



SYNTHESIS AND IDENTIFICATION OF AROMATIC POLY (ESTER-AMIDE) CONTAINING CHALCONE GROUPS IN BACKBONE CHAIN

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ABSTRACT

The purpose of this research is to synthesize a new monomer (E)-5-(3-(4-aminophenyl)-3-oxoprop-1-en-1-yl)-2-hydroxybenzoic acid and poly (ester-amide) polymer. Chalcone compound, α , β - unsaturated ketone is a new monomer that includes both the functional group (-CO-CH=CH-) and α , β - unsaturated carbonyl group of the present system. It is prepared via the condensation of aryl ketone with an aromatic aldehyde in the presence of suitable condensation agents which is known as condensation of aldol. The monomer was reacted with (phthalic anhydride and maleic anhydride) by solution polycondensation reactions to yield polymer. The synthesized monomer and polymer were characterized via FT-IR-spectra, Nuclear magnetic resonance¹³ C-NMR-spectra, ¹H-NMR-spectra] and DSC (Differential scanning calorimetry)]. The polymer demonstrated excellent thermal stability. The findings revealed that poly (ester-amide) was successfully synthesized by providing a good spectrum that improved the existing amide functional group (-CONH-) and ester functional group (-COO-) in the spectrum of prepared polymer, as well as the presence of chalcone functional groups(CO-CH=CH-) improved in the spectrum of monomer.

Keywords: poly (ester-amide) polymer, monomer, chalcone group.

INTRODUCTION

Two of the most common polymer types are polyesters (PEs) and polyamides (PAs). In polyesters, monomers are joined by ester linkages. For the time being, they are frequently employed as mass plastic, consumables, with good mechanical characteristics, biocompatibility as well as biomaterials. In general, because of their capacity to hydrolyze, they are used in medicine [1, 2]. Polyamides (monomers linked together by amide linkages) were a variety of fossil- and non-fossil-based compounds. Bio-based polyamides are available for use in a variety of applications, a variety of fields as biomedical, automotive, and other of commodity [3]. Polyamides containing amide groups in the main chain (-NH-CO-) are regarded as one of the most important polymers due to their considerable super-engineering design and superior mechanical qualities at high temperatures. They can withstand a wide range of temperatures because of their thermal stability. They are stiff [4, 5] as a result of the amide group's feature, inclusive hydrogen bonding. [6]

Because of its high mechanical strength and durability, aliphatic polyamide is used in a wide range of industrial and textile applications. Aromatic polyamides have excellent properties but poor solubility, whereas aliphatic-aromatic polyamides with a diacid or diamine and a flexible aliphatic segment have excellent properties as well as good solubility [7, 8, and 9]. Aromatic-aliphatic polyamides have higher melting and glass transition temperatures, as well as mechanical properties [9].

Researchers are increasingly turning to poly(ester amide)s (PEAs) in the hope of developing functional biomaterials with improved cell-matrix interactions. PEAs

are biodegradable synthetic polymers that include both ester and amide bonds along their polymer backbone, allowing them to integrate the good biodegradability of polyesters with the good thermo-mechanical properties of polyamides [10].

In recent decades, poly (ester amide)s have been the topic of substantial investigation [11-12]. These polymers, in fact, combine the benefits of both polyamides and polyesters. Polyesters are valued for their minimal environmental impact due to their biodegradability and ability to be manufactured from renewable resources [13, 14]. They may, however, have poor mechanical properties [15, 16]. Polyamides, on the other hand, generate a network of hydrogen connections between the amide functionalities, resulting in a high cohesive energy density and good mechanical characteristics [17, 18]. They are, however, either non-biodegradable or simply partially biodegradable. Furthermore, the ester/amide function ratio can be changed to alter the thermal and mechanical properties [19, 20].

Carothers produced the first PEAs in 1932 by polycondensing diols, diacids, and diamines [21], cyclic anhydrides with diisopropanolamine [22], lactones/lactams [23]. Various pathways based on ring opening of monomers (depsipeptides) [24] dicarboxylic acids with bis(2-oxazolines) [25] or acyclic diene metathesis polymerization [26] or spontaneous zwitterionic copolymerization of 2-oxazolines or 2-oxazines Polycondensation of monomers containing carboxylic acid, amine, ester, hydroxyl, or acyl halide groups by melt polycondensation, solution polycondensation, interfacial polycondensation, or solid/liquefied state polycondensation is the most common method for producing PEAs [27, 28].



