



Preparation and Identification of Aromatic Copolyester Containing Chalcone Groups



Huda Sabah Hassen^{1*}, Majida Hameed Khazaal², Nadia Sadiq Majeed², Ekhlal Sabah Hassan³

¹ Assistant professor in chemistry, Department of chemistry, Faculty of Education for Girls, University of Kufa, Iraq.

² lecturer in chemistry, Department of chemistry, Faculty of Education for Girls, University of Kufa, Iraq.

³ Assistant professor in pharmacology and therapeutics, Department of pharmacology and therapeutics, Faculty of Medicine, University of Kufa, Iraq.

Abstract

In the present paper, many unsaturated polyesters has been synthesized using maleic anhydride, phthalic anhydride and succinic anhydride for esterification with new monomer [E]-1-(4-hydroxyphenyl)-3-(3-methoxy-4-hydroxyphenyl) prop-2-en-1-one]. These polyesters were polymerized by condensation reaction. Their chemical structures were characterized using FTIR, ¹³C-NMR and ¹H NMR spectroscopy. Thermal properties have been analysed using Differential Scanning Calorimetry of synthesized polyesters. All the polymers showed well thermal stability and perfect data of glass transition temperature (T_g) also the results showed polyesters and monomer were successfully synthesized by giving well spectrum improved existing an ester functional group (-COO-) in spectrums each polymer prepared also existent Chalcone functional group(-CO-CH=CH-) in spectrum of monomer.

Keywords: Polymer, polyesters, monomer, poly condensation

1. Introduction

Unsaturated polyesters are commonly copolymers synthesized by polymerizing one or more diol with unsaturated and saturated dicarboxylic acids (fumaric acid, maleic acid.....) or their anhydrides. The unsaturated monomer supplies sites for cross-linking at the curing step. The choice of starting materials, such as unsaturated acid, saturated acid, and diol, as well as unsaturated comonomer, affects the polymer's behavior [1].

Polyesters (PEs) are a category of polymers with major application in several market strips, like specialty resins and elastomers [2,3], engineering plastics [4], textile fibers[5]. for the time being, the world output of PEs is one of the great among the most widespread polymers [6].

Unsaturated polyester resins (UPR) are vastly used for the industrialization of stuffing compounds which are binders in output of fiberglass and another

polymer composites [7-10] The vast application of these resins is because of their comparatively little cost, resistance to aggressive media, high corrosion resistance and good wetting ability, also amended deformation and physicomechanical properties [11,12].

For organic matrix fiber composites, UPEs are one of the most effective template resins. They're used in sports, the marine industry, manufacturing, and furniture. The beneficial mechanical properties of polymer composites have gained a lot of attention during their evolution. Physical or chemical approaches may be used to do this [13].

Also Polyester used as fabrics which prominently used in the textile sector due to excellent physical and chemical properties and low cost. Polyester fibers are highly compact and hydrophobic in nature and it is dyed with disperse dye at high pressure, as well as at high temperature [14,15], which is now regarded as the most ordinarily utilized fiber in clothes industry.[16]

*Corresponding author e-mail: ealkhazaaly@gmail.com; (Dr.Huda Sabah Hassen).

Receive Date: 24 December 2020, Revise Date: 05 March 2021, Accept Date: 09 April 2021

DOI: 10.21608/EJCHEM.2021.54469.3138

©2021 National Information and Documentation Center (NIDOC)

Aromatic polyesters are a significant category of engineering high performance polymers because of their stellar chemical, thermal properties in addition to mechanical properties. Their harsh structures can give them high melting, or glass transition temperatures and restricted their solubility in nonaggressive organic solvents, most aromatic polymers are risqué to this process. [17, 18, 19, 20]. Considering all these important aspects, we aimed in this research to: undertake the synthesis of new Unsaturated polyesters by solution polycondensation of diols and different anhydrides, evaluate their thermal properties in details and their characterization through Fourier transform infrared spectroscopy FTIR, ^1H NMR, ^{13}C NMR.

2. Experimental

Numerous methods has been applied in this paper, FTIR Spectra of the monomer and all polymers were tested by using KBr pellets on FTIR Bruker German, model Equionex 55 Spectrometer ($4000\text{--}400$) cm^{-1} .

Nuclear Magnetic Resonance (^1H NMR and ^{13}C -NMR) Spectra were determined in NMR Spectroscopy- Bruker company, 400MHZ for ^1H NMR, 100MHZ for ^{13}C NMR, 9.5 Tesla magnetic using $\text{CD}_3\text{C}(=\text{O})\text{CD}_3$ as solvent.

Thermal analysis of the polymers was tested by

using Instrument : METTLER TOLEDO (Switzerland), Model: DSC 1, Type of (Sample & reference) Pan: Aluminum Crucible Standard $40\mu\text{l}$ and Purity:99.999%, $\text{O}_2 < 50\text{ppm}$, $\text{H}_2\text{O} < 30\text{ppm}$, $\text{Ar} < 30$.

