924, 1664, 1597 and 1261. ^{1}H NMR (400 MHz, DMSO-d6) δ 9.69 (s, 2H), 7.36 (s, 2H), 7.24 (s, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.2 Hz, 2H), 3.84 (s, 6H), 3.06 (s, 3H).

1,5-bis(2-Hydroxybenzylidene)-1,4-pentandiene-3-one (B)

FTIR (cm^{-1}) 3356, 3070, 2960, 1647, 1608 and 1246. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.29 (s, 1H), 7.93 (d, *J* = 16.1 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 16.1 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H).

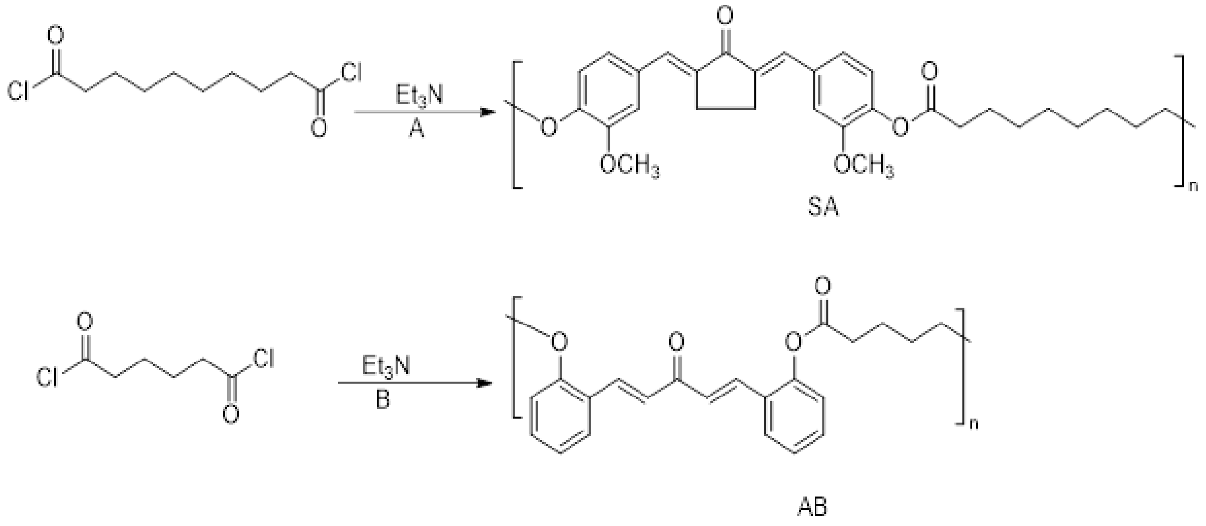
Table 1: Synthesis of curcumin A,B based on Scheme 1

Sym.	R_1	R_2	R_3	R_f	Yield (%)	Mp (˚C)	Ketone unit
A	H	OH	OCH_3	0.25	83	212-214	1
B	OH	H	H	0.14	72	154-156	2

2.4. Preparation of polyester

In a three necked round bottom flask, 0.002 mol of the chalcone compounds (A, B) and 0.004 mol of triethyl amine was dissolved in 30 mL of 1,2-dichloroethane. The resulting solution was left for stirring under argon atmosphere for an hour. then adipoyl chloride or sebacoyl chloride (0.002 mol, in a minimum amount of EDC) was added drop wise to this solution.

. The reaction mixture was left for 24 hours under constant stirring, where the formation of a yellow precipitate was observed. for complete precipitation of the polymers, 200 ml of n-hexane was added. the formed polymer was filtered and washed with n-hexane, and recrystallized from methanol. Scheme 3 shows the synthesis of polymers [9]



Scheme 2: Synthesis of Polyester

3. Results and discussion

3.1. FTIR Spectra of prepared polyester

Figures (1-2) show the FTIR spectra of prepared polymers and Table 2 shows the most important peaks of these polymers.

