



## Synthesis and Characterization of Monomer and Three Types of Polymers Containing Chalcone Groups in Main Chain



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### Abstract

This work was aimed to prepare new monomer (*E*)-1-(4-aminophenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one] and three types of poly (ester-amide) polymers. New monomer is Chalcone compound  $\alpha,\beta$ - unsaturated ketone contain functional group(-CO-CH=CH-) of presence system  $\alpha,\beta$ - unsaturated carbonyl group. It is prepared by condensation aryl ketone with aromatic aldehyde with presence of suitable condensation agents which called Aldol condensation. Monomer reacted with (phthalic anhydride maleic anhydride salicylic acid and succinic anhydride) Via solution poly condensation reactions to yield three types of polymers. The prepared monmer and polymers were characterized by [(FT-IR-spectra, Nuclear magnetic resonance <sup>1</sup>H.NMR-spectra , <sup>13</sup>C.NMR-spectra and Differential scanning calorimetry (DSC)] All the polymers showed good thermal stability and good data of glass transition temperature (T<sub>g</sub>). The results revealed that poly (ester-amide)s were successfully prepared by giving good spectrum which improved the existed amide functional group (-CONH-) and ester functional group (-COO-) in spectrum of each prepared polymer, furthermore the existed chalcone functional group(-CO-CH=CH-) is improved in spectrums of monomer.

**Keywords:** Polyester-amide polymer, , monomer, poly condensation .

### Introduction

Polyesters (PEs) and Polyamides (PAs) are two of the most important polymer kinds. Polyesters (monomers are connected through ester bonds) are often used as mass plastics for meanwhile and consumables, as well as for specific biomaterials in medicine due to their ability to hydrolyze, biocompatibility and good mechanical properties (1,2). Polyamides (monomers are connected through amide bonds) were a variety of fossil- and bio-based polyamides exist for applications in many fields (biomedical, automotive and commodities) (3).

Polyamides with amide groups -NH-CO- in the main chain are considered to be one of the most

significant super-engineering materials due to their excellent mechanical properties at elevated temperature because of their thermal stability (4,5), their rigidity because of the double-bond characteristic of the amide group coupled with inclusive hydrogen bonding. (6)

Polyamide's good abrasion resistance, toughness, low coefficient of friction make it an ideal surrogate for a wide diversity of applications, replacing can form between them. Due to these, and because the polyamide backbone is symmetrical and very order , polyamides are very good fibres also often crystalline (7,8) .

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Receive Date: 24 December 2019, Revise Date: 05 February 2020, Accept Date: 21 March 2020

DOI: 10.21608/EJCHEM.2020.21287.2276

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PEAs are prominent polymers, which can merge the stiffness and the excellent mechanical and thermal properties of polyamides with the favorable properties of PEs which biocompatibility and biodegradability (9,10). They have been scrutinized and used as biodegradable plastics for consumables (11).

Because of these properties, poly(ester amides) are an emerging group of very interesting polymers,(12) which have acquired an increasing impact within the few years ago, as composites ,smart materials and adhesives (13,14) .Many prepared polymers have been qualified for medical applications, as drug delivery, implants tissue engineering (15) .

Thus, the expansion and growth of aliphatic aromatic- PEAs work, both basic and used over the past few decades has been massive (16-17). The PEAs have potential applications as engineering polymers also high modulus fibres(18). For high thermal stability, more poly(ester amides) exhibit liquid crystalline properties (19).

For all these very interesting aspects we decided to undertake synthesis of new PEAs from new monomer with different anhydrides by solution poly condensation reaction and do their characterization through FTIR, 1H NMR, 13C NMR and DSC analysis.

This study aims to synthesize monomer and three types of polymers, as well as to characterize them by studying their thermal properties, behaviour and stability .

## Experimental Parts

### Materials and Methods

In this work, we prepared new monomer [ E)-1-(4-aminophenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one] and three types of poly (ester-amide) polymers. New monomer is Chalcone compound  $\alpha,\beta$ - unsaturated ketone contain functional

group(-CO-CH=CH-) of presence system  $\alpha,\beta$ -unsaturated carbonyl group. It is prepared by condensation aryl ketone with aromatic aldehyde with presence of suitable condensation agents which called Aldol condensation. Monomer reacted with (phthalic anhydride ,maleic anhydride ,salicylic acid and succinic anhydride) Via solution poly condensation reactions to yield three types of polymers.