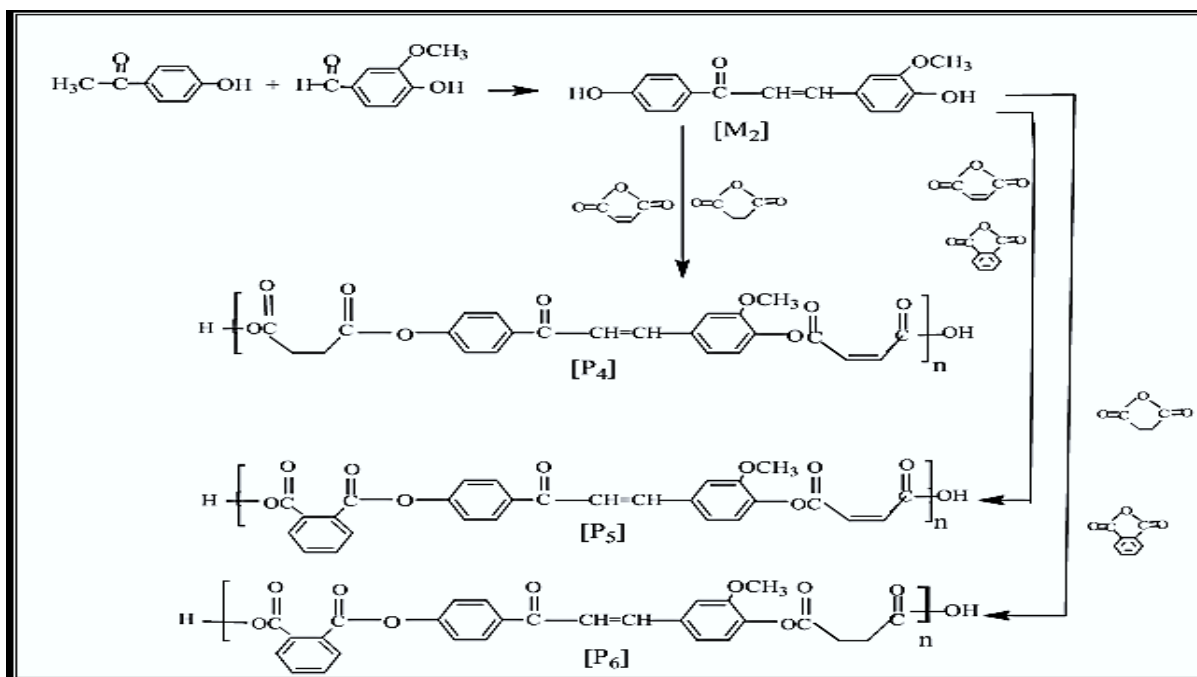
Materials and Methods

Preparation of Monomers and Polymers :-

4-hydroxy-3-methoxy benzaldehyde 0.01 mol and 4-hydroxy acetophenone 0.01 mol were dissolved in 30 ml absolute ethanol to make monomer [M₂]. The mixture was whisked for 5-6 hours after added 10% sodium hydroxide solution (5ml). Then it was put in the refrigerator overnight with continuous stirring. From ethanol, the precipitate was filtered, cleaned, and recrystallized.

Polymers [P₄, P₅, P₆] were synthesized by dissolving the reactants with acetone, then react them by reflux for (6hrs) with zinc chloride as catalyst via polycondensation reaction to give the products.

The reactants for prepared polymer [P₄] were monomer M₂ with succinic anhydride and maleic anhydride but the reactants for synthesized polymer [P₅] were M₂, maleic anhydride and phthalic anhydride while the reactants for prepared polymer [P₆] were monomer M₂, succinic anhydride and phthalic anhydride, scheme (2).



Scheme (1): synthesis of monomer[M₂] and polymers [P₄-P₆]

3- Results and Discussion:

In order to confirm the polyester that synthesized and to estimate matrix and obtained polyester, they were analysed by FTIR .

Figure 1 is offered an infrared spectra of in absorbance with a zoom in the zone in 1708 cm⁻¹ characteristic of vibration of the carbonyl (C=O) of ester group which exist in the polymer P4 backbone.

The structure of all PEs was assured by ¹H-NMR , ¹³C-NMR and FTIR spectroscopy. The synthesis of PEs was assured by the characteristic bands observed about 1700 , 1713 cm⁻¹ (>C=O stretching in the groups of ester) for P5,P6 respectively . 1230,1168 and 1170 cm⁻¹ (CO–C stretching absorptions, unsaturated ester P4 ,P5 and P6 respectively), 1595, 1584 and 1515 cm⁻¹ (aromatic in-plane ring C=C stretching vibration for polymers P4 ,P5 and P6 respectively), 1635 (C=O stretch of chalcon for monomer) also 1662,1665 and 1658 (C=O stretch of chalcon for Polymers P4 ,P5 and P6).

The FTIR spectrum of polymers offer distinctive absorption bands at 1168-1170 cm⁻¹ because of the stretching of OCH₃ methoxy groups. An absorption band at 3224-2800 cm⁻¹ ascribed to COOH stretching vibration of the hydroxyl group was seen in the spectrum of

polymer P4. The broad absorption of the COOH stretching show about 3255-2700 cm⁻¹ in the spectrum of P5. The FTIR spectrum of polymer P6 offered appear absorption bands at 3238-2805 cm⁻¹ (COOH stretching vibration) and disappear stretching vibration of hydroxyl group in all polymers that is obtain in monomer spectrum . The FTIR spectrum of monomer and polyesters are illustrated in Fig. (1-4).

¹H-NMR spectra :

¹H-NMR spectra means application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei through molecules of the substance, with a view to characterize the structure of its molecules.

Figures (5,7 and 9) attend the proton nuclear magnetic resonance spectra of the resultant [P4-P6].