Table 2: The FTIR of prepared polymer

Polymer	**v (cm^{-1})**				
	Stretching				
	C-H **Aromatic**	**C-H** **Aliphatic**	**C=O**	**C=C**	**C-O-C** **Ether**
SA	3074	2926	1690	1584	1758
AB	3069	2929	1665	1608	1752

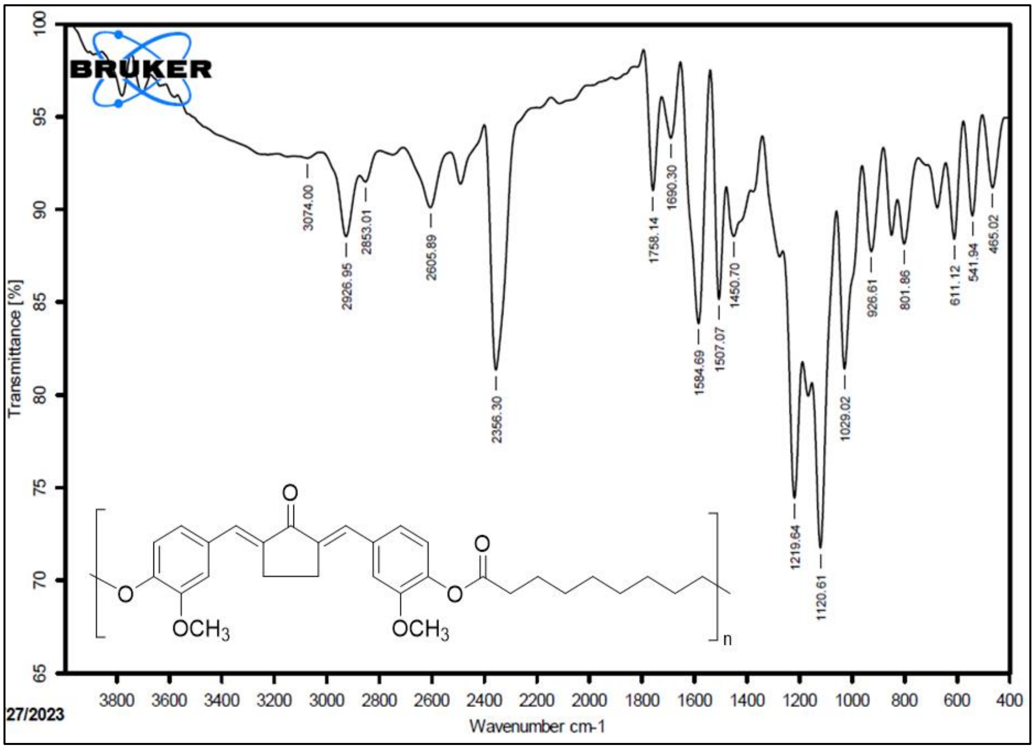


Fig. 1: FTIR spectrum of SA polymer

The FT-IR spectrum of synthesized polyesters showed the presence of common bands in the prepared polymers. Conclusive evidence of the formation of the polymers is shown by the observation that new bands in the FTIR spectra of the polymers appear at 1752-1758 cm^{-1} assigned to ester bond. Also, the decay of the band belonging to the hydroxyl groups is an indication of the correctness of preparing the polymers. In addition to a group of bands resulting from the stretching and bending vibration of the active groups present in its composition, such as the double bond, the carbonyl ketone group [10].