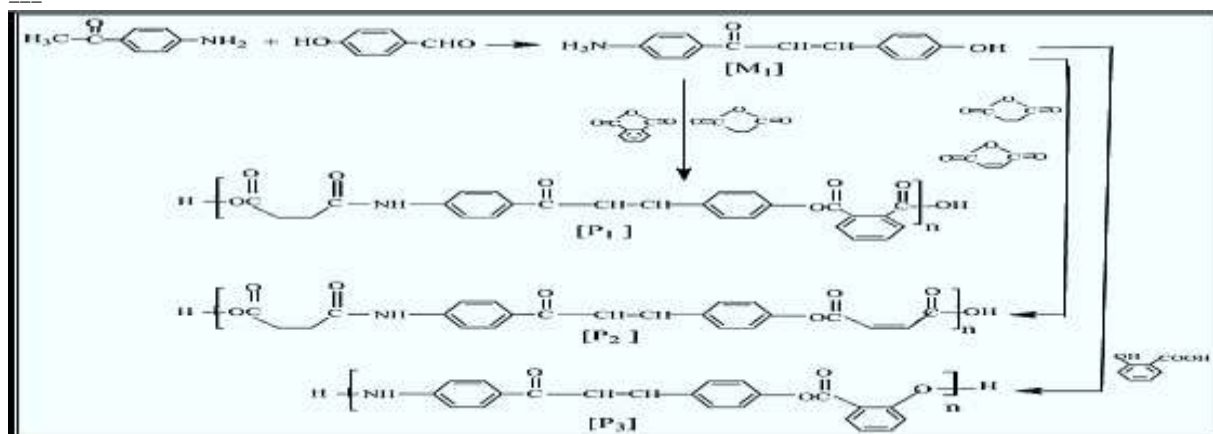
### Preparation of Monomer and Polymers :

Monomer [M1] was prepared from 4-aminoacetophenone (0.02 mol) and 4-hydroxy benzaldehyde (0.02 mole) dissolved in (30 ml) absolute ethanol and sodium hydroxide solution 10% (10 ml) was added gradually with stirring of the mixture for 5-6 hrs . Then constant stirring was done after that the mixture put in refrigerator overnight . The obtained precipitate was filtered ,washed and recrystallized from ethanol.

Polymer [P1] was synthesized by reaction monomer M1 with succinic anhydride and phthalic anhydride with solvent ( acetone ) by refluxing for (6hrs) with z **Polymer [P<sub>1</sub>]** was synthesized by reaction monomer M<sub>1</sub> with succinic anhydride and phthalic anhydride with solvent ( acetone ) by refluxing for (6hrs) with zinc chloride as catalyst through condensation reaction to give polymer[P<sub>1</sub>].

**Polymer [P<sub>2</sub>]** was synthesized by reaction M<sub>1</sub>, succinic anhydride and maleic anhydride in presence of acetone with reflux for (6hrs) with zinc chloride as catalyst via polycondensation reaction to give polymer[P<sub>2</sub>].

**Polymer [P<sub>3</sub>]** was prepared by reaction between monomer M<sub>1</sub> and salicylic acid with zinc chloride as catalyst in presence of acetone and reflux for (6hrs) through condensation reaction to give polymer[P<sub>1</sub>], scheme(1).

Scheme(1):synthesis of monomer [M<sub>1</sub>],[ P<sub>1</sub>- P<sub>3</sub>]

## RESULTS AND DISCUSSION:

In this work we synthesized and characterized the structure of monomer and three type polymers . Synthesis of polymers were done from new monomer which reacted with various compounds like (succinic anhydride , maleic anhydride ,phthalic anhydride, salicylic acid ) to form various polymers .

The structures of monomer and these prepared polymers were confirmed by mean of FT-IR ,<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy and their thermal behaviour was studied.

### FT-IR –spectra:

Table. 1:FT-IR data (cm<sup>-1</sup>) of the monomer & polymers.

Comp.	(COO) ester	(-CO-) Chalcone	CH=CH Alkene	Other Functional groups
[M <sub>1</sub> ]	-----	1654	3090	(NH <sub>2</sub> )of amine:3396, 3335, (OH)hydroxyl group:3228
[P <sub>1</sub> ]	1700	1685	3100	(NH)of amide:3444, (CH) aliphatic:2900, (C=C)aromatic:1570
[P <sub>2</sub> ]	1720	1694	3050	(NH)of amide:3334,(CH) aliphatic:2924, (C=C)aromatic:1595
[P <sub>3</sub> ]	1700	1675	3100	NH)of amide:3330, (CH) aliphatic :2950, (C=C)aromatic:1588

### <sup>1</sup>H-NMR spectra :

<sup>1</sup>H-NMR spectra is the application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei in the molecules of a substance, with a view to identify structure of its molecules.