The structure of reiterate units in the polyester chain was as well characterized by ¹³C-NMR (table 3). The signals positioned at 3.63-3.84 ppm were attributed to the carbons of CH=CH alkene of chalcon, those identical to carbons of the phenyl rings were existing around 6.44-7.90 ppm, these assigned to carbons of aliphatic and aromatic esters were spotted at 2.06-2.45 ppm in the ¹H -NMR spectra of all polyesters.

Table 1 : FT.IR data (cm⁻¹) of the polymers and monomers.

Comp.	(COO) ester	(-CO-) Chalcone	CH=CH Alkene chalcon	Other Functional groups of
[M ₂]	-----	1635	3035	(OH)hydroxyl group:3487, 3388
[P ₄]	1708	1662	3060	(COOH)of carboxyl: 3224-2800 ,(CH) aliphatic:2910,(OCH ₃):1169 (C=C)aromatic:1595
[P ₅]	1700	1665	3012	(COOH)of carboxyl:3255-2700 ,(CH) aliphatic:2910,(C=C)aromatic:1584,(OCH ₃):1168
[P ₆]	1713	1658	3085	(COOH)of carboxyl:3238-2805 ,(OCH ₃): 1170,(C=C)aromatic:1585

Table 2: ¹H- NMR data (ppm) of the polymers

Comp.	Ph-rings	CH=CH Alkene of chalcon	Other signals
[P ₄]	6.88-7.90	3.63, 3.75	CO-CH=CH-CO: 2.06, 2.08 CO-CH ₂ -CH ₂ -CO: 2.30, 2.42
[P ₅]	6.92-7.90	3.74, 3.84	CO-CH=CH-CO: 2.10, 2.08
[P ₆]	6.44-7.90	3.62, 3.84	CO-CH ₂ -CH ₂ -CO: 2.34, 2.45

The ¹³C-NMR spectra: Carbon-13 (¹³C) nuclear magnetic resonance is the application of nuclear magnetic resonance (NMR) spectroscopy to the carbon and it is a paramount tool in chemical structure illustration. The ¹³C NMR spectra of the

polyesters were recorded in acetone solvent and offered the chemical shifts in range at (195.80-196.04 ppm) were related to carbon of (COO) ester , showed signals at (123.63-152.78ppm) for carbon Ph-rings and manifest signals at (110-115 ppm)

related to carbon of CH=CH alkene of chalcon and the assignments [21, 22, 23,24] for the diverse peaks observed are presented in Table (3) . Figures (6,8

and 10) attend the The ^{13}C -NMR spectra of the resultant [P₄-P₆]

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

Comp	(COO) ester	Ph-rings	-CO- Chalcon	CH=CH Alkene of chalcon	Other signals
[P ₄]	195.80	130.9-152.75	206	110.19, 115.28	OCH ₃ : 55.59 CO-CH=CH-CO: 126, 129 CO-CH ₂ -CH ₂ -CO: 23.0, 24.0
[P ₅]	196.04	126.17-148.13	206.35	110.27, 115.17	OCH ₃ : 55.65 CO-CH=CH-CO: 119.03 , 123
[P ₆]	196.29	123.63-152.78	206.59	110.29, 115.18	OCH ₃ : 55.67 CO-CH ₂ -CH ₂ -CO: 25.51, 28.53

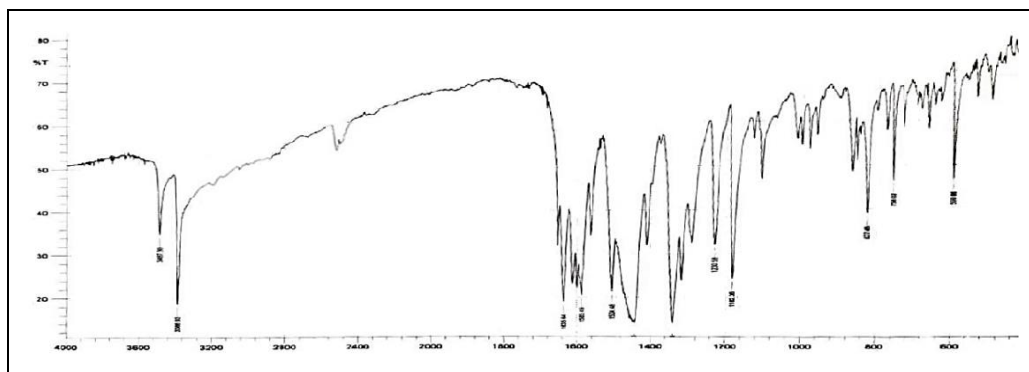


Figure (1) : FT.IR of monomer [M₂]

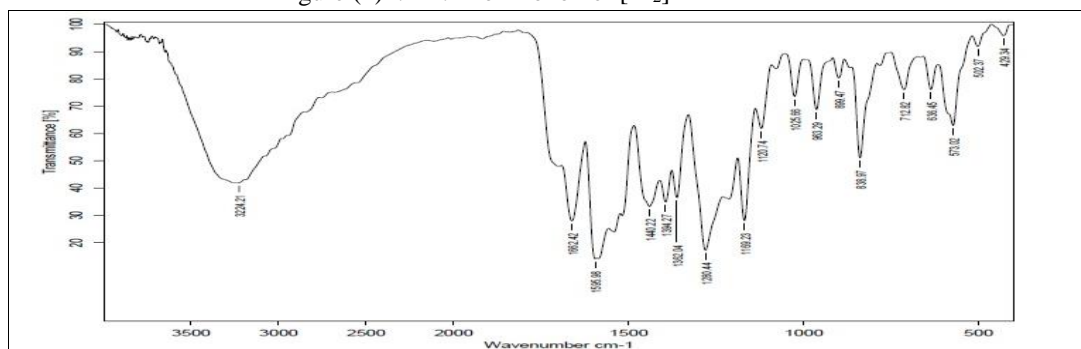


Figure (2):. FT.IR of polymer [P₄]