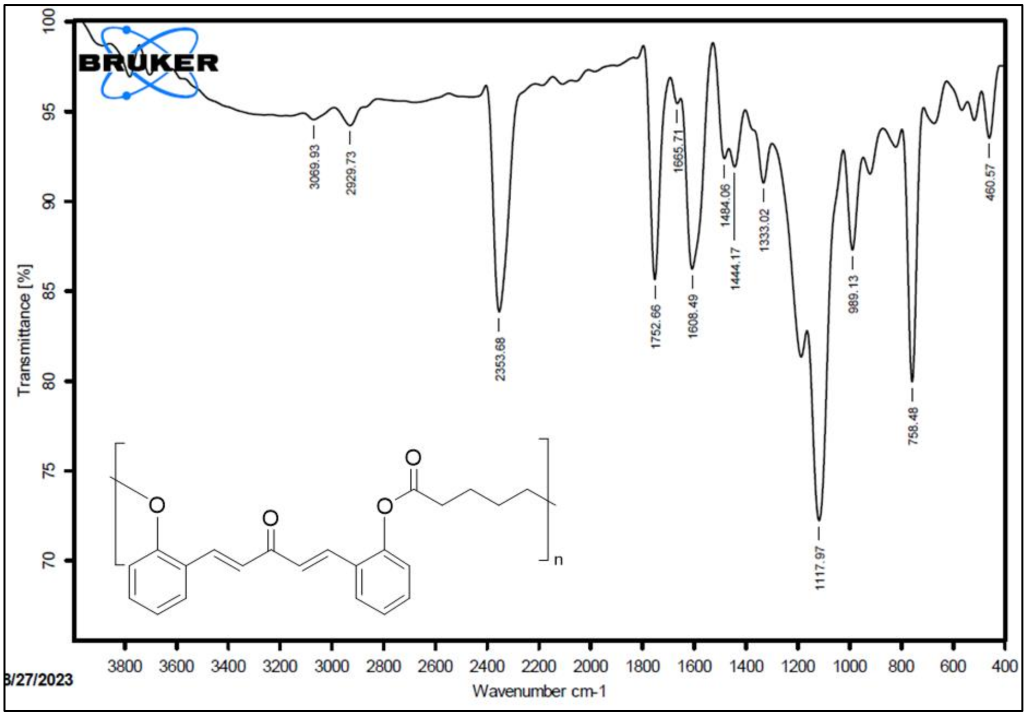


Fig. 2: FTIR spectrum of AB polymer

3.2 Thermal study of prepared polymers

One of the fundamental aspects of research in polymer science is the study of polymer thermal stability because one of the characteristics that distinguishes polymers is the change in their properties as a function of temperature, and this characteristic depends on the majority of polymer manufacturing processes and their various uses. Thermal dissociation of polymers is the reaction a polymer exhibits to a rise in temperature, at which point the polymer starts to break down or disintegrate along with the release of gases that are specific to the type and content of the polymer [11], [12]. In addition to the length of the polymeric chain (molecular weight), the degree of crosslinking between the polymeric chains, and the presence of aromatic structures, the chemical composition of the polymer, particularly the composition of the repeating unit, has a major impact on the polymer's thermal resistance[13]. The objective of measuring the thermal analysis of the prepared polymers is to calculate many important functions in understanding the thermal behavior of polymers, and among these functions is calculate the weight loss percentage at any temperature and the percentage of the remaining polymer after the Char residue process. Calculate the decomposition temperature (which can be set in two degrees It is the initial degree of dissociation (T_i) and the final degree of dissociation (T_f)[14].The thermogravimetric analysis of the prepared polymers was measured in the range (30-600 ˚C) with a constant heating rate (20˚C.min^{-1}) in the presence of an inert atmosphere of nitrogen gas. From the (TGA) curves (Figures 3-4) for the prepared polymers. Table 3 shows the most important values obtained from the thermo gravimetric analysis curves of the prepared polymers. The polymer SA had one stages of decomposition was at (377-545 ˚C), while the polymer AB had two stages decomposing the first one was at (280-424 ˚C) while the second decomposing was at (451-549 ˚C). Observing the results, it can be seen that the synthesized polymers decompose at various rates and have a high degree of stability. The different chemical structures of the chalcone polyethers polymer are what cause the variations in the stages of breakdown. The stability is improved by the presence of aromatic structures. The produced polymers' exceptional heat stability is shown by the substantial residual polymer content. The initial phase of weight loss was attributed to the elimination of tiny molecules like water based on the degradation curves. Due to the removal of bigger molecules such aromatic rings and other fragments of the polymer backbone, the second face of weight loss was discovered. Non-volatile ash is among the residual materials above the ultimate temperature [15], [16]. From the TGA graphical figures and data for the prepared polymers, the activation energy (Ea) was determined using Broido 1965 model as showed in the equation below [17]:

$$\ln \ln \left\{\frac{1}{Y}\right\} = -\frac{Ea}{RT} \text{........} 1$$

Where:

$$Y = \frac{Wt - W\infty}{Wi - W\infty}$$

Wi= The initial weight of the polymer

Wt= Weight at any temperature of the polymer

R= General constant of gases

T= The temperature range measured at Wt

Plotting graphs between ln[ln(1/y)] vs 1/T gives a straight line. The slope is related to the activation energy W∞= The final weight of the polymer.

Table 3: Values obtained from TGA curves to prepared polyesters

Sym.	Decomp. Stage	T_i (˚C)	T_f (˚C)	T_{op} (˚C)	Weight loss (%)	Rate of Decomp. ($\%.min^{-1}$)	Char Residue 530 ˚C (%)	Activation Energy $KJ.mol^{-1}$	Temp. Range for Activation Energy (˚C)
SA	1st Decomp.	377	545	430	44.085	2.02	56	57.91	380-490
AB	1st Decomp.	280	424	370	16.631	0.97	72	-	-
	2st Decomp.	451	549	500	9.534	0.43		63.01	420-475