Figures (5,7 and 9) presents the proton nuclear magnetic resonance spectra of the resultant [P<sub>1</sub>-P<sub>3</sub>].The chemical shifts in range at (9.89- 9.58 ppm) due to proton of (CO-NH) amide in polymer P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub> ,The signals at 6.36-7.98 ppm are assigned to the aromatic protons of phenyl

### The <sup>13</sup>C-NMR spectra:

Carbon-13 (<sup>13</sup>C) nuclear magnetic resonance is the application of nuclear magnetic resonance (NMR) spectroscopy to carbon. It is an important tool in chemical structure elucidation .The <sup>13</sup>C NMR spectra of copolymers were recorded in acetone solvent and given the chemical shifts in range at

FT-IR spectra recorded from pellets of KBr mixed with respective polymers as shown in figures (1-4), an absorption band at (1652, 1644 cm<sup>-1</sup>) due <sup>[10-12]</sup> to carbonyl of amide (CO-N) in polymer P<sub>1</sub>, P<sub>2</sub> respectively , bands at (3255-2800 cm<sup>-1</sup>) due to hydroxyl of carboxyl group (COOH) in all polymers [P<sub>1</sub>-P<sub>3</sub>].Formation of ester bond during the poly condensation can be showed from the spectral data( 1700 -1720) for all synthesied polymers .Other peaks at (1654-1694 cm<sup>-1</sup>) were related to stretching vibration of (-CO-) chalcone groups and speared bands at (3050-3100 cm<sup>-1</sup>) due to (CH=CH ) alkene of chalcone ,also the absorptions at (1570-1795 cm<sup>-1</sup>) is assigned to (C=C) aromatic ,this showed in Table (1)

riings ,The signals at (3.21-3.68ppm) are assigned to (CH=CH) alkene of chalcon , other peaks showed in Table (2)

Table. 2: <sup>1</sup>H- NMR data (ppm) of the polymers

Comp.	Ph-rings	CH=CH Alkene	Other signals
[P <sub>1</sub> ]	6.70-7.98	3.73, 3.63	CO-CH <sub>2</sub> -CH <sub>2</sub> -CO: 2.10, 2.31
[P <sub>2</sub> ]	6.61-7.96	3.66 ,3.68	CO-CH=CH-CO: 2.06, 2.08, CO-CH <sub>2</sub> -CH <sub>2</sub> -CO: 2.30, 2.42
[P <sub>3</sub> ]	6.36-7.93	3.21, 3.47	NH of amine:5.87

(169-173 ppm) were related to carbon of (COO) ester , showed signals at (115-159 ppm) for carbon Ph-rings and appered signals at (112-115 ppm) related to carbon of CH=CH alkene of chalcon and the assignments [12-15] for the various peaks observed are given in Table (3) . Figures (6,8 and 10) represents the The <sup>13</sup>C-NMR spectra of the resultant [P<sub>1</sub>-P<sub>3</sub>].

Table. 3:  $^{13}\text{C}$ - NMR data (ppm) of the polymers

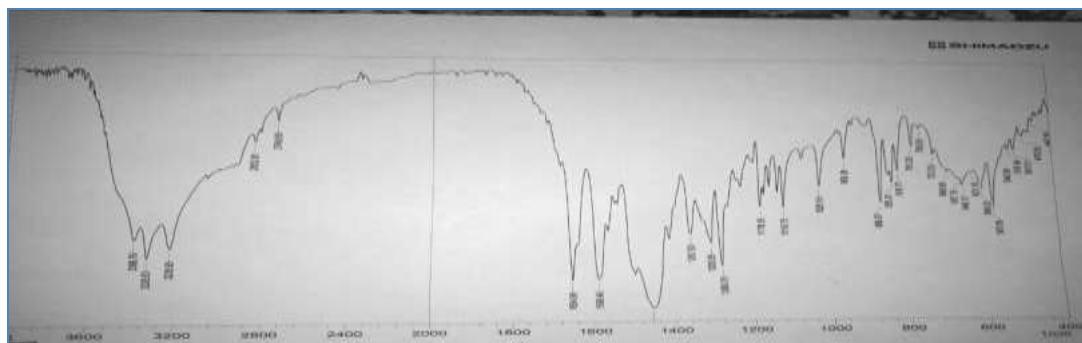
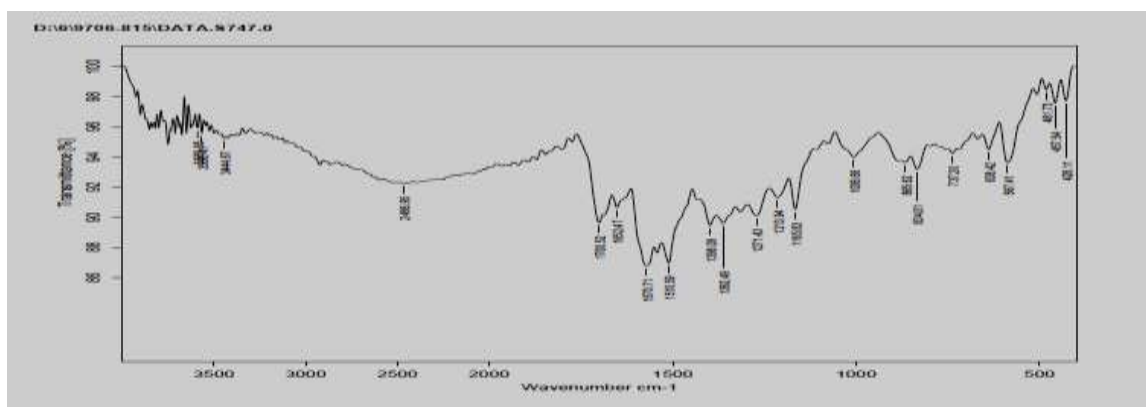
Comp	(COO) ester	Ph-rings	-CO- Chalcon	CH=CH Alkene of chalcon	Other signals
[P <sub>1</sub> ]	173.49	122.8-159.8	206.19	113.16,118.58	(CO-N)amide: 163.18 , CO-CH <sub>2</sub> -CH <sub>2</sub> -CO:25.6, 25.67
[P <sub>2</sub> ]	170	115.26-143	205.49	112.04, 113.04	(CO-N)amide: 159.7 CO-CH=CH-CO:25.08, 25.54
[P <sub>3</sub> ]	169.03	119.2-159.83	206.03	115.2, 116.53	

