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Synthesis and Characterization of Some New Copolyester from Curcumin Mono-Carbonyl Analogues

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ABSTRACT

Nine copolyesters were prepared from a dicarboxylic acid, curcumin analogues (monocarbonyl) and phenophthalene dye in the mole ratio of 2:1:1 by direct polycondensation using triethylamine (Et_3N) as the condensation agent. The dicarboxylic used is 2,6-Pyridine dicarbonyl dichloride acid. The curcumin analogues were prepared by acid catalyzed Aldol condensation reaction. These copolyesters were characterized by FT-IR. The fluorescence of the synthesized copolyesters was also investigated. Furthermore, Thermo gravimetric analysis (TGA) was used to investigate the thermal stability of these copolymers.

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1. Introduction

Polyesters are containing at least one group of ester per repeating unit within the main polymer chain (Deopura, et al., 2008). Polyester is considered as one of the most important industrial polymers because of its excellent properties. The polyesters are either natural or industrially prepared (Valerio, et al., 2018; Goodlaxson, et al., 2018). The natural polyesters are characterized by their ability to biodegradation, while the industrially polyester prepared are mostly non-biodegradable (Yousif, et al., 2012), and possess high moisture resistance, fire resistance, good thermal properties and environmentally stable (Mittal, 2011).

Polyesters have been classified according to the structure of their main chain into aliphatic and aromatic compounds (Oral, et al., 2018; Hongsriphan & Sanga, 2018). Such polymers can be synthesized via a variety of reactions, the most important of which is the interaction of dicarboxylic acids and dihydroxy compounds or their derivatives, as well as other reactions such as (Budriene, 2002):

1. The reaction between dicarboxylic acids and di-alkyl halides
2. The reaction between dihydroxy compounds with halides of organic acids (Lecomte & Jérôme, 2011)

Polyesters are used in high-tech industrial applications such as production and energy conversion devices, textile materials, biomedical devices (Oral, et al., 2018; Hongsriphan & Sanga, 2018), as well as in the manufacture of chips, tapes, seals and wire insulation. Composite materials were used that depend on polyester resins supported with glass fibers. In the manufacture of car body parts and watercraft (Rachchh & Trivedi, 2018). Polyesters are used as biomaterials in medical applications such as surgical sutures and scaffolds within tissue engineering (Ahlinder, et al., 2020; Ahlinder, et al., 2018). In this study, we were interested to preparation and characterized certain copolyester possessing curcumin mono-carbonyl analogues moiety in the polymer.

2. Materials and Methods

2.1. Chemicals

The chemicals P-hydroxybenzaldehyde, Ortho-Vanillin, Salicylaldehyde, cyclopentanone, cyclohexanone, triethylamine, 2,6-pyridine dicarbonyl dichloride and

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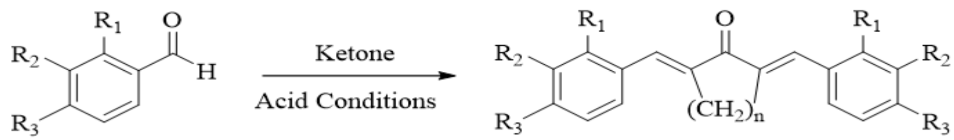
phenolphthalein were purchased from Sigma-Aldrich company while acetone and dichloromethane were purchased from VWR company and hydrochloric acetic acid and n-hexane were purchased from Barker company and used as received.

2.2. Preparation of Curcumin Mono-Carbonyl Analogues

A mixture of appropriate ketone (0.005 mol) and appropriate aldehyde (0.01 mol) was placed in one neck round flask and dissolved in absolute ethanol (15 ml). To this solution, a mixture of glacial acetic acid and anhydrous hydrogen chloride was added (10:1, ratio) drop wise and the mixture was left under continuous stirring for two hours, a clear solution of violet color was formed. Then, the mixture was left to stand for two days (eleven days for the compound C) at room temperature where a green precipitate was filtered, washed with 5 ml of cold distilled water and dried. Purification was carried out by recrystallization using ethanol, and a green precipitate of (A, B, C, D, E and F) compounds and yellow precipitate of (G, H and I) compounds were obtained. Scheme 1 shows synthesis of curcumin mono-carbonyl analogues.



A : (n = 3 , R_1= R_2=H, R_3= OH)

B : (n = 2 , R_1= R_2=H, R_3= OH)

C : (n = 0 , R_1= R_2=H, R_3= OH)

D : (n = 3 , R_1=OH, R_2= R_3= H)

E : (n = 2 , R1=OH, R2= R3= H)

F :(n = 0 , R1=OH, R2= R3= H)

G : (n = 3 , R1=OH, R2=OMe, R3= H)

H : (n = 2 , R1=OH, R2=OMe, R3= H)

I :(n = 0 , R1=OH, R2=OMe, R3= H)

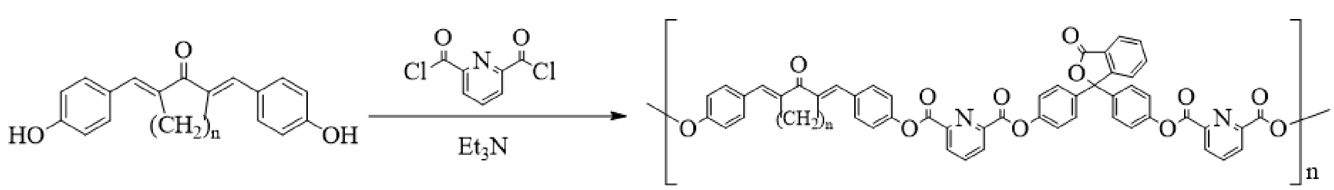
Scheme 1 Synthesis of curcumin mono-carbonyl analogues
Source: Du, et al., (2006)