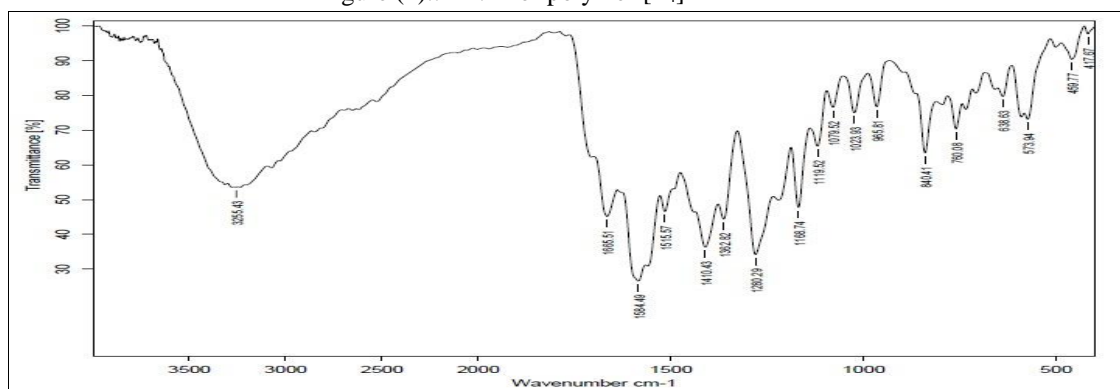


Figure (3) : FT.IR of polymer [P₅]

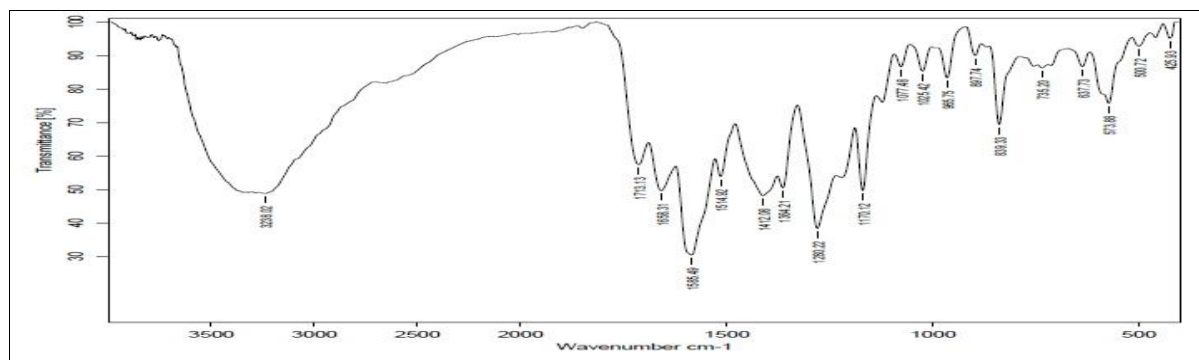


Figure (4): FT-IR of polymer [P₆]

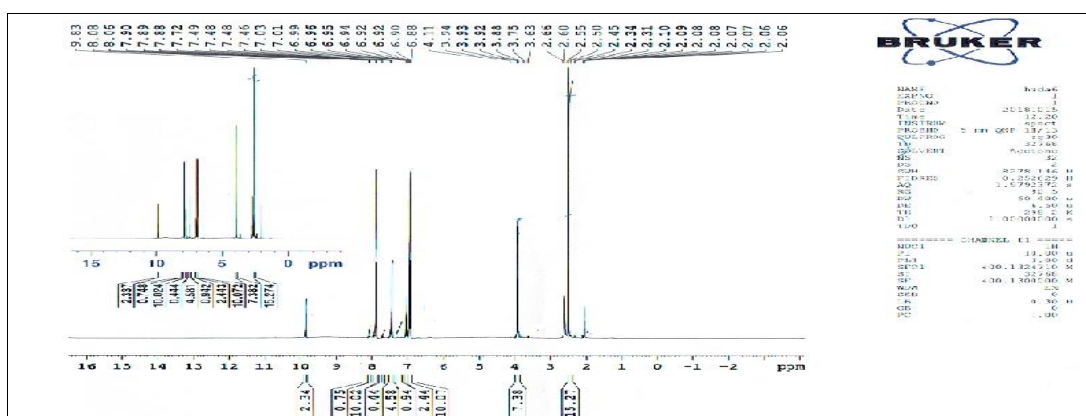


Figure (5) : ¹H-NMR of polymer [P₄]