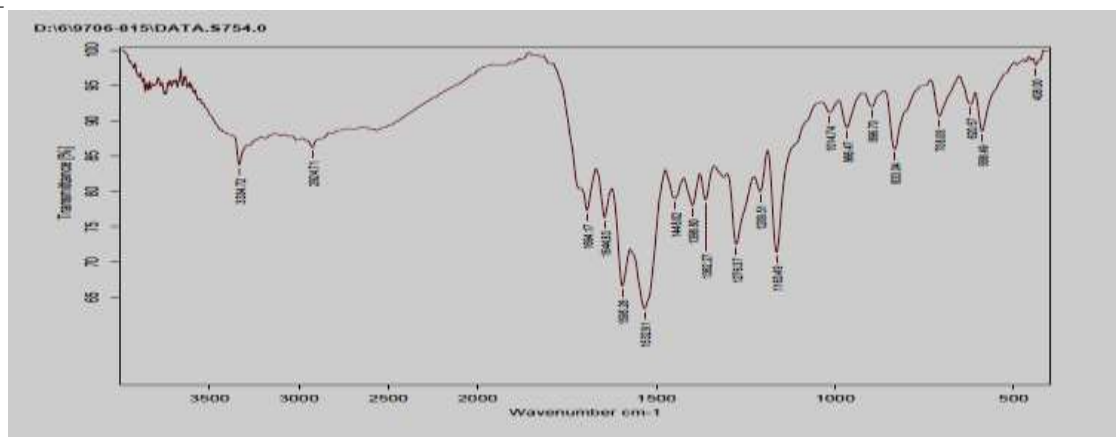
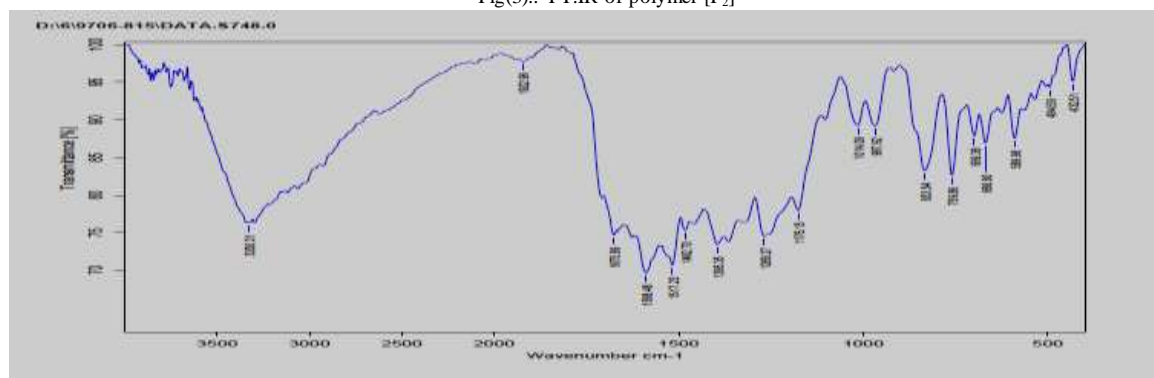
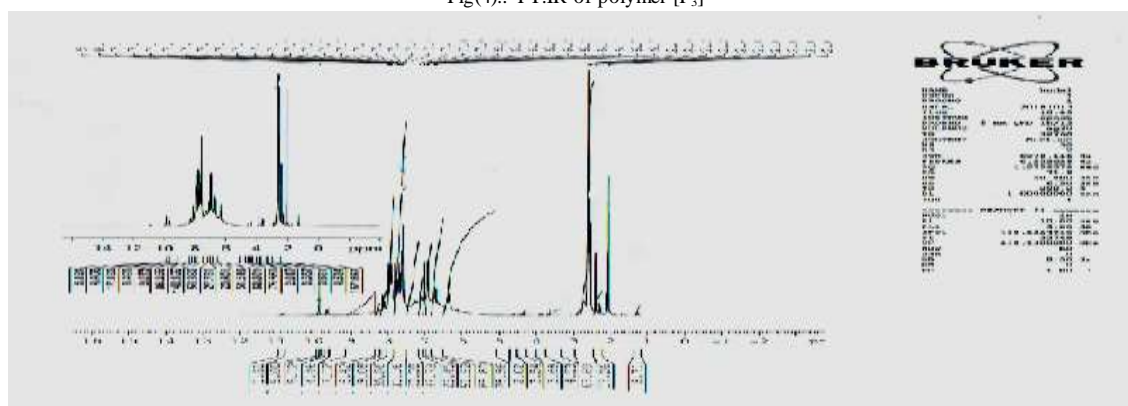
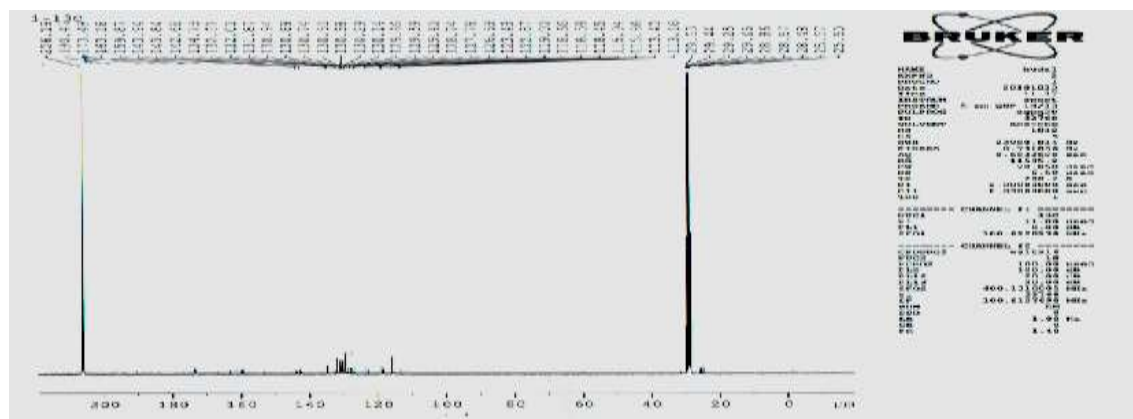
From our results , disappearance of some signals [15] and formation of new signals due to formation of polymers.