2.3. Preparation of Copolymer Compounds (PA1-PI1)

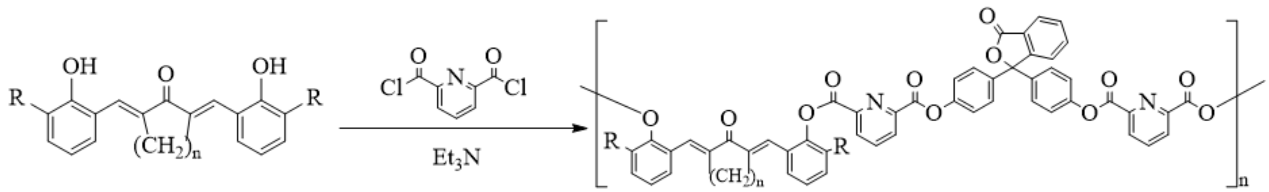
The polymers (PA1-PI1) were prepared by dissolving an appropriate curcumin analogue (0.002 mol) and phenolphthalein (0.002 mol) in dichloromethane (50 ml). Then, the mixture was placed in a three-nick round flask under constant stirring at room temperature (Morgan, 1964). Triethylamine (0.008 mol) was added, and the mixture was stirred continuously for 90 minutes at 10 °C, making the reaction environment inert by shedding nitrogen gas and tightly closing the flask nozzles. After that, 2,6-pyridine dicarbonyl dichloride (0.004 mol) dissolved in dichloromethane (50 ml) was added dropwise to the mixture for 60 minutes at 10 °C, and the reaction was left for 24 hours with continuous stirring. The resulting polymer was precipitated by adding the solution to a beaker containing 300 ml of (n-hexane) and waiting for a while for the sedimentation to complete. The polymer was then filtered, washed with n-hexane, and allowed to dry at room temperature. Table 1 shows the quantities of monomers used and the yield of the polymerization reactions, while Schemes 2, 3, & 4 show the preparation reactions:

Table 1
The quantities of monomers used and the yield of the polymerization reaction

Sym	Curcumin amount (gm)	2,6-pyredinedicarbonyldichloride amount (gm)	Yield %
PA1	0.61	0.82	88.852
PB1	0.60	0.82	71.868
PC1	0.53	0.82	83.102
PD1	0.73	0.82	71.721
PE1	0.70	0.82	78.414
PF1	0.65	0.82	75.026
PG1	0.61	0.82	80.862
PH1	0.60	0.82	67.849
PI1	0.53	0.82	87.565

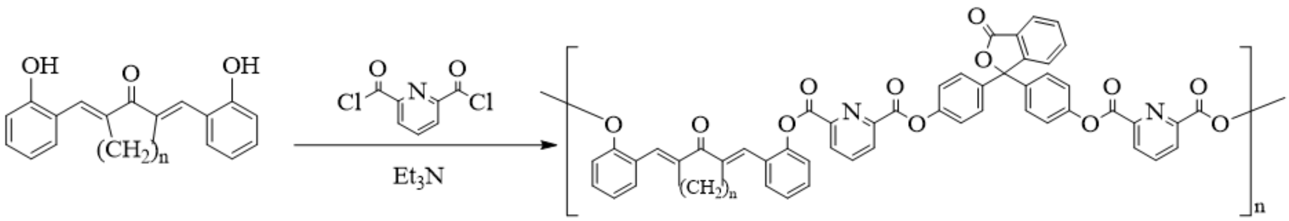


Scheme 2 Preparation equation of A, B and C copolyesters



D: n=3, E: n=2, F: n=0 , R=OMe

Scheme 3 Preparation equation of D, E and F copolyesters



G: n=3, H: n=2, I: n=0

Scheme 4 Preparation equation of G, H and I copolyesters

3. Results and Discussion

3.1. FT-IR Spectra of Prepared Polymers (PA-PI)

The FT-IR spectrum of synthesized copolyesters showed the presence of common bands in all the prepared polymers, and the Table 2 shows the locations of the bands, and Figures from 1 to 9 to the FT-IR spectra of the prepared polymers, where it was observed that absorption bands appeared at (1754-1763 cm^{-1}) indicating the formation of the 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 (Silverstein, 1974).

