Ministry of Higher Education
and Scientific Research

Journal of Kufa for Chemical Sciences

A refereed

Research Journal Chemical Sciences
Vol.2 No.8 Year 2022
ISSN 2077-2351

Address:
Iraq-Najaf-University of Kufa
Box(190)

www.Edu_girl.Kuiraq.com

E-mail:Edu_grils@kuiraq.com

Synthesis And Characterization Of New Long Chain Aliphatic Polyesters Derived From Dicarboxylic Acid With Diols Using *p*-Toluene Sulfonic Acid As Catalyst

Thaer.A.Jwaid[1], Moayad.N.Khalaf [2], Hana.S.Abbo[2]

[1] Fuel and Energy Department, Engineering Technical Collage, Southern Technical University,Basra,Iraq.

[2]Department of Chemistry, College of Science, University of Basra, Basra, Iraq.

Abstract

The recent research in the polymers area concern with the synthesis of aliphatic biodegradable polyester- based polymers with long chain which can be degraded usefully. The aliphatic based polyester was receiving special attention due to sensitivity to degradation. A new series of long-chain linear co-polyesters with up to 20 carbon atoms were designed and synthesized in this study by condensation polymerization catalyzed by *p*-toluene sulfonic acid using toluene as solvent.

Copolyesters containing various structure aliphatic diols were prepared as decan-1,10-dioic acid-co–cis-buten-2,4-dioate (**P1**), dodecane-1,10-dioic acid -co-1,10- decanedioate (**P2**), 1,4-cyclohexane-co-1,4-butandicarboxylate (**P3**) and 1,4-cyclohexan-co-1,10-decancarboxylate (**P4**).

The linear copolyesters were characterized by variety of techniques such as FTIR, ^{1}H- and ^{13}C-NMR spectroscopy. The average molecular weight (Mw), number average molecular weight (Mn) and poly dispersity index for these poly esters were measured by gel permeation chromatography techniques, The influence of the different polyesters middle block on microstructure, the structures and crystallization properties of the copolymers was investigated. **P1** copolymer showed the highest weight average molecular weight (Mw) of 17771 g/mole and copolymer **P2** showed number average molecular weight (Mn) 5484 g/mole , while poly disparity index(PDI) was 3.78 for copolymer **P1** .

Keyword: aliphatic polyester, biodegradable polyester, linear aliphatic polyester.

1. Introduction

Aliphatic polyesters have gained increasing attention in solving “white pollution” concerns which caused by conventional non-biodegradable polymers as well as their use as particularity polymers in biomedical field applications [1][2].Up to now, polyesters are considered the most competitive biodegradable polymers commercialized. Poly (alkylene dicarboxylate) comprise a particular family of polyesters as it can be obtained from renewable resources. Generally, The aliphatic poly esters with long chain repeating unit was prepared early by Carothers[3], long chain monomers are considered to consist of chain 14 carbon atoms or longer, but are a rather general agreement that 10-15 carbon atoms the lower limit of linear long chain compounds[4]. However, the long chain reap unit were some advantage and used widely in industry such as the plasticization modification of linear poly ester with poly vinyl chloride(PVC)[5], also it obtaining sufficient molecular weight to achieve some properties of mechanical strength[6].They are usually applied to synthesize perfumes, special nylon engineering plastics[7],hot melt adhesives[8],coatings[9], plasticizers, senior lubricants[10],drag reduction agent[11],Biopolymers produced from renewable source raw materials provide an environmentally friendly and many other chemical products[12]. Molecular weight calculation (molecular weight distribution) for long chain polyester is very important because of influencing on crystallization behaviors, ratio of degradation and melting point [13], most polyesters made from DA and diols are crystalline polymers. For impact modification or elastomer applications, amorphous flexible polyesters are often more desired as they can provide better chain flexibility than crystalline counterparts [14].