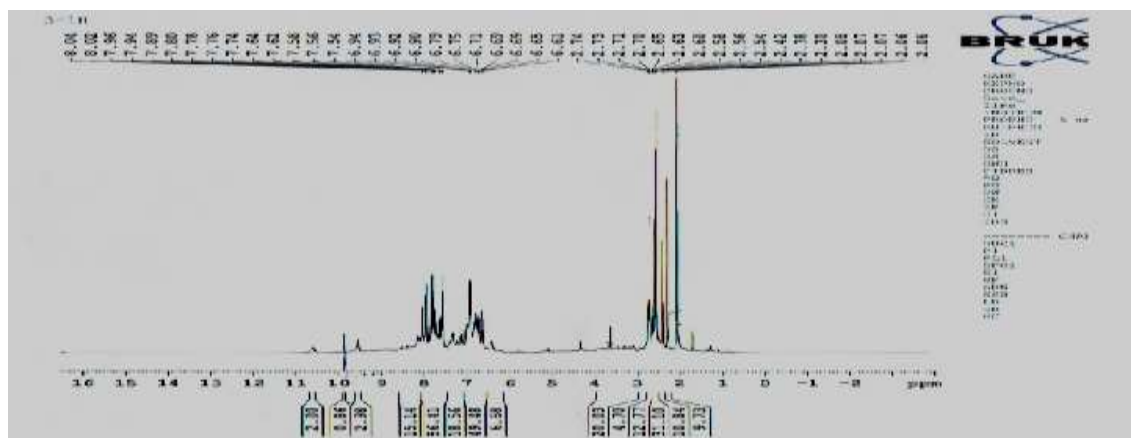
#### Thermal Studies:

The thermal analysis embraces a group of analytical methods in which a physical properties are determined . The thermal stability of poly(ester-amide)s were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG) of the PEAS could be determined from the heating scan of DSC analysis . The data reveal that glass transition temperature (T<sub>g</sub> ) of these polymers are not very high with values ranging from 48.42 °C to 67.21 °C and that could be related to the segmental movement in the noncrystalline area [20].