The polycondensation of a carboxylic diacid and amino alcohol is one of the simplest processes for producing PEA on a big scale. A repeat unit with an ester and an amide function is created in this situation, but without any control over the amino alcohol insertion into the poly(ester-amide), and therefore without control over the polymer microstructure. Thermomechanical characteristics are therefore influenced directly, according to Goodman *et al.* [29].

The purpose of this research was to synthesize a new monomer (E)-5-(3-(4-aminophenyl)-3-oxoprop-1-en-1-yl)-2-hydroxybenzoic acid and poly (ester-amide) polymer.

EXPERIMENTAL SECTION

Materials and Instruments

The FTIR Spectra of the polymer and monomer was measured using KBr pellets on an FTIR Bruker German model Equionex 55 Spectrometer (4000-400 cm^{-1}), which was used to measure the FTIR Spectra of the monomer and all polymers. A variety of other methodologies were also used in this work.

Nuclear Magnetic Resonance (^1H NMR and ^{13}C NMR) Spectra were obtained utilizing NMR Spectroscopy-Bruker company equipment at 400MHz for ^1H NMR and 100MHz for ^{13}C NMR, and 9.5 Tesla magnetic employing $\text{CD}_3\text{C}(=\text{O})\text{CD}_3$ as the solvent for the experiments.

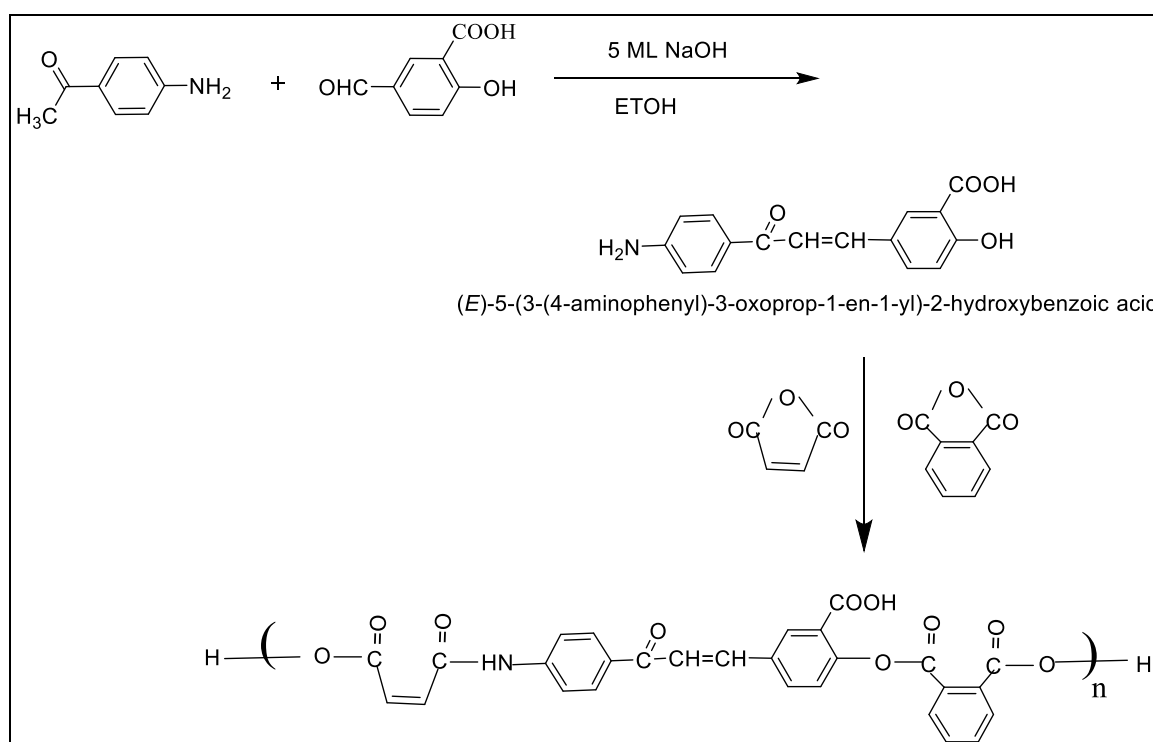
The thermal analysis of the polymers was performed using an instrument manufactured by METTLER TOLEDO (Switzerland) and designated as DSC 1. Instances of (examples and references) Pan: Aluminum Crucible Standard 40L with 99.999 percent purity, O_2 concentration of 50ppm, H_2 concentration of 30ppm, and Ar concentration of 30ppm.