Reactions involving the condensation of organic materials are called poly condensation. The prepared polyesters are one of the classes of condensation reactions that include two types of monomers such as di carboxylic acid and diols to form alternative copolymers.

In the work, we investigated the poly condensation of di carboxylic acid with diols to form copolymers by using *p*-toluene sulfonic acid (PTSH) as catalyst. A basic catalyst to remove water output from reaction and use toluene as solvent [15]. Several polyesters have been synthesized on the basis poly (decan-1,10-dioic-co-cis-2-buten-2,4-dioate) **P1** from monomer Sebacic acid and cis-2-butene 1,4-diol.in a similar way was synthesis copolymer (dodecandioic acid-co-1,10-decandioate) **P2** also prepared long chain co-polyester that contain unsaturated rings such as poly(1,4-cyclohexane-co-1,4-butancarboxylate) **P3** and poly(1,4-cyclohexane-co-1,10-decancarboxylate) **P4** from monomer 1,4-cyclo hexandiol. These compounds were discussed structures, characterization and molecular weight distribution for all synthesized polyesters.

2-Experimental

2.1-meterials:

Sebacic acid (99%), *p*-toluene sulfonic acid (PTSA), cis-2-butene1,4-diol (98% BHD), dodecanedioic acid (99%), 1,10-decandiol (98%), adpatic acid (98% BHD) and 1,4-cyclohexanediol

(98% BHD), toluene, sodium hydroxide (0.01N), argon gas. All materials were purchased from Sigma Aldrich and were used without further purification.

2.2- synthesis of polyesters

2.2.1-Synthesis of copolymer (decan 1,10-dioic acid - co – cis,2-buten 1,4-dioate)(**P1**)[16][17].

Sebacic acid (10 gm ,49 mmol), 2% w\w of *p*-toluene sulfonic acid in 50 ml anhydrous toluene were charged into 250 round bottom flask fitted with Dean Stark apparatus equipped with a separating funnel and inlet class tube for argon gas, Argon gas is bubbled through a reaction mixture at ambient pressure for 5 min. Then the mixture was heated to its boiling point .the reaction was stopped after water collecting in graduated tube of dean stark flask. The mixture was cooled and washed with 0.01N solution of sodium hydroxide to extracted residual of *p*- toluene sulfonic acid, also washed with water five times and evaporated by rotary evaporator to obtain (60 %) weight solid yellow product, At the same procedure method synthesis copolymer (Dodecane 1, 10-dioic acid -co-1,10-decan dioate)(**P2**).

2.2.2- synthesis copolymer (1,4-cyclo hexane - co - 1,4-butane di carboxylate) (**P3**).