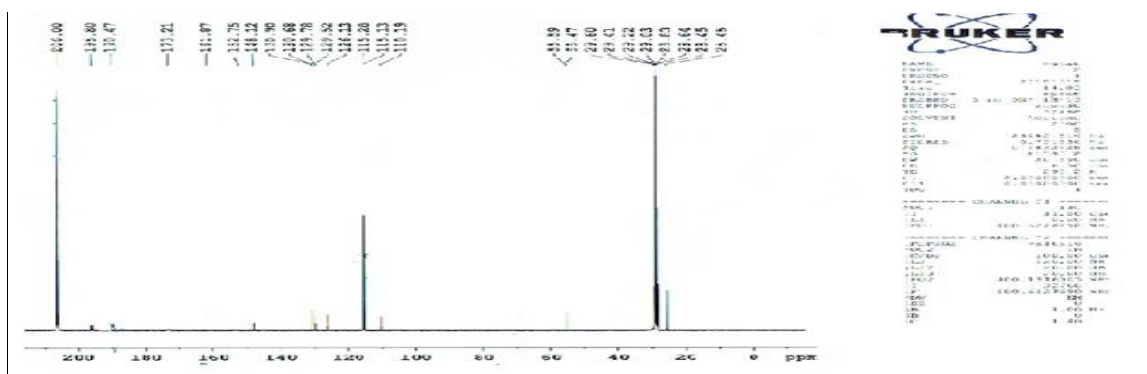


Figure (6): ¹³CNMR of polymer [P₄]

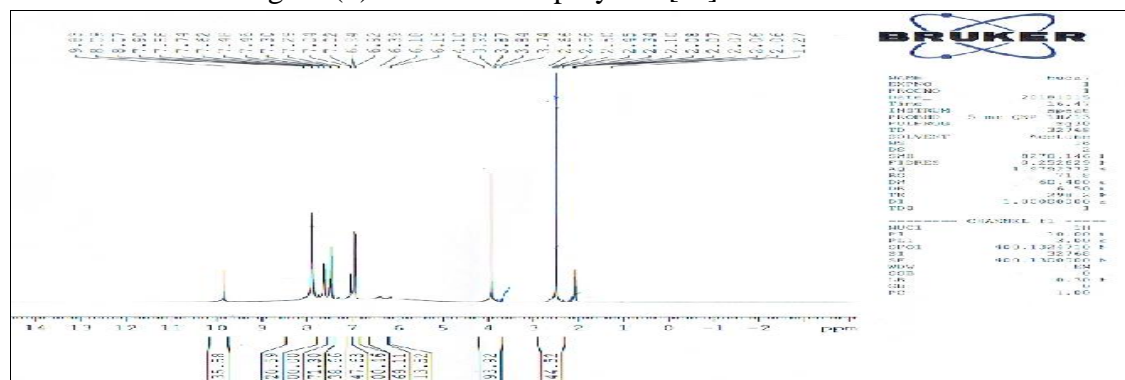
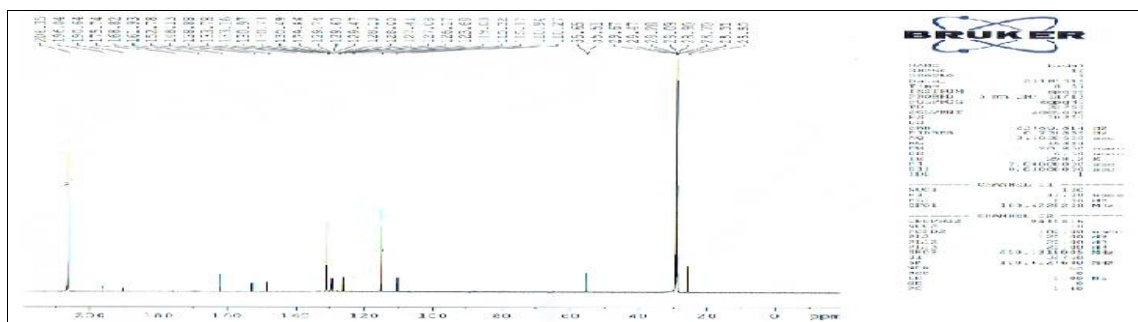
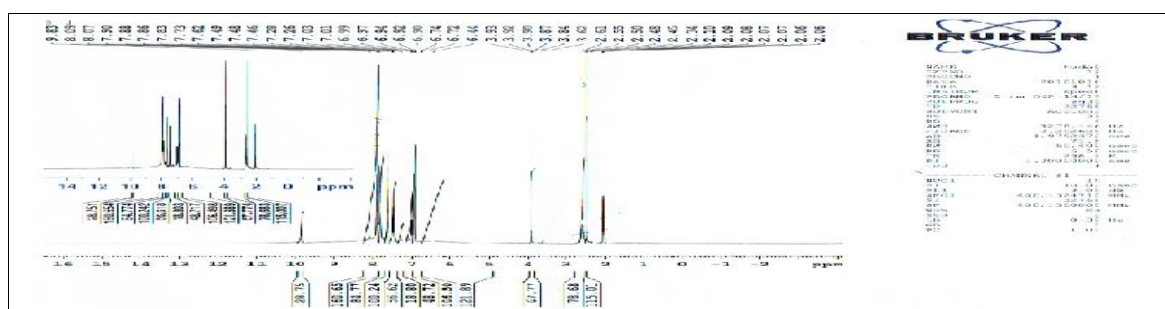
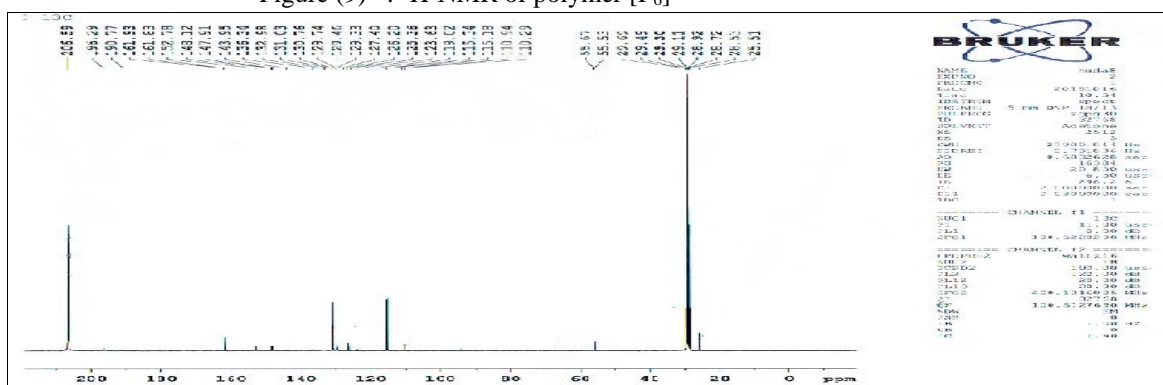