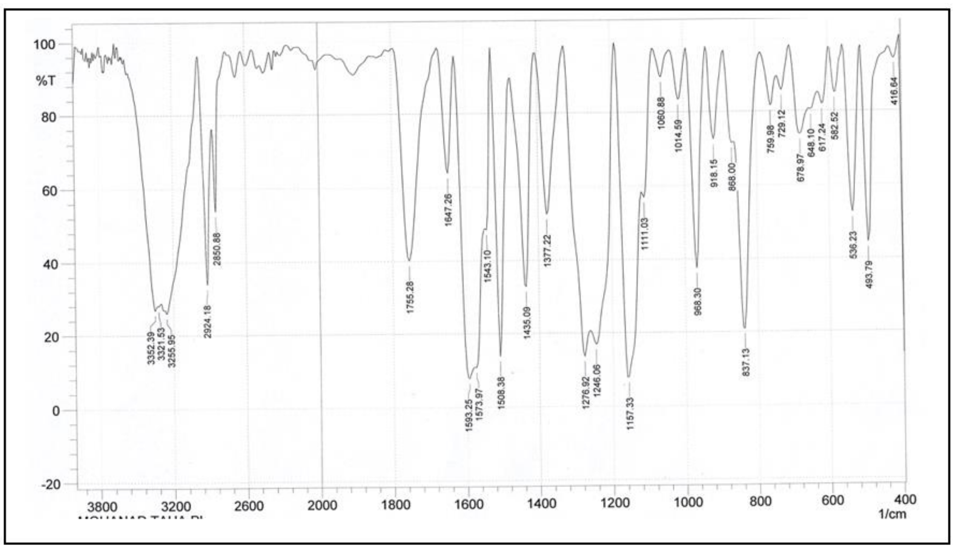


Fig. 1. FT-IR spectrum of PA polyester

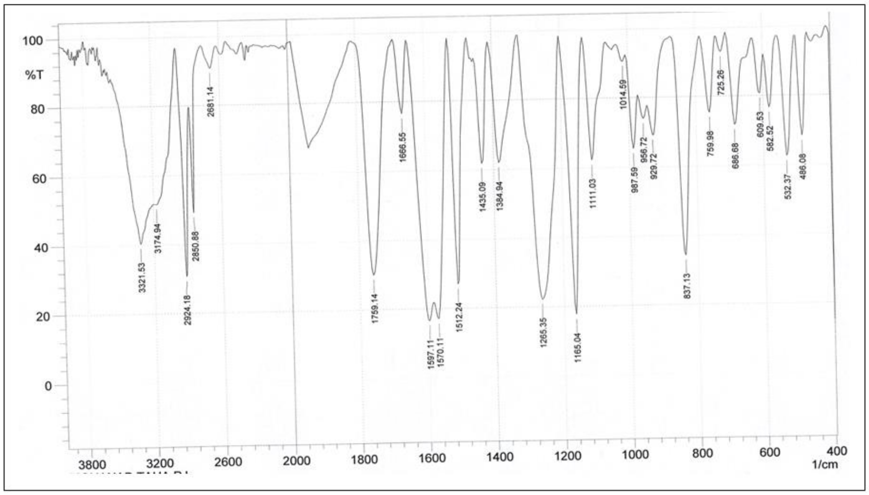


Fig. 2. FT-IR spectrum of PB polyester

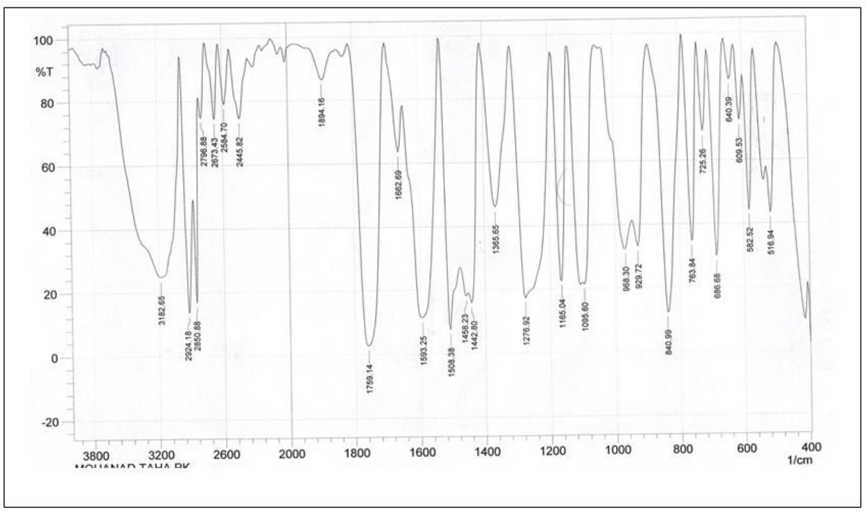


Fig. 3. FT-IR spectrum of PC polyester

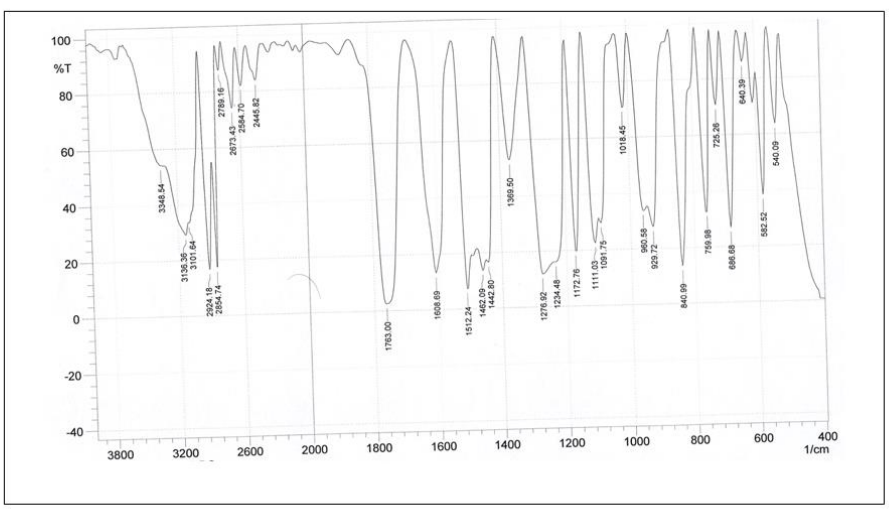


Fig. 4. FT-IR spectrum of PD polyester

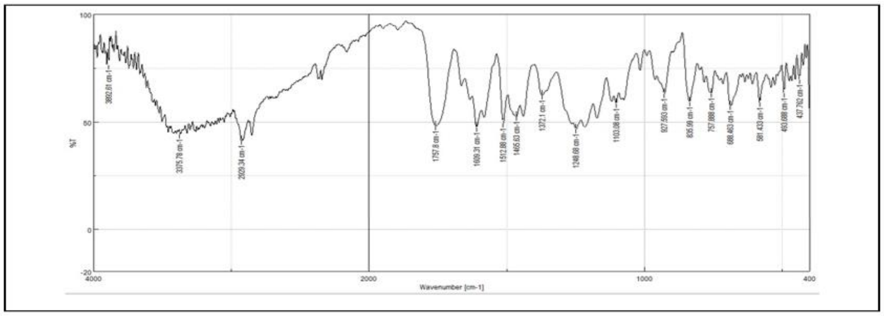


Fig. 5. FT-IR spectrum of PE polyester

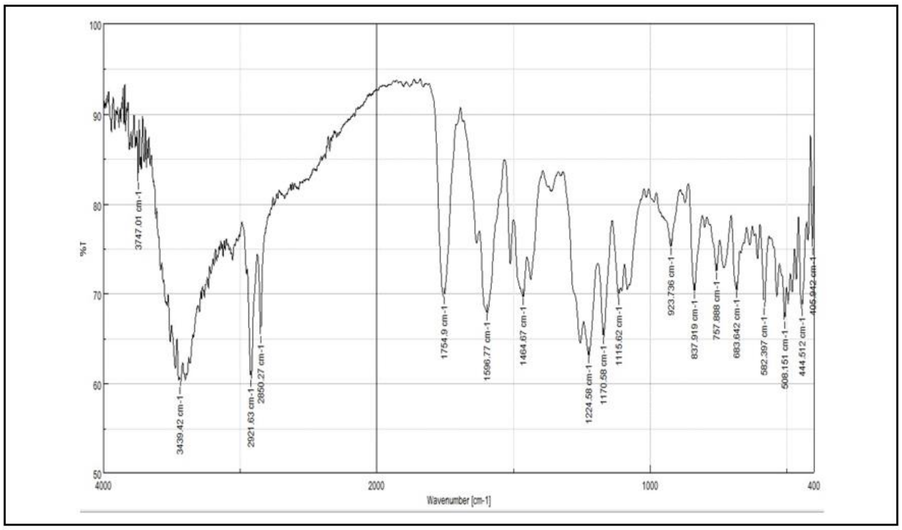


Fig. 6. FT-IR spectrum of PF polyester

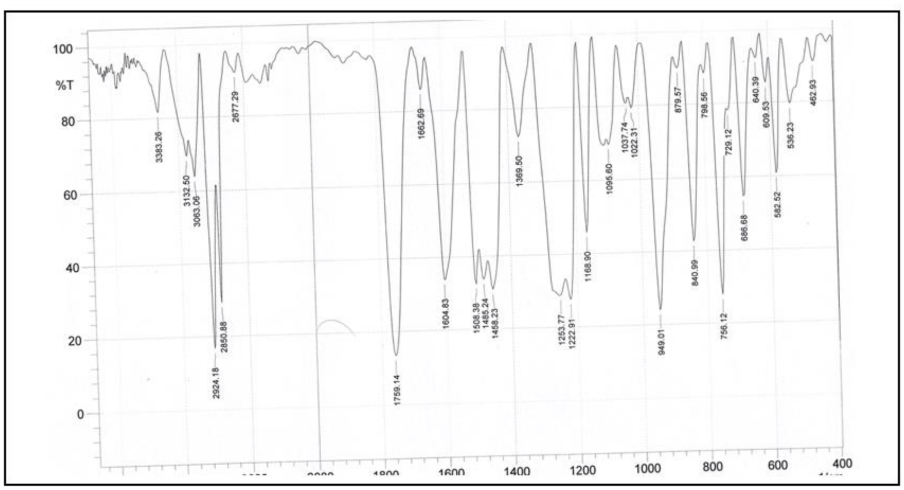


Fig. 7. FT-IR spectrum of PG polyester

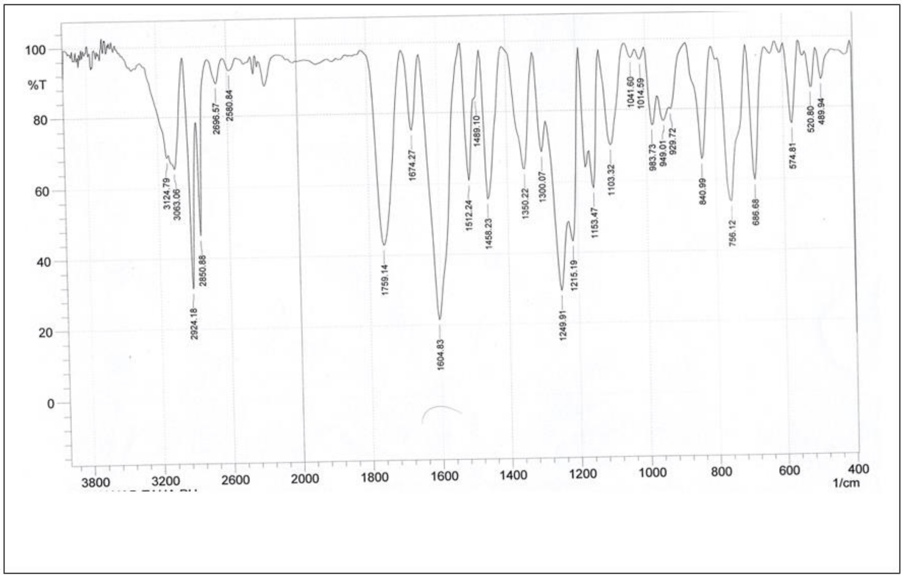


Fig. 8. FT-IR spectrum of PH polyester

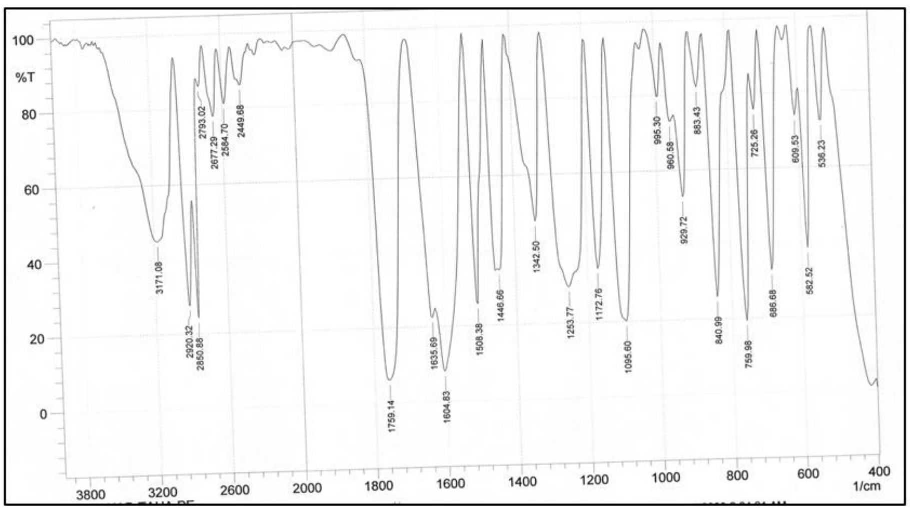


Fig. 9. FT- IR spectrum of PI polyester

Table 2
IR data of prepared polymers (PA-PI) phph

SYM			υ (cm⁻¹) Stretching		
	C-H Ar	C-H Al	C=O ester	C=C	C=O
PA	3255	2924	1755	1647	1593
PB	3174	2924	1759	1666	1597
PC	3182	2924	1759	1662	1593
PD	3136	2924	1763	1608	1512
PE	3375	2929	1757	1609	1512
PF	3439	2921	1754		1596
PG	3063	2924	1759	1662	1604
PH	3063	2924	1759	1674	1604
PI	3171	2920	1759	1635	1604

3.2. Thermal Study of Prepared Polymers

The study of thermal stability of polymers is one of the basic features of research in polymer science, because one of the distinguishing characteristics of polymers is the change of their properties as a function of temperature, and this characteristic depends on most methods of manufacturing polymers and their various uses (Menczel & Prime, 2009; Al-Lami, et al., 2017).

Thermal dissociation of polymers is defined as the response shown by the polymer towards the rise in temperature, at which the polymer begins to decompose or disintegrate accompanied by the liberation of gases that depend on the nature and composition of the polymer (Al-Mayyahi, et al., 2017). The thermal resistance of the polymer depends mainly on the chemical composition of the polymer, especially the composition of the repeating unit, in addition to the length of the polymeric chain (molecular weight), the amount of crosslinking between the polymeric chains and the presence of aromatic structures (Schick, 2009).