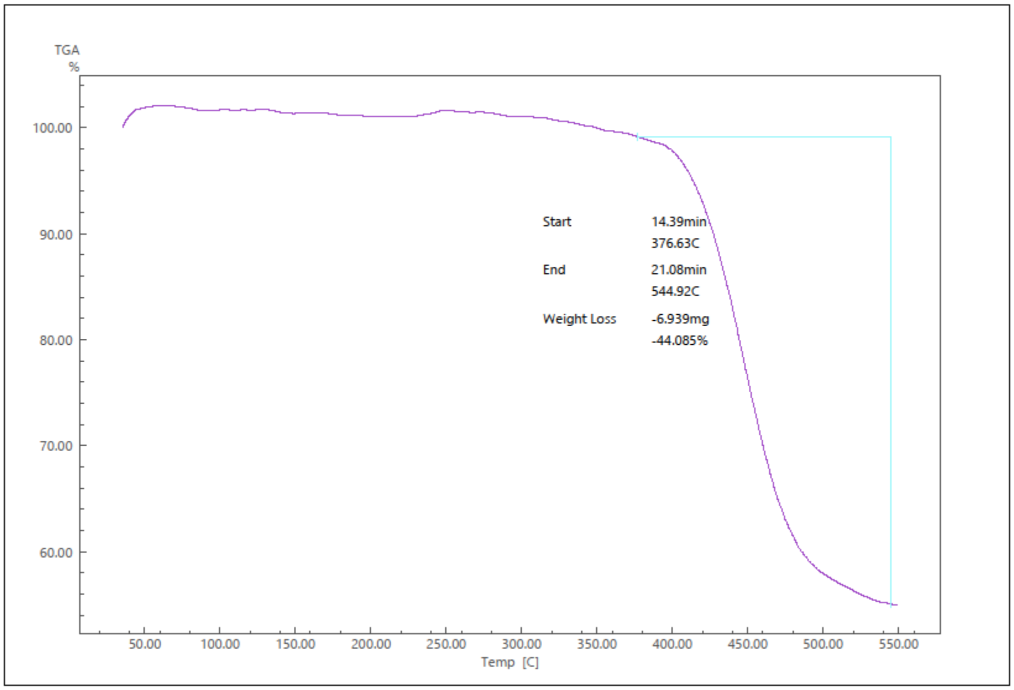


Fig. 3: TGA of SA polymer

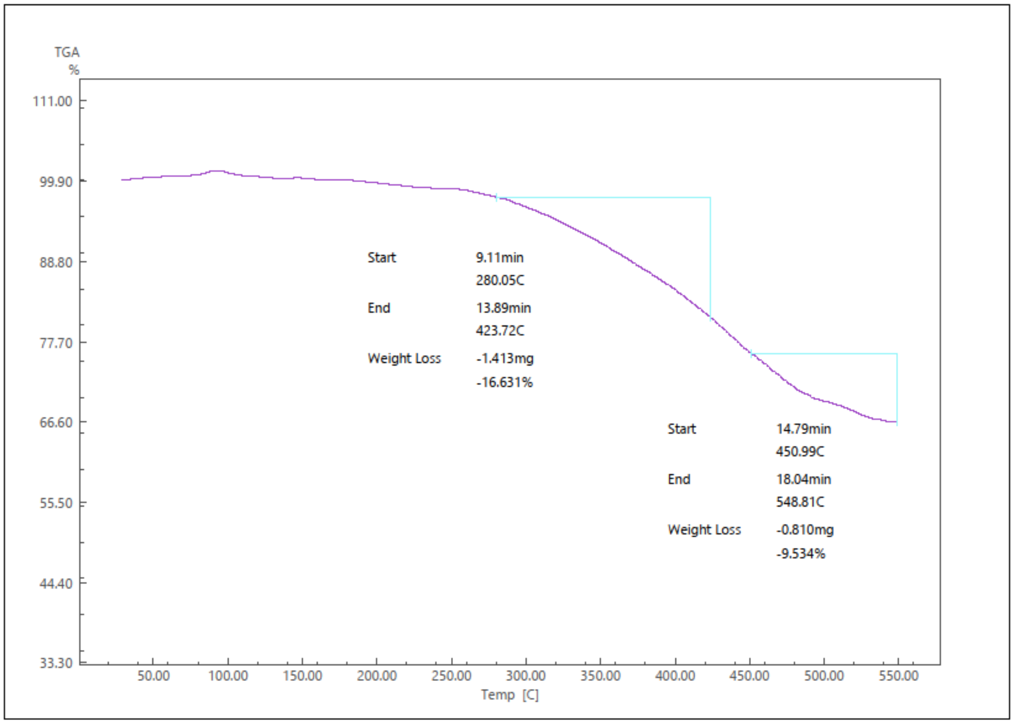


Fig. 4: TGA of AB polymer

3.3. Evaluation of the solubility of the prepared polymers

The solubility of the prepared polymers was conducted in most commonly used organic solvents. The test results showed that prepared polymers dissolved in the two aprotic solvents, namely DMSO and N-methyl pyrrolidone. polymers gave negative results with acetone (aprotic solvent), ethanol, methanol (protic solvents), toluene, chloroform, tetrahydrofuran, and dichloromethane, but their solubility in DMF (aprotic solvent) varied between total solubility in some polymers and partial solubility in other polymers.

Table 4: The solubility of polymers in different solvents

Sym.	**Solvents**			
	DMSO	**DMF**	**N-methyl pyrrolidone**	***Solvents**
SA	+	$+^*$	+	-
AB	+	$+^*$	+	-

(+) soluble; (-) insoluble; ($+^*$) partial soluble

3.5. The photophysical properties

The UV-vis absorption and Fluorescence spectra of the prepared polychalcones were recorded in diluted dimethyl sulfoxide solutions (Figures 5-6). Table 5 summarizes the spectral data and Energy gap values which obtained from these curves. The absorption spectra of prepared polymers show the appearance of absorption peaks at low energy (high wavelength) and this is due to the electronic transition ($\pi \rightarrow \pi^*$) regarding to double bonds. The higher the number of successive double bonds in the polymer leads to the higher the value of the maximum wavelength. An increase in the length of the chromophore and the presence of substituents such as (OH and OCH_3) in some polymers leads to an increase in wavelength.