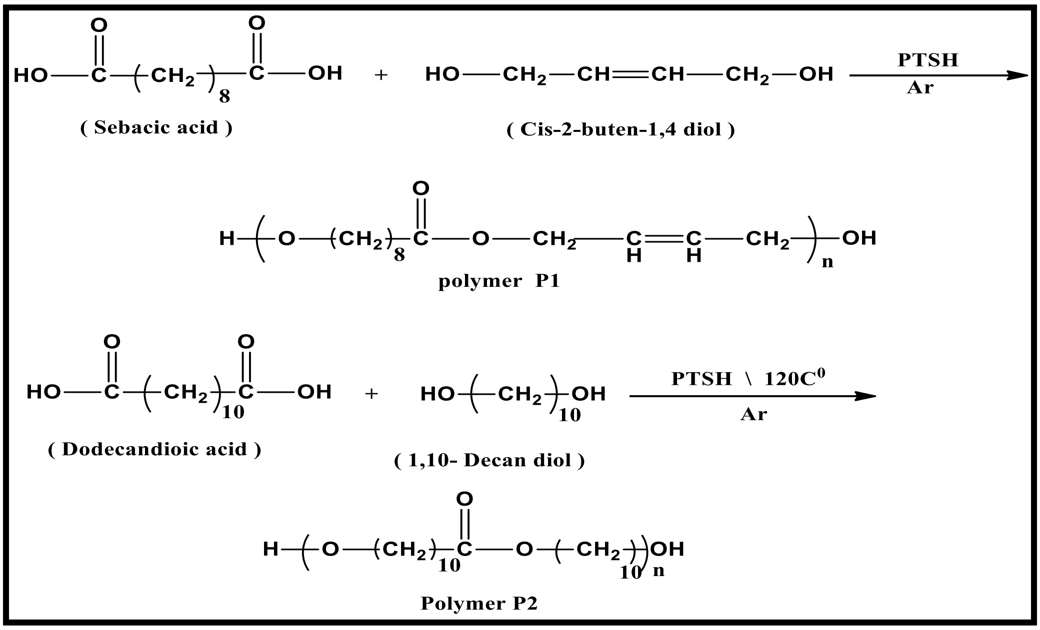
1,4-cyclohexandiol (2.8 gm, 24 mmol) dissolved in 50 ml toluene,then added (3.9 g, 24 mmol) adipatic to solution in a round bottom flask (250 ml) fitted with Dean-Stark apparatus. The reaction mixture was heated to 150 C^0 for 10 min, then 2% of *p*-toluene sulfonic acid was added under inert argon gas and the reaction mixture was left refluxed for 4 hours. At the end of the reaction, the mixture was cooled and p-toluene sulfonic acid was extracted with a suitable solvent such as diethyl ether or toluene, washed first with 50 ml of 0.01N NaOH and with 10 ml acetone-methanol (1:1) and finally washed with distilled water. the product is concentrated through evaporation and afterward subjected to vacuum to obtained brown waxy solid (45%) **P3.** The copolymer (1, 4-cyclohexane-co-1,10-decancarboxylate)**P4** was prepared using the same procedure as above.

3-Characterization:

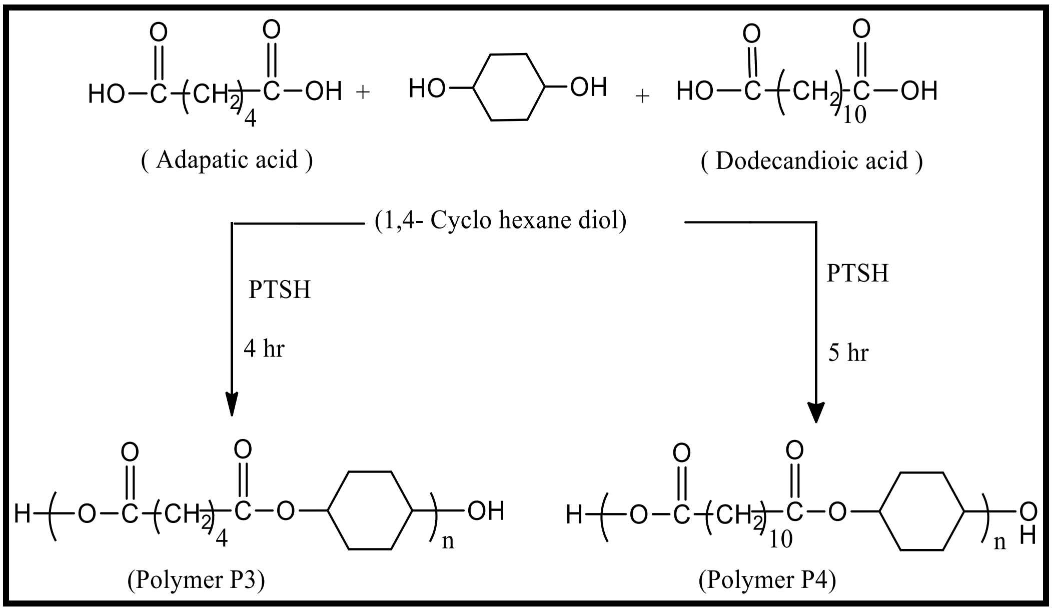
The chemical structures of the co-polymers were confirmed by nuclear magnetic resonance (NMR) and Fourier transformation infrared spectroscopy (FT-IR). The FTIR spectra of the synthesized polymers were recorded on Shimadzo FTIR spectrometer 4800A (Japan) as KBr discs in the range of 400–4000 cm-1 with a resolution of cm^{-1}.