3.3. Thermal Gravimetric Analysis (TGA)

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 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), and it is also possible to calculate the weight loss percentage at any temperature and the percentage of the remaining polymer after the Char residue process (Coats & Redfern, 1963), in addition to calculating the activation energy.

The Broido1969 method was used to calculate the activation energy from the analysis curves Thermogravimetric for all polymers prepared according to the following equation:

$$\ln[-lny] = -\frac{Ea}{RT}$$

Where :

$$y = \frac{wt - w\infty}{w\circ - w\infty}$$

$W_\circ$ = the initial weight of the polymer

W_t = the weight of the residual polymer at any temperature

W_∞ = the final weight of the polymer remaining at the end of dissociation

R = the gas constant

T = the measured temperature when calculating Wt.

And by plotting a graphic relationship between In[-lny] and 1/T we get a straight line where the slope represents the activation energy (Menczel & Prime, 2009). Thermogravimetric analysis of the prepared polymers was measured with a temperature range (25-800) °C and a constant heating speed (50 °C /min) in the presence of an inert atmosphere of nitrogen gas.

By observing the Figures 10 to 15, we note that the dissolution of the prepared polymers begins at (172-483) °C, and this indicates the great thermal stability enjoyed by the prepared polyesters, and the reason for this is due to their containing the compositions aromatics located along the polymeric chain. The high amount of residual polymer is an indication of the great thermal stability of the prepared polymers (Coats & Redfern, 1963).

By reviewing many previous researches (Crompton, (2013; Al-Lami, et al., 2017), and observing the dissociation curves, we conclude that the dissolution of the prepared polymers begins with the loss of small molecules such as CO_2 and CO, followed by the loss of large molecules such as acetone and some aromatic rings such as phenol and carboxylic acid . and the Table 3 shows the most important values obtained from the thermo gravimetric analysis curves for all the prepared polymers.