From the obtained values, we note the variation in the fluorescence intensity of the polymer, as the polymer SA possessed a high fluorination density while the polymer AB had a lower density, and this is due to several factors. Among these factors is the chemical composition, in which the presence of effective electron-driven aggregates such as (OCH_3, OH) leads to a shift towards a higher wavelength (red shift), which leads to green emission and, accordingly, leads to an increase in the intensity of fluorescence. As we can see that the prepared polymers have different structures which is resulted from the condensation reaction of different monomers. This will be reflected on the nature of the resulting Spectra and the extent to which the polymer is affected by the intensity of radiation. This difference between the prepared polymers in terms of the nature of the fluorescence and absorption spectra may be due to many factors. One of the factors is the molecular weight of the prepared polymers, as is known for polymers, an increase in molecular weight leads to an increase in viscosity. As an increase in molecular weight means an increase in the lengths of polymer chains, which leads to a decrease in the movement of those chains, and therefore the rate of collisions between large polymer molecules decreases, and this reduces energy dissipation and increases the intensity of florescence. One of the factors that lead to reducing the intensity of florescence is the ultraviolet radiation used to excite the sample to lead to the breakdown or disintegration of the fluorescence compound, and intramolecular or intermolecular reactions, including excited state reactions and energy dissipation, reduce the intensity of florescence [18], [19].

Table 5: Absorption and Fluorescence data of polyesters

Sym.	**Absorption**		**Fluorescence**	
	λ max)nm(	**Eg (ev)**	**λ max)nm(**	**I max**
SA	**395**	**2.55**	**524**	**25723**
AB	**322**	**3.23**	**403**	**19097**