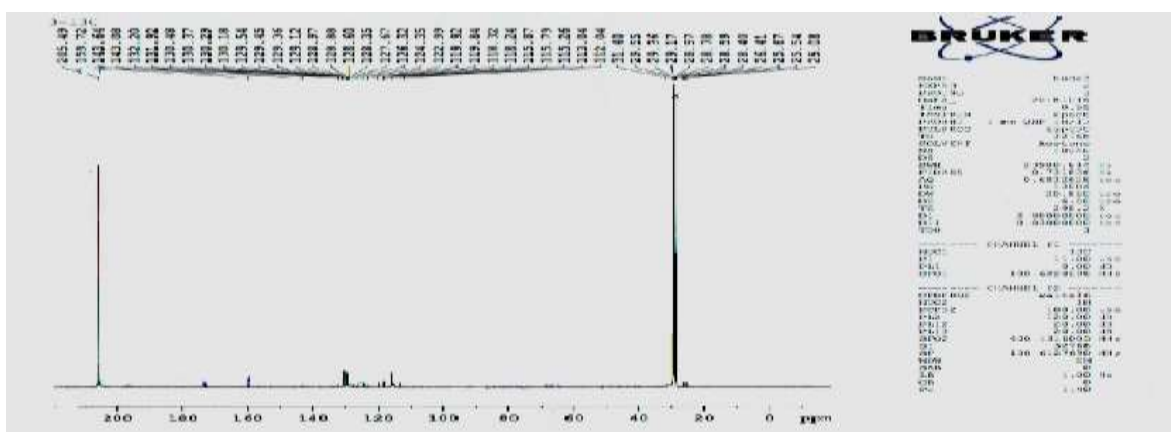
This may be attributed to the enhanced free rotation of the chromophore through the more flexible spacer ,and the higher chromophore concentration being without any added plasticizer .This observation indicates that the polymer is capable to form a stable amorphous or semicrystalline with low T<sub>g</sub> and free volumes for the ordered sequence ,that explain why T<sub>g</sub> for polymer [ P<sub>1</sub>] was the higher one . The DSC thermograms of the **investigated** polymers [P<sub>1</sub>-P<sub>3</sub>] in Figures (11-13) .These Thermograms show glass transition temperature (T<sub>g</sub>) at 67.21 °C for polymer [P<sub>1</sub>] ,48.42 °C for polymer [P<sub>2</sub>] , 65.81 °C for polymer [P<sub>3</sub>].

Fig(1): FT-IR of monomer [M<sub>1</sub>]Fig(2): FT-IR of polymer [P<sub>1</sub>]

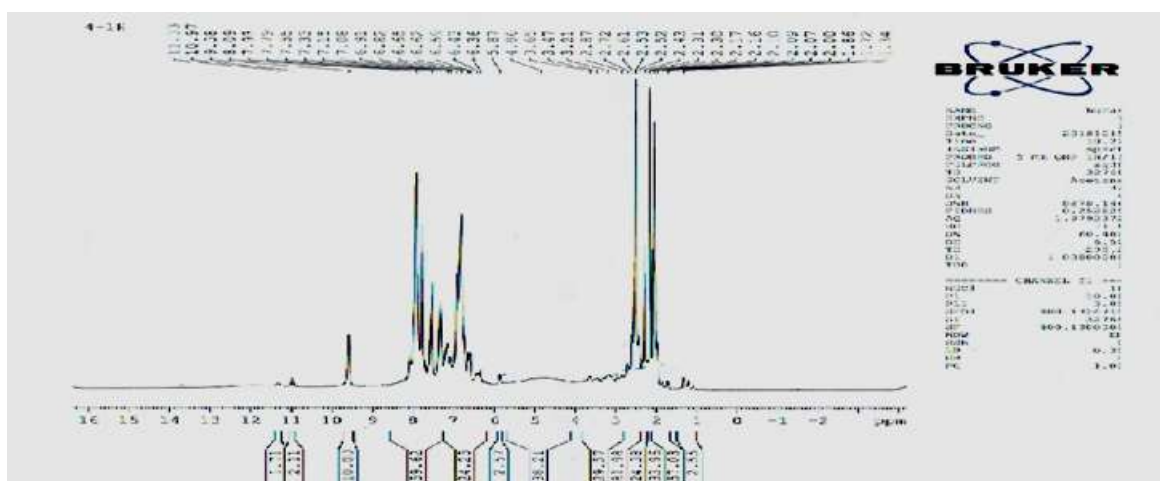
Fig(3): FT-IR of polymer [P<sub>2</sub>]Fig(4): FT-IR of polymer [P<sub>3</sub>]Fig(5): <sup>1</sup>H-NMR of polymer [P<sub>1</sub>]Fig(6): <sup>13</sup>CNMR of polymer [P<sub>1</sub>]



