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Synthesis, Characterization and Thermal Study of Some new Copolyesters from mono-carbonyl analogues of Curcumin and Thymol blue dye

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الخلاصة:

حضرت سلسلة من البوليمرات بمفاعلة حامض ثنائي الكاربوكسيل مع مشتقات الكركمين (احادية الكاربونيل) وصبغة الثايمول الزرقاء(thymol blue dye) بنسبة 2:1:1 عن طريق تفاعل البلمرة التكثيفي المباشر بأستخدام ثلاثي اثيل امين (Et₃N) كعامل مكثف الحامض ثنائي الكاربوكسيل المستخدم هو (Leopy dictor) مينا مكاربوكسيل مع مشتقات الكركمين بواسطة تفاعل تكاثف الدول (Aldol condensation) في الوسط الحامضي . شخصت هذة المركبات بتقنية (TGA) للتحقق من الاستقرار الحراري لهذة البوليمرات .

Abstract:

A series of copolyesters were prepared from a dicarboxylic acid, curcumin analogues (monocarbonyl) and thymol blue 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 .

Keyword: copolyester, curcumin analogues, polycondensation, fluorescence

1. Introduction:

Polyesters are possessing at least one group of ester per repeating unit within the main polymer chain[1]. Because of its excellent properties polyester is considered as one of the most important industrial polymers. There are two type of polyesters natural and industrially prepared [2], [3]. The natural polyesters are characterized by their ability to biodegradation, while the industrially polyester prepared are mostly non-biodegradable [4], and possess high moisture resistance, fire resistance, good thermal properties and environmentally stable [5].

Polyesters are used in high-tech industrial applications such as production and energy conversion devices, textile materials, biomedical devices [6], [7], as well as in the manufacture of chips, tapes, seals and wire insulation.

For nearly two decades, arylidene - ketones have attracted the interest of macromolecular chemists, and their conjunction to the polymeric main chain has imparted a thermo-fed liquid crystal property to polymeric materials[8]

Moreover, aromatic polyesters composed of fully solid linear aromatic ester units possess a high melting temperature [9]

Composite materials were used that depend on polyester resins supported with glass fibers. In the manufacture of car body parts and watercraft [10]. polyesters are used as biomaterials in medical applications such as surgical sutures and scaffolds within tissue engineering [11], [12].

On the other hand, copolyester containing curcumin monocarbonyl analogues in its main chain has been used as an antibacterial[13] as well as an anti-fungal[14] in addition to having high stability and semiconductor properties[15] as well as distinguished fluorescent properties[16]

In this study we were interested to preparation and characterized certain copolyester possessing curcumin mono-carbonyl analogues moiety in the polymer.

2. Experimental: 2.1. Chemicals:

The chemicals P-hydroxybenzaldehyde, Ortho-Vanillin, Salicylaldehyde, cyclopentanone, cyclohexanone, triethylamine, 2,6-pyridine dicarbonyl dichloride and thymol blue 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:[17]

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) dropwise 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) show synthesis of curcumin mono-carbonyl analogues.



Scheme (1) synthesis of curcumin mono-carbonyl analogues

2.3 Preparation of Copolymer Compounds :(PA1-PI1) :[18]

The polymers (PA1-PI1) were prepared by dissolving an appropriate curcumin analogue (0.002 mol) and thymol blue (0.002 mol) in dichloromethane (50 ml). Then, the mixture was placed in a three-nick round flask under constant stirring at room temperature. 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:

SYM	Yield %
РА ТВ	67
РВ ТВ	86
РС ТВ	80
PD TB	75
PE TB	81
PF TB	63
PG TB	58
РН ТВ	70
РІ ТВ	80

table (1) the quantities of monomers used and the yield of the polymerization reaction

(TB) : Thymol bluo

(PA - PI) : Curcumin monocarbonyl analogues

% (TB : PA – PI) 1 : 1



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 (1590-1680 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[19]

So, as a result of the presence of the huge succession in the final polymeric structures due to the presence of double bonds and aromatic rings along the polymeric chains of the prepared polyester, so we notice a displacement of the carbonyl band belonging to the ester group and the appearance of a wide band in the region ranging from (1590-1680 cm⁻¹) which shows the overlap of the carbonyl band with the returning bands To the other groups that we see in this region, we also note the absence of these broad bands in the spectra of the primary compounds.

	$\upsilon (cm^{-1})$									
	Stretching									
S I M	C-H	C-H	C=O	C=C	C=O					
	Ar	Al	ester							
PA	3255	2924	1597	1438	1508					
PB	3059	2924	1597	1450	1508					
PC	3136	2924	1597	1450	1512					
PD	3394	2917	1624	1471	1540					
PE	3397	2935	1626	1474	1550					
PF	3365	2917	1601	1480	1508					
PG	3418	2918	1602	1456	1502					
PH	3441	2924	1600	1453	1500					
PI	3372	2916	1601	1480	1505					

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

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[20], [21].

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[22]. 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[23].

3.3 Thermal Gravimetric Analysis (TGA) :

Thermogravimetric analysis of the prepared polymers was measured with a temperature range (25-800) $^{\circ}$ C and a constant heating speed (50 $^{\circ}$ 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[24].

By reviewing many previous researches [25][21], 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 and DTG of PB

Fig (11) TGA and DTG of PD

Fig (12) TGA and DTG of PE

Fig (13) TGA and DTG of PF

Fig (14) TGA and DTG of PG

Fig (15) TGA and DTG of PH

Table	(2)	Value	abtained	frame	Taa	an marca f		10 10 01	nomod	nal	
гаре	1.71	vanies	oplamed	пош	I YX	curves in	or some	Dre	рагео	DOIY	vmers.
	(\mathbf{v})		0.000000000		- 5"					P ~	

SYM	Decomp.	Ti	T _f	Тор	T ₅₀	Rate of	Activation	Temp.	Weight	Char
	stage	(°C)	(°C)	(°Ĉ)	(°C)	Decomp.	Energy	Range for	Loss	Residue
						%/min	KJ.mol ⁻¹	activation	%	
								Energy		
								(°C)		
PB.TB		180	540	326.8	350	4.83	10.570	265-295	85.26	14.74
PD.TB		251	530	270.8	390	5.8	13.891	280-315	74.49	25.51
PE.TB	1 st decomp.	160	430	250.32	430	6.28	8.025	195-235	94.97	5.03
	2 nd decomp.	440	800	617.3	430					
PF.TB		230	390	321.4	350	2.75	3.009	280-310	89.51	10.49
PG.TB		115	400	317.8	340	5	6.204	250-315	81.26	18.74
PH.TB		210	395	314.2	351	3.85	9.554	240-285	86.76	13.24

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 (16) to (21) 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-TB	470-640	530	2.0
PD-TB	454-625	515	6.6
PE-TB	471-640	540	1.7
PF-TB	520-645	550	1.2
PG-TB	471-655	535	2.3
PH-TB	470-645	530	2.0

Fig (16) Fluorescence of PB

Fig (17) Fluorescence of PD

Fig (18) Fluorescence of PE

Fig (20) Fluorescence of PG

4. CONCLUSION:

A new copolyesters were synthesized through direct polycondensation reaction between curcumin analogues and thymol blue dye 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 stability. Also, 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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