Procedure: Preparation of Monomer and Polymer

They consisted of the following steps:

To prepare monomer [M], 0.596gm, 0.001ml of 3-carboxy-4-hydroxybenzaldehyde was added slowly to a solution of 1gm, 0.001mol of 4- aminoacetophenone in 30ml of absolute ethanol. Then, with steady stirring on the magnetic stirrer, 5ml of a 10 percent NaOH solution was added slowly to the solution. Using absolute ethanol, we added the solution of the first stage and stirred continuously for 6 hours. The reaction was then followed by (TLC) using Ethanol: dry benzene ((1:4)), and the product was cooled, filtered, and recrystallized with absolute ethanol.

In order to synthesize polymer [P], the reactants which included monomer, maleic anhydride, and phthalic anhydride dissolved in acetone then react at high temperature for six hours with zinc chloride as a catalyst in a polycondensation process to obtain the product, according to the reaction scheme (1).



Scheme-1. Synthesis of monomer [M] and polymer [P].



RESULTS AND DISCUSSIONS

They were analyzed using FTIR to identify the new polyester that was synthesized as well as to evaluate the matrix and resulting polyester.

The FT-IR spectroscopy approach was used to confirm the chemical structures of produced substances. The monomer and polymer FT-IR spectra were recorded as KBr pellets in the 650- 4000 cm⁻¹ range. The aromatic C-H stretching vibration occurred in the range 2822-2733 cm⁻¹ in the infrared spectra of M under investigation, and a band at 3475cm⁻¹ matched the -OH of the non-hydrogen-bonded groups. In 1307 cm⁻¹ and 1120 cm⁻¹, respectively,

the aromatic C-H in-plane bending and out-of-plane bending vibrations emerged. While the bands in the 1500cm⁻¹ region matched the aromatic C=C stretching vibration of aromatic rings, the C=C stretching vibration of the alkene group created the other band in the 1583cm⁻¹ region. Due to the carbonyl group C=O of carboxylic acid, the M displayed a band of approximately 1662 cm⁻¹. The carbonyl group C=O of chalcone vibration caused the band at 1643cm⁻¹. The NH₂ stretching vibration was attributed to the bands found in the M's FT-IR spectrum in the range 3421, 3448 cm⁻¹.