Figure (7) : ¹H-NMR of polymer [P₅]

Figure (8) : ^{13}C NMR of polymer [P₅]Figure (9) : ^1H -NMR of polymer [P₆]Figure (10) : ^{13}C NMR of polymer [P₆]

Thermal properties :

Differential scanning calorimetry (DSC), which measures the heat flow into and out of a polymeric material with temperature, supply a convenient way to determine the crystalline properties of polymers and subsequently to prophesy certain processing and end-use characteristics. Knowing of the thermal properties of polymers is fundamental for developing the best methods for processing the materials into beneficial products and predicting execution during product lifetimes.

Thermal properties of the polyesters DSC, was used to appraise the thermal properties

of the novel polyesters. Confirming the amorphous nature of the polyesters in the DSC analysis .The glass transition temperature (T_g) showed for these PEs was in the range of 65.02 - 71.24 °C. As can be seen, P₄ showed the lower T_g because of its lower molecular weight [25]. As well widely It is attributed to the more readily chain mobility as the lessening of the molecular weights and the irregularity of the chain. The T_g was consistent with a material that has an amorphous (non-crystalline) structure. which contain high levels of benzene rings, are familiar to be wholly amorphous.

There is a lot of mobility for the polymers above the glass transition. they never stay for very long

in one place. When they hit a temperature that is right.

They're accumulating enough energy to switch into very organized configurations, which we call, of course, crystals . They give off heat as polymers fall into these crystalline arrangements . crystallization temperature T_c for synthesized polymers [P4, P5, P6] are 96.29 °C, 161.68 °C, 140.66 °C respectively .

Heat can cause crystals to form in the polymer, but too much of it can be undone. If we keep heating the polymer past its T_c , we will eventually hit another thermal transition called melting. These polymer crystals begin to fall apart when reaching the melting temperature of the polymer, or T_m . That is, they melt. The chains emerge from their organized arrangements and start moving

about freely. On a DSC plot. , we can spot this happening.

melting temperature (T_m) at 116.90 °C, 243.14 °C and 225.58 °C for prepared polymers [P4, P5 and P6] respectively and decomposition temperature (T_d) at 146.62 °C for P4 while T_d for P6 at 265.08 °C .

The DSC thermograms of the polymers [P4, P5 and P6] are presented in Fig. (11-13) These Thermograms show the heat capacity 1.06 Jg⁻¹K⁻¹ for P4, 0.85 Jg⁻¹K⁻¹ for P5 and 0.63 Jg⁻¹K⁻¹ for P6 .

The DSC can reasonably easily calculate the change in the heat capacity at the glass transition (Δc_p) of even small amounts.

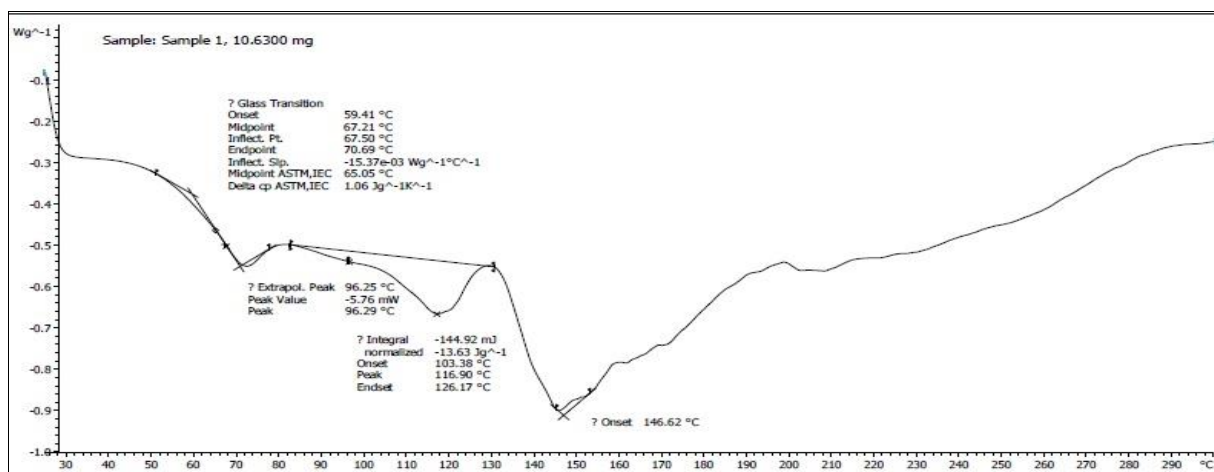


Figure (11): DSC of polyesters Spectrum[P4]