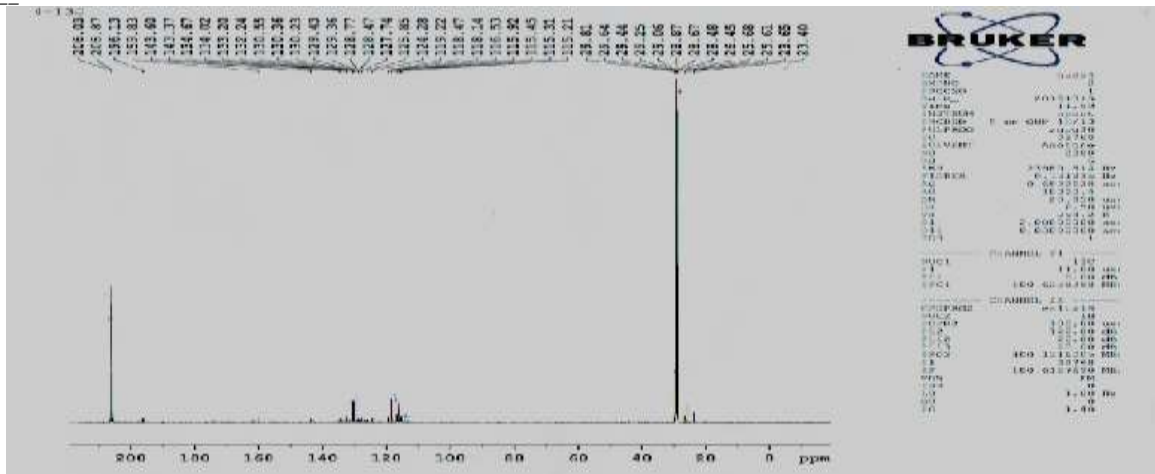
Fig(7): <sup>1</sup>H-NMR of polymer [P<sub>2</sub>]



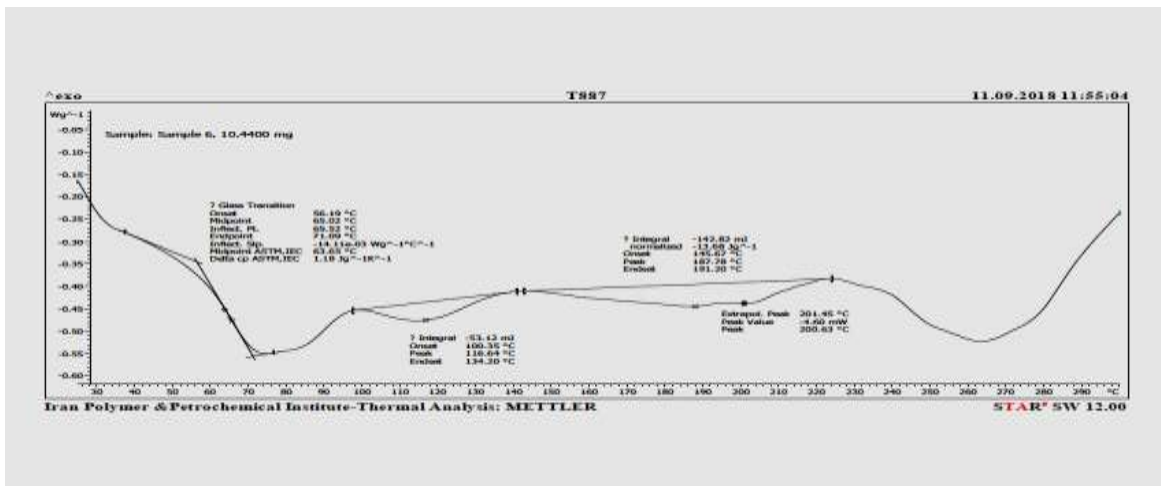
Fig(8): <sup>13</sup>C-NMR of polymer [P<sub>2</sub>]



Fig(9): <sup>1</sup>H-NMR of polymer [P<sub>3</sub>]