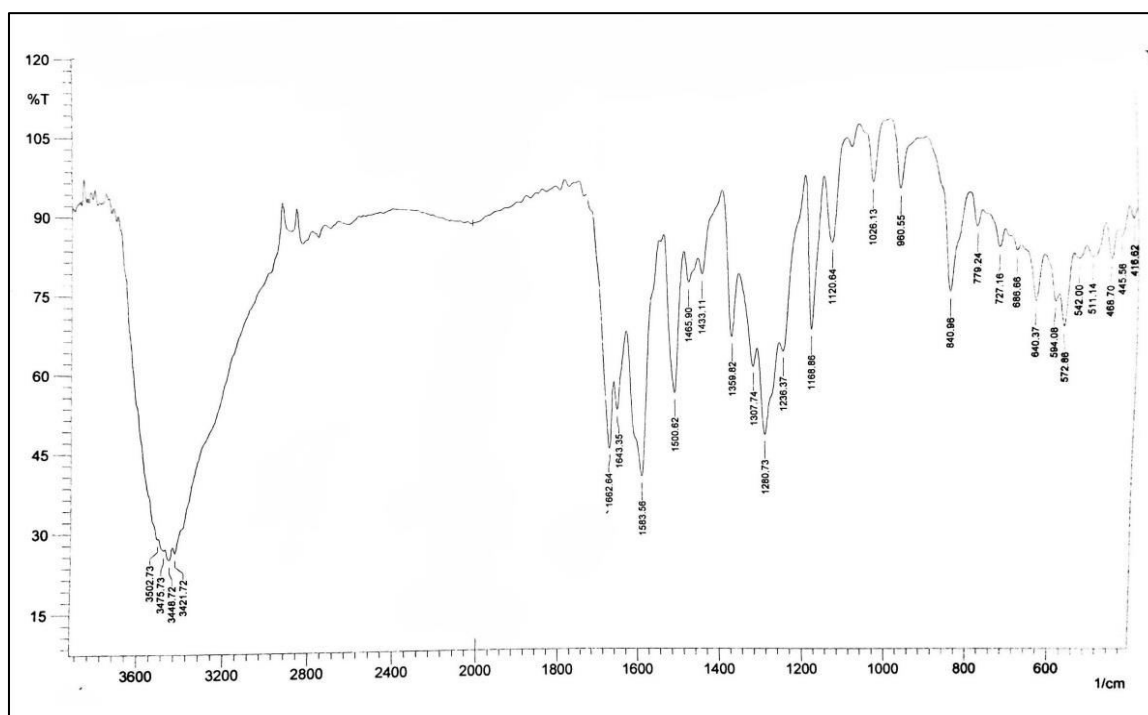


Figure-1. FT-IR of monomer.

In order to confirm the (polyester-amide) that was synthesized and to estimate the matrix and obtained polymer, they were analyzed by FTI. Figure-1 is offered an infrared spectrum of absorbance in (1660 cm⁻¹)[30-32] due to carbonyl of amide (CO-N) which exists in the polymer backbone. The structure of PEAs was assured by ¹H-NMR, ¹³C-NMR, and FTIR spectroscopy. 1118 cm⁻¹ (CO-C stretching absorptions, unsaturated ester, 1501 cm⁻¹ aromatic in-plane ring C=C stretching vibration, 1578C=O stretch of chalcon for Polymer.(The FTIR spectrum of polymer offers distinctive absorption bands at

1163 cm⁻¹ because of the stretching of OCH₃ methoxy groups and speared bands at (3055-3100 cm⁻¹) due to (CH=CH) alkene of chalcone. The broad absorption band at 3006-2826 cm⁻¹ is ascribed to COOH stretching vibration of the hydroxyl group and disappear stretching vibration of the hydroxyl group in a polymer that is obtained in the monomer spectrum. The absorption of the NH amide stretching show about 3300 cm⁻¹ in the spectrum. The FTIR spectrum of monomer and polyester is illustrated in Figures (1, 2).