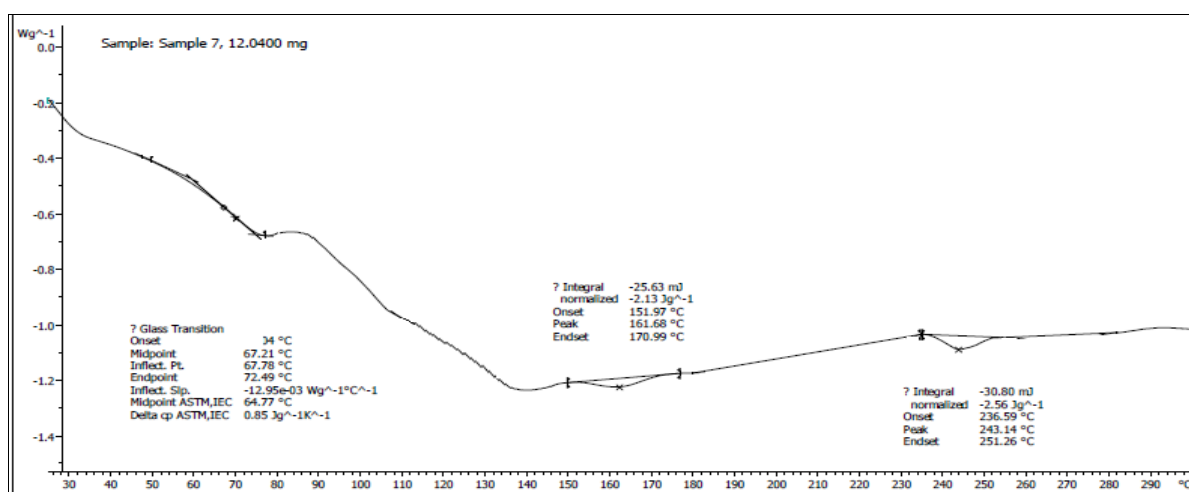


Figure (12): DSC of polyesters Spectrum[P5]

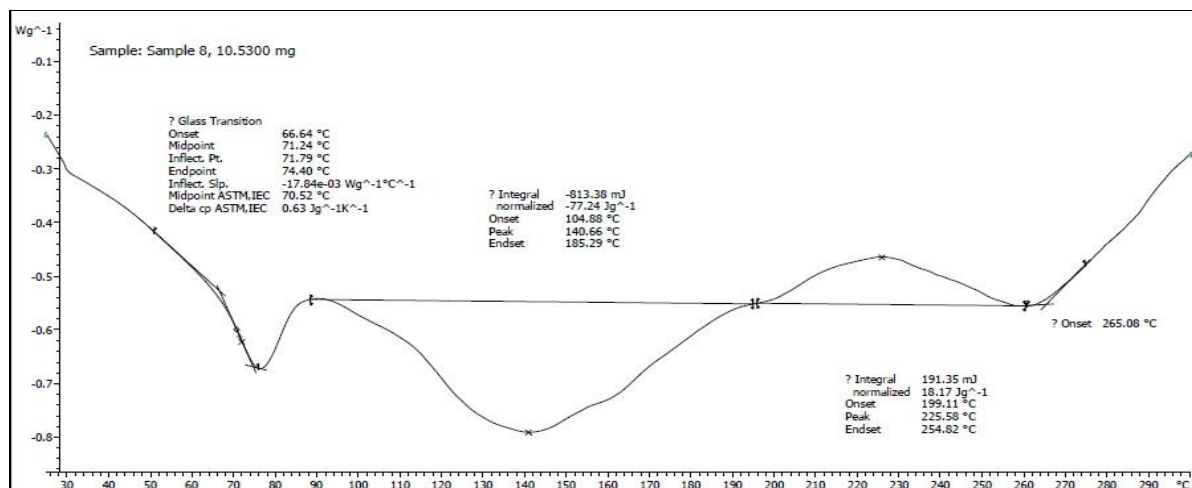


Figure (13): DSC of polyesters Spectrum[P6]

4. Conclusion

This paper reports the successful synthesis of Polyesters containing Chalcone groups in main chains by solution polycondensation of new monomer [E)-1-(4-hydroxyphenyl)-3-(3-methoxy-4-hydroxyphenyl) prop-2-en-1-one] with several aromatic and aliphatic anhydrides in the existence of Zinc chloride as the condensing agent. Overall analytical investigations detect important, structural characteristics of the new monomer and PEs were assured by FT-IR, ¹H- and ¹³C-NMR spectroscopy. Thermal constancy of the obtained polymers was reported as well as glass transition temperatures varied in the range 65.02 - 71.24 °C .