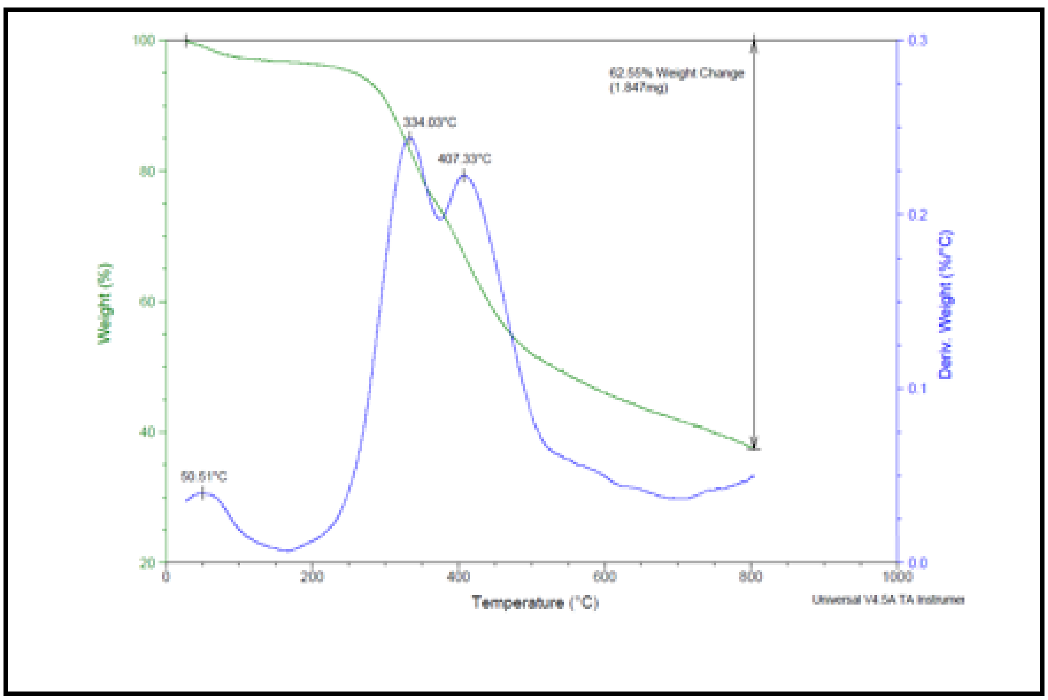


Fig. 10. TGA of PB polyester

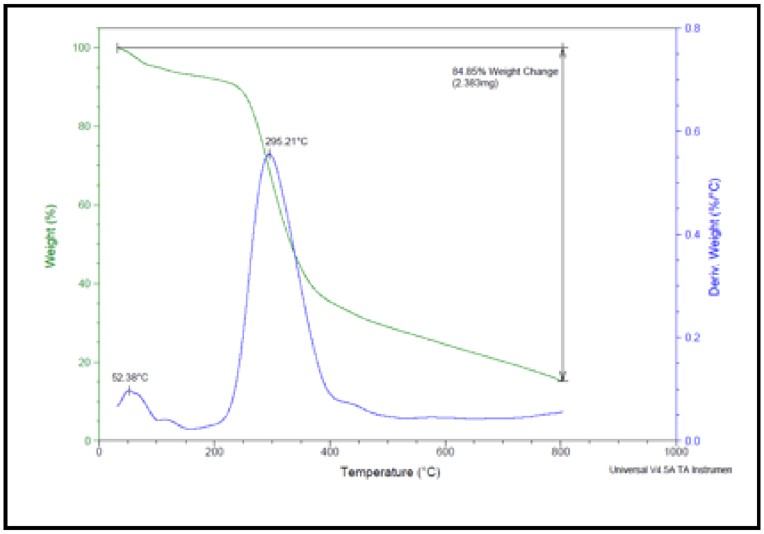


Fig. 11. TGA of PD polyester

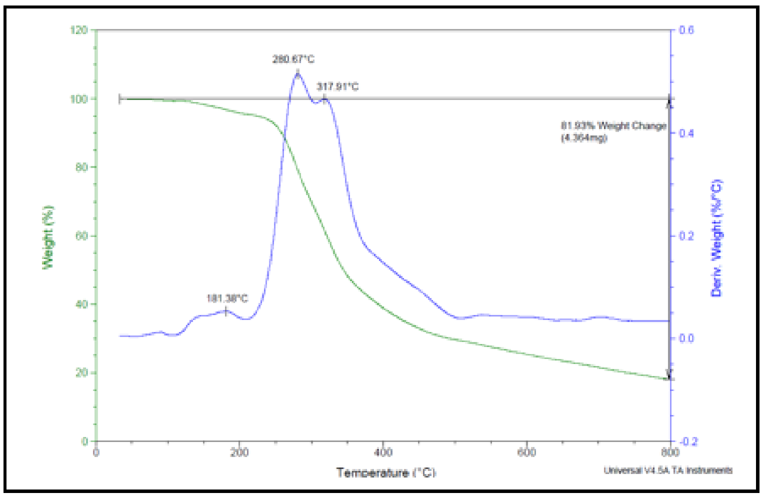


Fig. 12. TGA of PE polyester

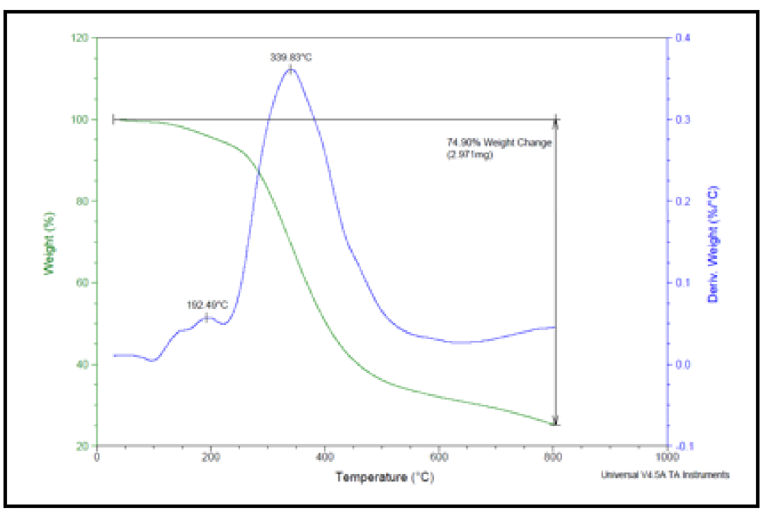


Fig. 13. TGA of PF polyester

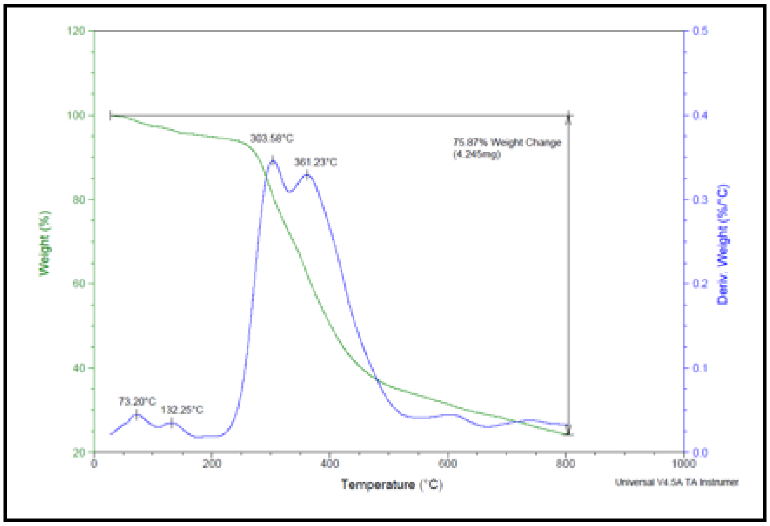


Fig. 14. TGA of PG polyester

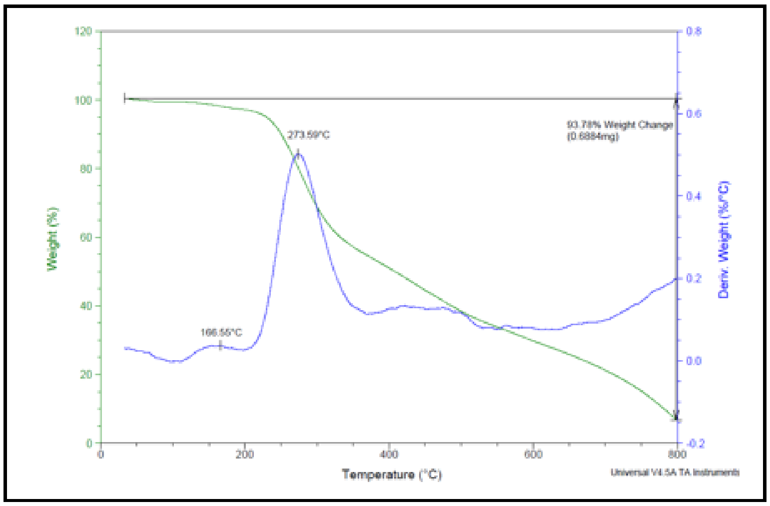


Fig. 15. TGA of PH polyester

Table 3
Values obtained from Tga curves for some prepared polymers

SYM	T_i (°C)	T_f (°C)	Top (°C)	T_{50} (°C)	Rate of Decomp. %/min	Activation Energy KJ.mol^{-1}	Temp. Range for activation Energy (°C)	Weight Loss %	Char Residue
PB.phph	160	615	370.68	540	7.4	5.547	320-370	62.55	37.45
PD.phph	150	500	295.21	330	5.31	10.292	260-285	84.85	15.15
PE.phph	210	510	299.29	340	4.52	8.0252	260-280	81.93	18.07
PF.phph	220	570	339.83	340	5.73	10.409	270-310	74.9	25.1
PG.phph	215	540	332.4	400	5.36	4.85	330-370	75.87	24.13
PH.phph	200	370	273.59	400	3.95	10.389	250-280	93.78	6.22

3.4. Fluorescence of the Prepared Polymers

The fluorescence spectrum of polymer PB depends on the basis of 2,6-pyridine dicarbonyl dichloride acid monomer with curcumin analogues as shown in Figure 17, where the polymer is dissolved in dimethyl sulfoxide. The emission spectra were recorded between (400-670) nm. The fluorescence spectrum of the polymer PB showed a wide emission band that ranged between (450-550) nm and the highest emission intensity was at wavelength 500 nm. Figures 17 to 22 show the fluorescence spectrum of the polymers prepared in this study, while Table 4 shows all the information related to the fluorescence spectrum of the prepared polymers. Through the values, we note the variation in the fluorescence intensity of the prepared polymers, and this in turn is due to several factors. It can be suggested at least two processes responsible for reducing the intensity of fluorescence, as the increase in concentration decreases the fluorescence because the collision between the particles of the material increases, and thus the energy loss increases in a non-radiative manner, Non-fluorescent molecules may absorb the fluorescence spectrum from fluorescent molecules. Also, the ultraviolet rays used to excite the sample sometimes lead to dissociation of the fluorescent compound, and this can be avoided by choosing a longer wavelength or quickly measuring the fluorescence.