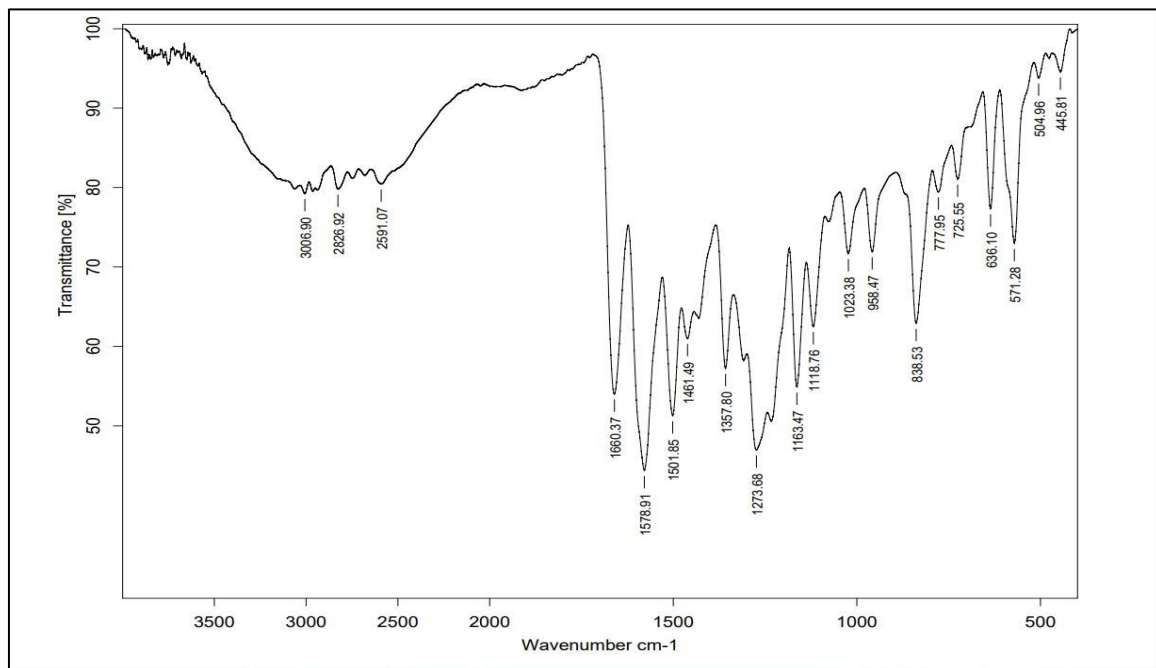


Figure-2. FT. IR of polymer.

¹H-NMR Spectra

The application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei in a substance's molecules in order to identify the structure of its molecules is known as ¹H-NMR spectra.

The proton nuclear magnetic resonance spectra of the resultant polymer were shown in Figure-3. The chemical shifts in the (9.56 ppm) range were caused by the proton of (CO-NH) amide in polymer, the aromatic

protons of phenyl rings were assigned to the signals at 6.90-7.84 ppm [33].

The signals at (3.83ppm) were assigned to the (CH=CH) alkene of chalcon, and those at 2.06-2.46 ppm were assigned to carbons of aliphatic and aromatic esters in the ¹H -NMR spectra of polyester. Figure-3 depict the proton nuclear magnetic resonance spectra of the resulting polymer.

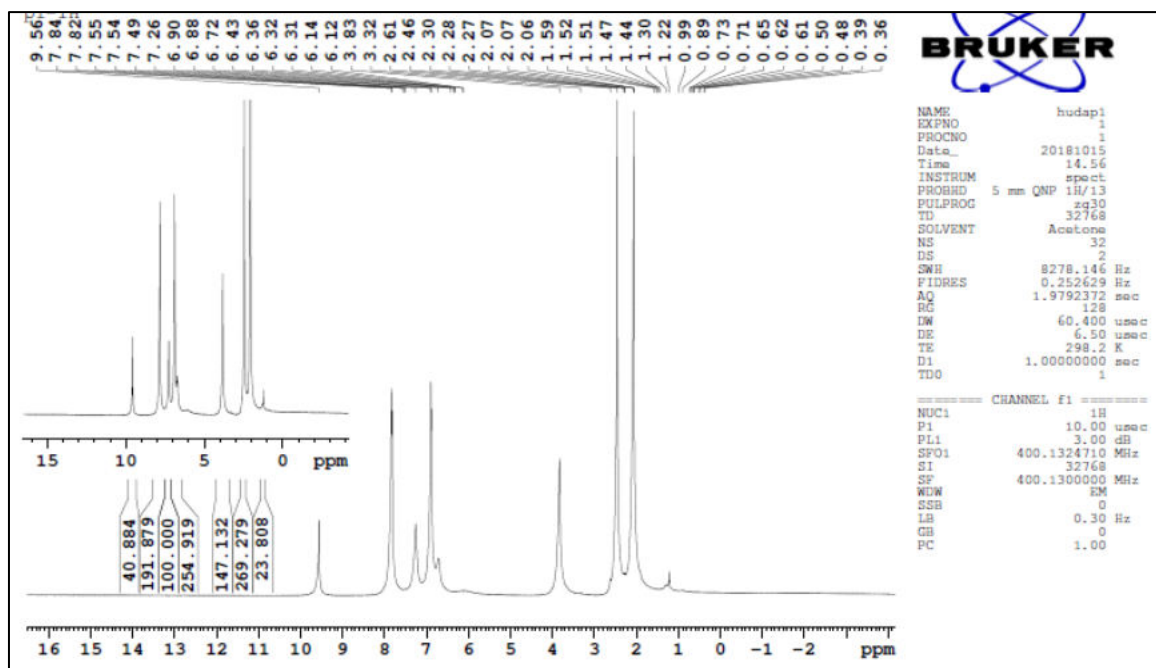


Figure-3. ¹H-NMR of polymer.