5. Conflict of Interest: There is no any Conflict of Interest for authors.

6. Formatting of funding sources

Self funding

7. Acknowledgments

The author is thankful to Head of Kufa University for providing laboratory facilities

8. References

- [1]-Abdeen Ahamad, Mary Lubic., Abhilash Mohan, Mohamed Safer and Eby Thomas Thachil. " Synthesis of unsaturated polyester resin — effect of anhydride composition ", *Designed Monomers and Polymers*, 2001, 4(3): pp. 261–268 .
- [2]- Shin JH, Lee HK, Kim KM, Lee KH. "Reactive compatibilization of an immiscible polyester/polyolefin blend with PP-g-MAH and PMPI dual compatibilizers. *Journal of Applied Polymer Science*. 2014;131(10): 40232 (1-6).
- [3]- Nakagawa T, Goto M. "Recycling thermosetting polyester resin into functional polymer using subcritical water. *Polymer Degradation and Stability*. 2015;115:16-23.
- [4]- Wiebeck H, Harada J. *Plásticos de Engenharia: tecnologia e aplicações.*; 2005.
- [5]- Pinho EB, Da Costa HM, Ramos VD. "Technical analysis of the use of polyester wastes in textile industry". *Polímeros*. 2013;23(5):654-660. <http://dx.doi.org/10.4322/polimeros>.
- [6]- Aizenshtein EM. "Still no crisis for polyester fibres". *Fibre Chemistry*. 2010;42:1-9.
- [7]- Diana Katruk , Volodymyr Levytskyi , Ulyana Khromyak, Volodymyr Moravskyi , and Andrii Masyuk " Physicochemical Principles of Synthesis and Modification of Unsaturated Polyester-Polyvinyl Chloride Composites and the Properties of Materials Derived from Them", *International Journal of Polymer Science*, 2019 , Article ID 2547384, 9 pages. <https://doi.org/10.1155/2019/2547384>
- [8]- U. Poth, "Polyester und Alkydharze", 2., überarbeitete Auflage, *Vincentz Network, Hannover*, 2014.
- [9]- Y.-W. Mai and Y. Zhong-Zhen," Polymer Nanocomposites", *Woodhead Publishing Limited, Cambridge, UK*, 2006.
- [10]- V. K. Thakur, M. K. Thakur, and A. Pappu. "Hybrid Polymer Composite Materials", *Woodhead Publishing Limited, Cambridge, UK*, 2017.
- [11]- Kusmono and Z. A. M. Ishak, "Effect of clay addition on mechanical properties of unsaturated polyester/glass fiber composites," *International*

- Journal of Polymer Science*, 2013, Article ID 797109, 7 pages.
- [12]- V. Chaudhary, A. K. Rajput, and P. K. Bajpai, "Effect of particulate filler on mechanical properties of polyester based composites," *Materials Today: Proceedings*, 2017, 4 (9) : pp. 9893–9897.
- [13]- Ayman M. Atta^{1,*}, Sayed I. Elnagdy², Manar E. Abdel-Raouf¹, Shimaa M. Elsaed¹ and Abdel-Azim A. " Compressive Properties and Curing Behaviour of Unsaturated Polyester Resins in the Presence of Vinyl Ester Resins Derived from Recycled Poly(ethylene terephthalate)", *Journal of Polymer Research*, 2005, 12(5): pp 373–383 .
- [14]- Hearle JW. & Morton W E." Physical properties of textile fibres. *Elsevier*, (2008)
- [15]- Burkinshaw, S. M. "Chemical principles of synthetic fibre dyeing". *Springer Science & Business Media*, (1995).
- [16]- Conca, James. "Making Climate Change Fashionable - The Garment Industry Takes On Global Warming". *Forbes*. Retrieved 12 December 2018.
- [17]- Liaw DJ, Chen P. "Preparation and properties of polyesters derived from 4,4'- sulfonyl dibenzoyl chloride by solution polycondensation ", *J. Polym. Sci., A: Polym. Chem.* 1996,34 (5) :pp 885. [https://doi.org/10.1002/\(SICI\)1099-0518\(19960415\)34:5%3C885::AID-POLA17%3E3.0.CO;2-E](https://doi.org/10.1002/(SICI)1099-0518(19960415)34:5%3C885::AID-POLA17%3E3.0.CO;2-E)
- [18]- Hsiao SH, Chiou JH. "Polyarylates Containing Sulfone Ether Linkages".*Polym. J.* 2001,33:PP 95-101.
- [19]- NECHIFOR M. "Aromatic polyesters with photosensitive side chains:Synthesis, characterization and properties", *J. Serb. Chem. Soc.*, 2016,81 (6) :PP 673–685 .
- [20]- Hassen H S., Majeed N S., Mohsein H F., Hassan E S. "Synthesis and Characterization of Monomer and Three Types of Polymers Containing Chalcone Groups in Main Chain". *Egypt. J. Chem.* ,2020, 63(11) : pp. 4195 – 4203.
- [21]- Fonseca A. C. , Gil M. H. and Simões P. N. "Biodegradable poly(ester amide)s—A remarkable opportunity for the biomedical area: Review on the synthesis, characterization and applications". *Prog. Polym. Sci.*, 2014,39:1291–1311.
- [22]- Ghosal K, Latha MS, Thomas S. "Poly (ester amides)(PEAs)—scaffold for tissue engineering applications ". *Eur Polym J.* 2014;60:58–68.
- [23]- Galan AR, Franco L. and Puiggali J." Degradable Poly(ester amide)s for Biomedical Applications" . *Polymers*,2011, 3(1) : 65–99. [DOI:10.3390/polym3010065](https://doi.org/10.3390/polym3010065)
- [24]- Ulery BD, Nair LS and Laurencin CT." Biomedical Applications of Biodegradable Polymers" *J. Polym. Sci., Part B: Polym. Phys.* 2011, 49, 832–864. <https://doi.org/10.1002/polb.22259>
- [25]- Jamshidi K., Hyon S-H., Ikada Y."Thermal characterization of polylactides". *Polymer*, 1988, 29(12): 2229–2234 . [https://doi.org/10.1016/0032-3861\(88\)90116-4](https://doi.org/10.1016/0032-3861(88)90116-4)