Fig(10): <sup>13</sup>CNMR of polymer [P<sub>3</sub>]



Fig(11):DSC of polyesters Spectrum[P<sub>1</sub>]

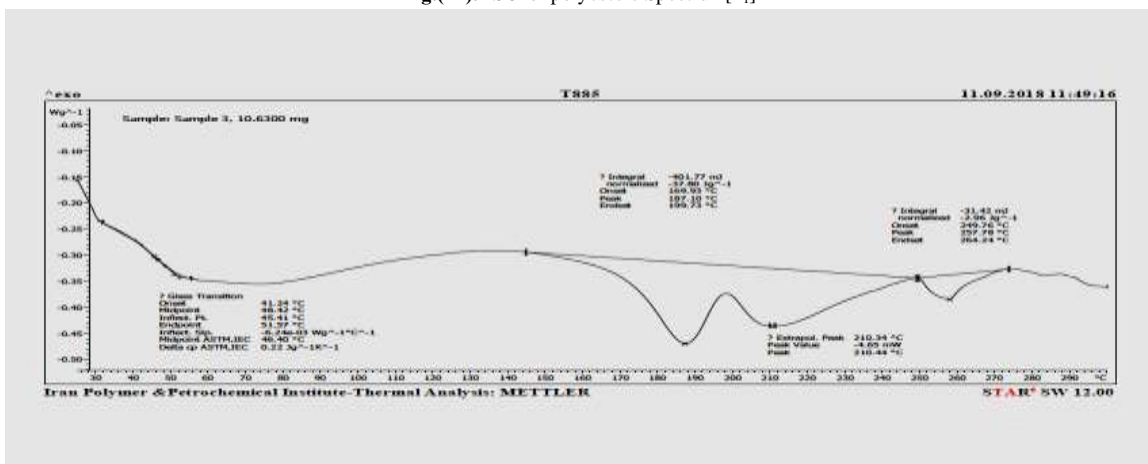


Fig. (12):DSC of polyesters Spectrum[P<sub>2</sub>]

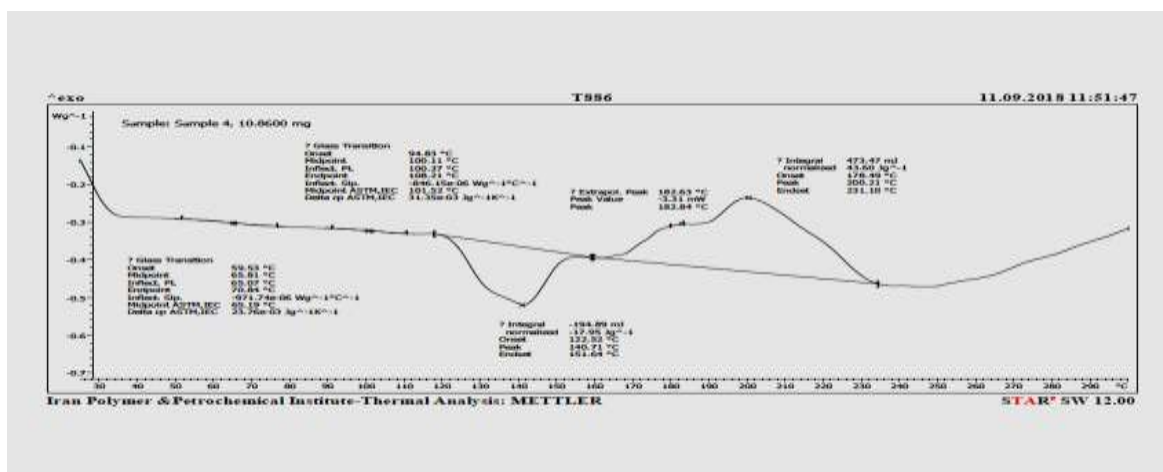


Fig.(13):DSC of polyesters Spectrum[P<sub>3</sub>]

### Conclusions:

This paper reports the successful synthesis of Poly(ester-amide)s containing Chalcone groups in main chains by solution polycondensation of new monomer [E)-1-(4-aminophenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one] with different aromatic and aliphatic anhydrides in the presence of

**Conflict of Interest:** There is no any Conflict of Interest

**Ethical clearance:** Ethics committee refer that there is no plagiarism and there is no mistakes or wrong results in this work.

**Source of funding:** Self funding

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Zinc chloride as the condensing agent. Extensive analytical investigations revealed important, structural characteristics of the new monomer and PEAs were confirmed by FT-IR, 1H- and 13C-NMR spectroscopy. Thermal stability of the obtained polymers was reported as well as the glass transition temperatures varied in the range 48.42 °C to 67.21 °C.

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