Spectra of ^{13}C -NMR

Spectra of ^{13}C -NMR: Carbon-13 (^{13}C) nuclear magnetic resonance is the application of nuclear magnetic resonance (NMR) spectroscopy to carbon and is an essential tool in chemical structure illustration. The ^{13}C NMR spectra of the polyesters were recorded in acetone solvent and provided chemical shifts in the range of (195.31-188.49ppm) for the carbon of (COO) ester,

showed signals at (128.06-150.65 ppm) for carbon Ph-rings, and manifest signals at (108.02-115.62 ppm) for the carbon of $\text{CH}=\text{CH}$ alkene of chalcon, the chemical shifts in range at (164.41 ppm) for (CO-N) amide, and appeared signals at (205.51 ppm) for the carbon of $\text{C}=\text{O}$ of chalcone [34]. Figure-4 shows the ^{13}C -NMR spectra of the resulting polymer.

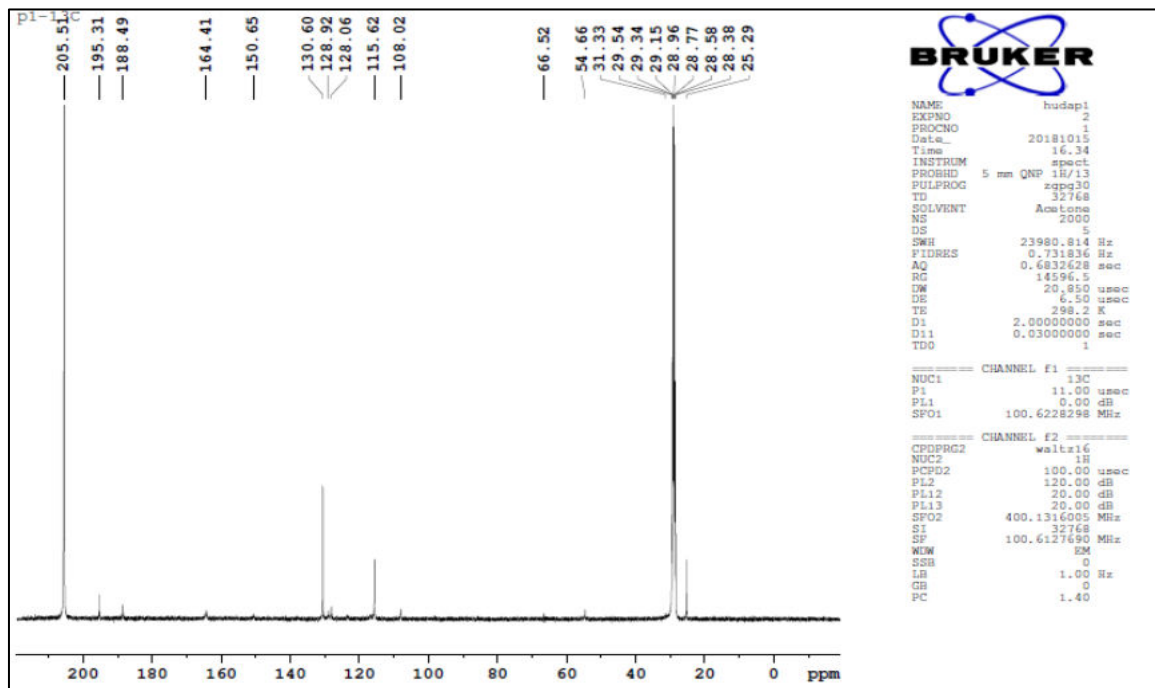


Figure-4. ^{13}C NMR of polymer.