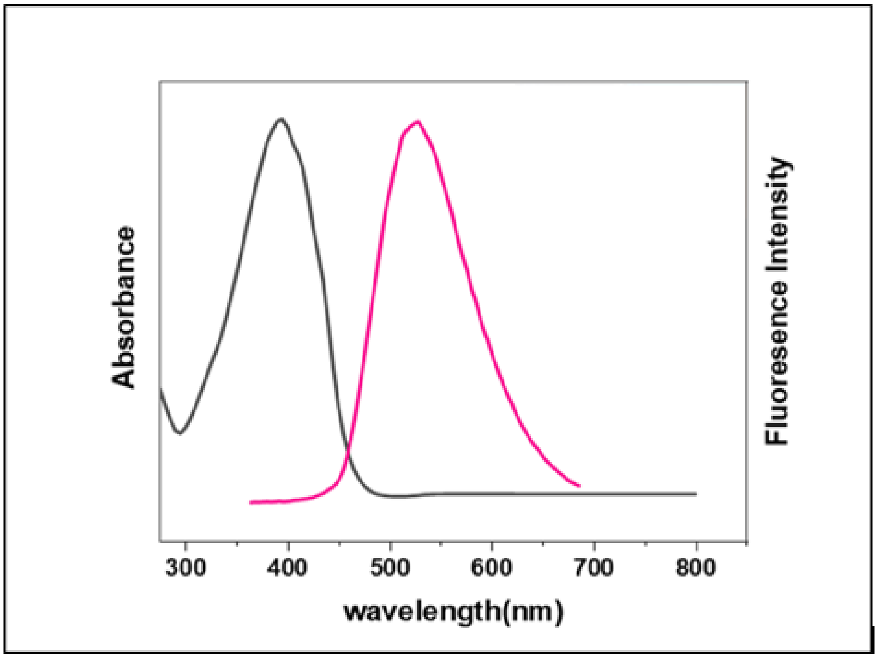


Fig.5: Fluorescence of SA polymer

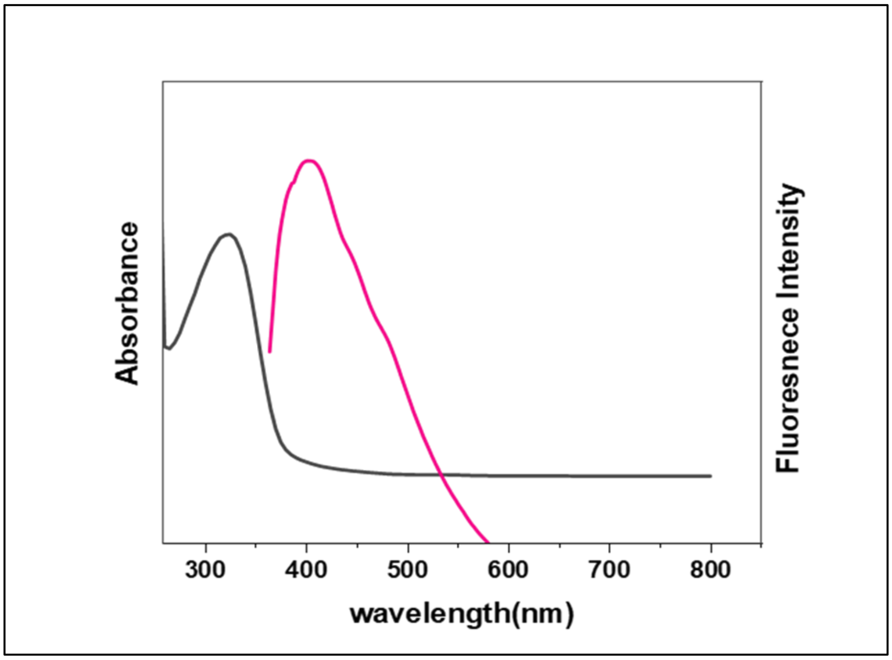


Fig.6: Fluorescence of AB polymer

4. Conclusions

In this study a new chalcone polyesters was synthesized by the condensation polymerization of curcumin analogs monomers with diacid halide. These polymers were then analyzed using infrared spectroscopy and their stability was assessed using thermal gravimetric analysis. The results indicated that the chalcone polyesters showed stability holding up well between 280-450 °C. This suggests that they could be potentially useful, as thermoplastics, in fields, including medicine. Moreover, the two synthesized polyesters exhibited fluorescence when dissolved in solution of DMSO although the intensity and absorption varied based on the properties of each polymer.

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تحضير، تشخيص، ودراسة التألق لبولي استرات جديدة مشتقة من نظائر الكركمين

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المستخلص

يصف هذا البحث تحضير وتشخيص وتقييم سلسلة جديدة من البوليسترات. تم تحضير البوليسترات عن طريق بلمرة التكثيف باستخدام نظائر الكركمين كاحد المونمرات بينما كان المونومر الآخر عبارة عن كلوريد السيباكويل وكلوريد الاديبويل. تم تحضير مونومرات الجالكونات بواسطة تفاعلات تكاثف الالدول. تم تشخيص تراكيب البوليسترات المحضرة باستخدام أطياف الاشعة تحت الحمراء FTIR. تم قياس الثبات الحراري للبوليمرات الجديدة عن طريق التحليل الحراري الوزني. كما تمت دراسة قابلية ذوبان البوليمرات في المذيبات العضوية. وقد وجد أن البوليسترات المحضرة تمتلك خواص التألق وبعضها له خواص انبعاثية جيدة.