Table 4
Fluorescence spectrum of the prepared polymers

SYM	Wavelength range (nm)	λ max (nm)	I_{max}
PB	452-660	500	25.3
PD	439-670	525	13.9
PE	436-640	500	4.3
PF	420-640	505	2.7
PG	430-670	490	97.8
PH	450-615	535	5.5

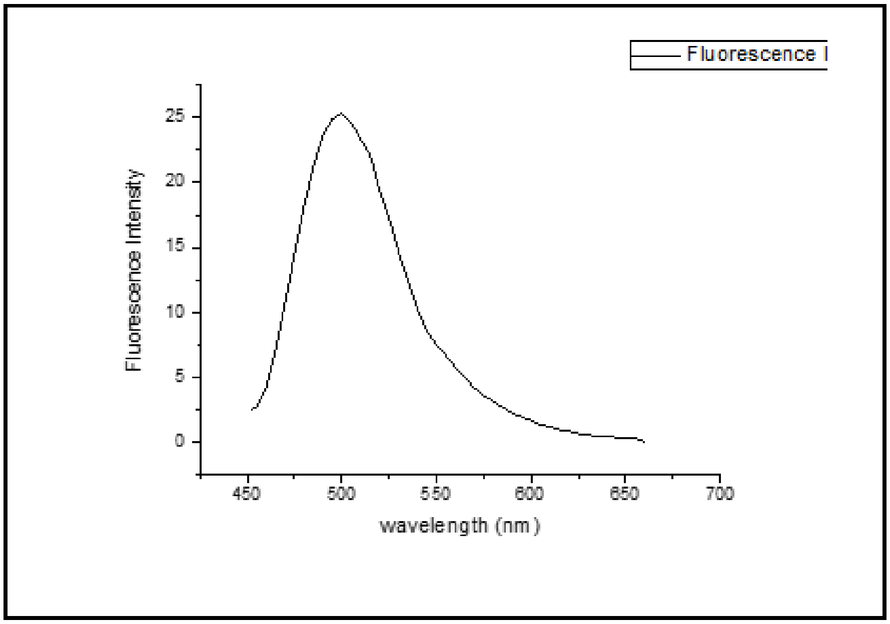


Fig. 17 Fluorescence of PB polyester

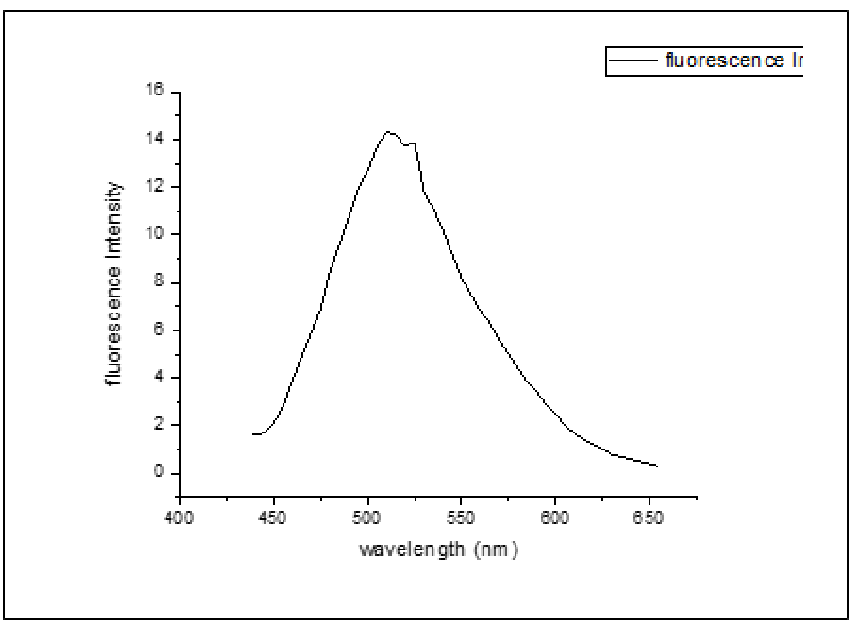


Fig. 18. Fluorescence of PD polyester

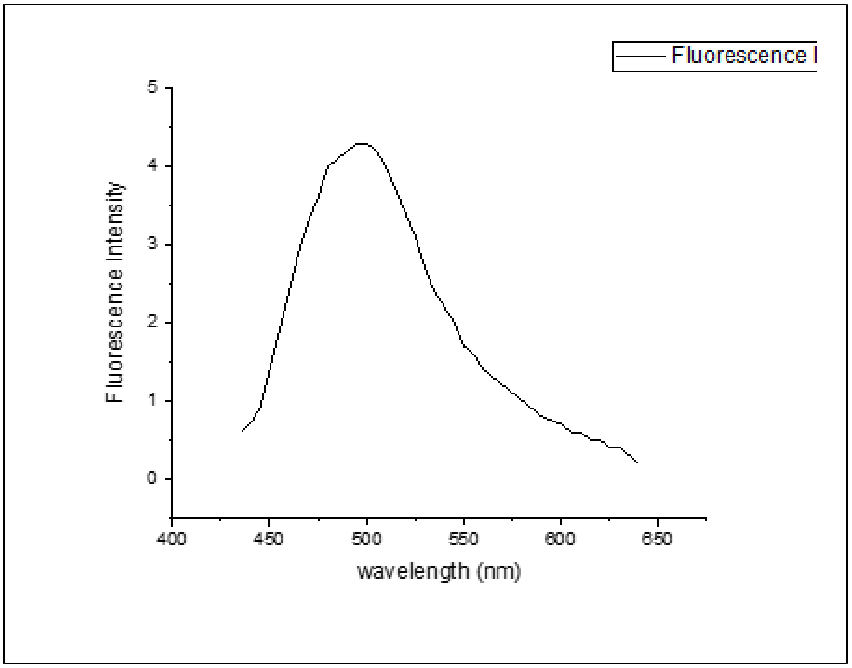


Fig. 19. Fluorescence of PE polyester

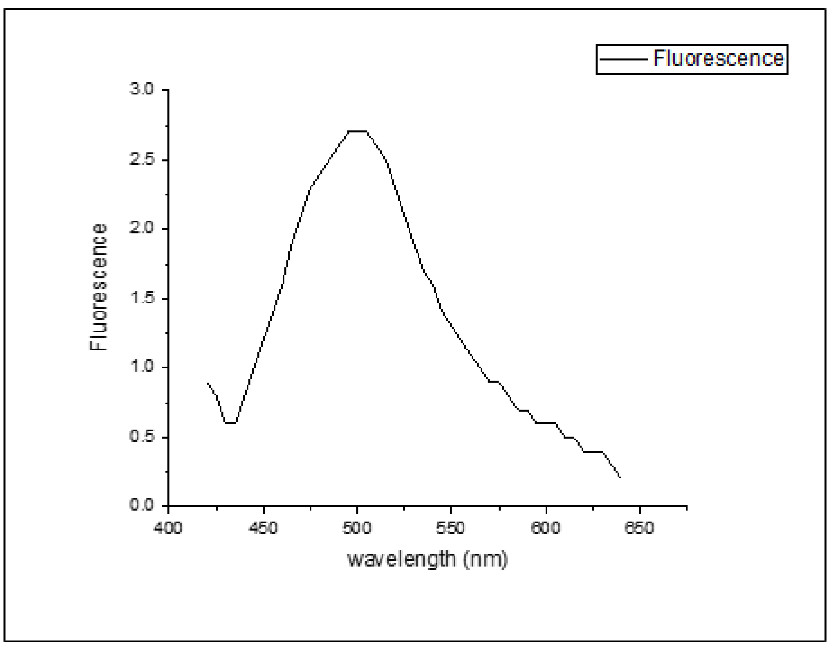


Fig. 20. Fluorescence of PF polyester

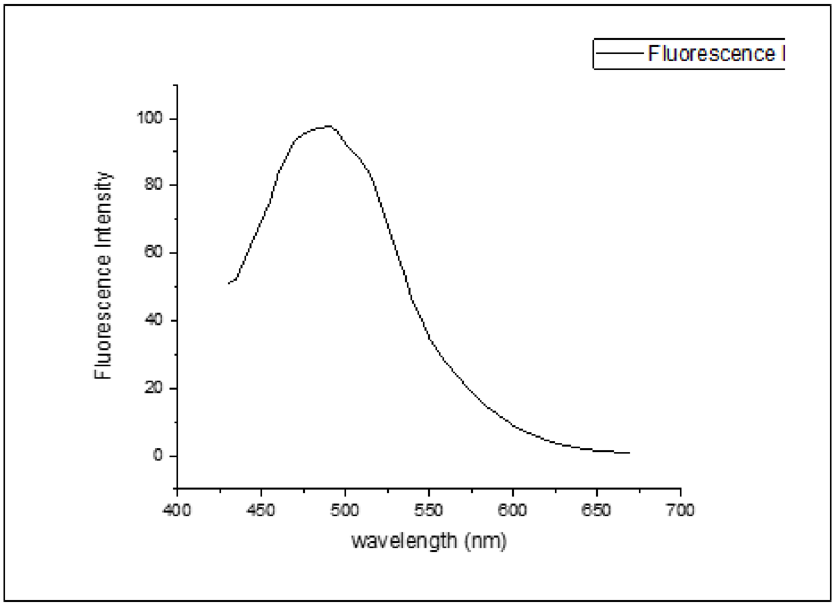


Fig. 21. Fluorescence of PG polyester

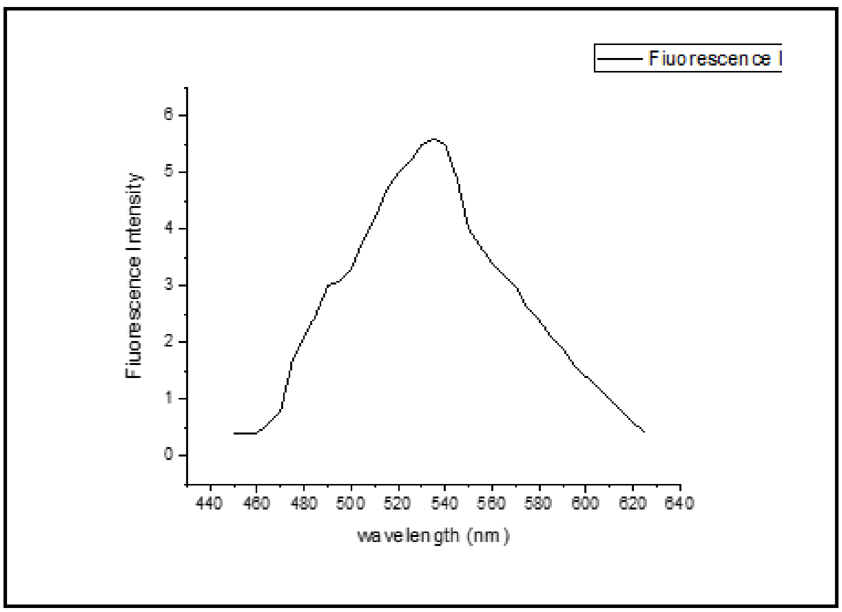


Fig. 22. Fluorescence of PF polyester

4. Conclusion

New copolyesters were synthesized through direct polycondensation reaction between curcumin analogues and phenolphthalein and triethylamine in methylene chloride. The dicarboxylic acid used is 2,6-pyridine dicarbonyl dichloride acid. TGA data reveals that the polymers are high thermal stability materials due to their aromatic compositions, which increase their thermal stsbility. In addition, the prepared polyester possess fluorescence properties based on the results of the measurement of fluorescence spectra. The synthesized copolyesters were characterized by FT-IR. Thermal transition temperatures of copolyesters were determined from TGA thermograms. The prepared copolyesters may be utilized for flame retardant applications because of their high thermal stability.

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