Thermal Properties

It is possible to detect the heat flow into and out of a system using differential scanning calorimetry (DSC). Temperature, as well as the availability of a polymeric substance a simple method for determining the crystalline structure of a substance as a result of the polymer's characteristics and as a result of forecasting the individual processing and end-use requirements .characteristics.

Understanding the thermal characteristics of materials, and the use of polymers is essential for the advancement of technology. The most effective means of transforming commodities into items that are advantageous, as well as forecasting and execution throughout the product's useful life Investigations into the thermal characteristics of DSC polyesters were carried out to determine the thermal characteristics of materials. The brand-new polyesters are made to Assuring the success of the polyesters used in the DSC have an amorphous structure [35].

As they accumulate enough energy, they'll be able to transition into highly ordered structures, which we'll refer to as crystals, of course. As polymers fall into these crystalline structures, they emit heat as a result of the process. The crystallization temperature T_c for the synthesized polymer is 75.22 degrees Celsius. In the polymer, heat can cause crystals to form; but, if too much of this occurs, it can be undone. The polymer will eventually undergo another thermal transition known as melting if the temperature is maintained above its T_c .

When the polymer crystals reach the melting temperature of the polymer, which is denoted by the letter T_m , they begin to break apart. In other words, they melt. The chains break free from their pre-arranged formations and begin to move freely. On a DSC plot, we can see that this was taking place [36].

The melting temperature (T_m) of the produced polymer was 129.60 degrees Celsius. Figure-5 shows the DSC thermograms of the polymer under various conditions.

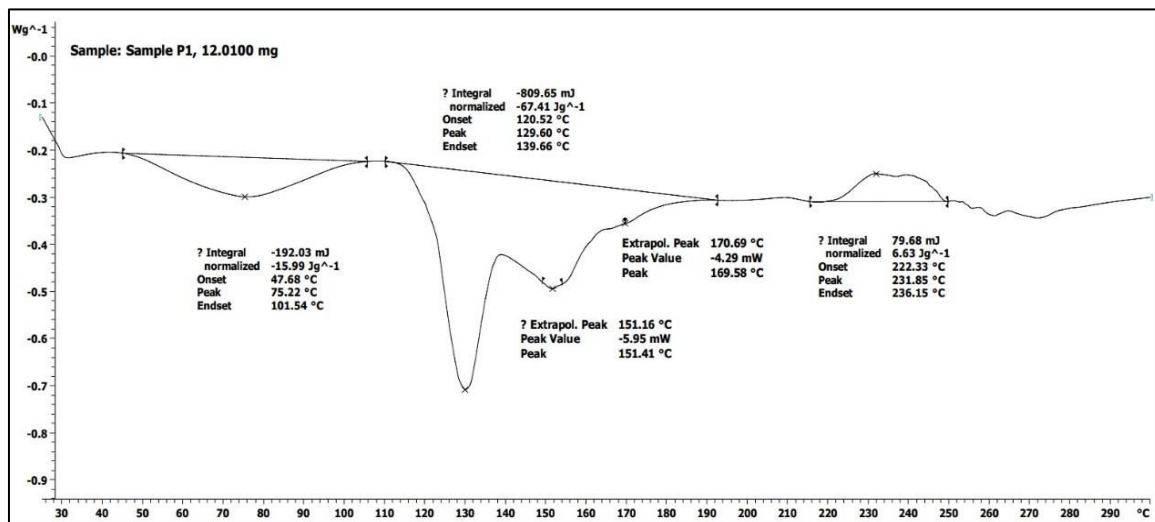


Figure-5. DSC of polymer spectrum.

CONCLUSIONS

This research described the successful synthesis of polyesters with Chalcone groups in the main chains via solution polycondensation of a new monomer (E)-5-(3-(4-aminophenyl)-3-oxoprop-1-en-1-yl)-2-hydroxy benzoic acid with various aromatic and aliphatic anhydrides in the presence of Zinc chloride as the condensing agent. Overall, FT-IR, ¹H, and ¹³C-NMR spectroscopy were used to detect important structural characteristics of the new monomer and PEAs. The thermal stability of the obtained polymer was reported.

Conflict of interest

The authors declare that there is no conflict of interest.

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