1H- and 13C-NMR spectra of the samples were recorded on 500 MHz JEOI-JNN-EX advance ultra-shield instrument spectrometer (Japan) and Bruker 125 MHZ type advance III DRX 500 (Germany), respectively, using deutrated dimethyl sulfoxide (DMSO-d6) as solvent in the University of Tabriz, (Iran). The chemical shifts were reported in part per million (ppm) and using internal standard tetra methyl silane (TMS).

The molecular weights of the synthesized polymers were determined by gel permeation chromatography (GPC). GPC was run on a Waters Breeze system equipped. THF as a mobile phase was eluted at a flow rate of 1.0 mL/min at 25°C. Polystyrene standards in the molecular weight range of 600–20,000 Dalton were also run to obtain a calibration curve. The molecular weights of the polymers were calculated from the retention times of the polymers using the calibration curve.



Scheme1 synthetic of long chain aliphatic polyesters P1, P2.



Scheme 2 synthetic of long chain aliphatic polyesters P3,P4.

4. Result and discussion

Synthesis of long-chain aliphatic polyester was obtained by direct esterification of dicarboxylic acids and diols in an A2+B2 polycondensation with removal of the liberated water (Scheme 1and 2). The direct esterification proceeds very slowly even at high reaction temperatures. Thus, for the preparation of high molecular weight polyesters the presence of a catalyst is generally required Metal salts and oxides, as well as organometallic compounds have been used as active catalysts [18][19].The long-chain polyester was characterized by IR spectroscopy, Fig1 and fig2, display the spectra of **P1** which show a band at 1732 cm^{-1} attributed to the carbonyl group (C=O)[20]. Strong bands at 1176 cm^{-1} and 1215 cm^{-1} are assigned to the carbonyl ester group (C-O)[21], while copolymer **P2** shows the same bands at 1168 cm^{-1} and 1219 cm^{-1}. A weak absorption band at 1631 cm^{-1} for copolymer **P1** attributed to stretching vibration bond (C=C) so attributable absorption band at 3444 cm^{-1} for copolymer **P1** that intermolecular bonded carboxyl group, while appearance the same ban for copolymer **P2** at 3448 cm^{-1} and 3525 cm^{-1} for inter carboxylic acid group[22].

P3 and, **P4** copolymer containing cyclo compounds were showed spectra vibration band at (415,1419) cm^{-1} respectively for streching (-CH2-) group scissoring cyclo compounds[23] .

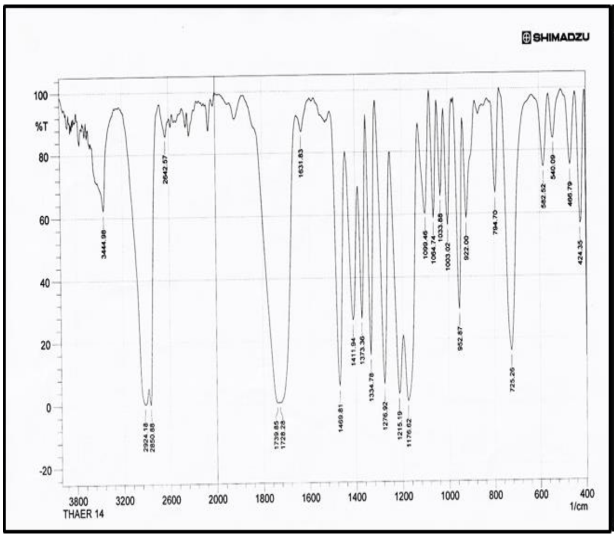


Fig1 infrared spectra for copolymer P1

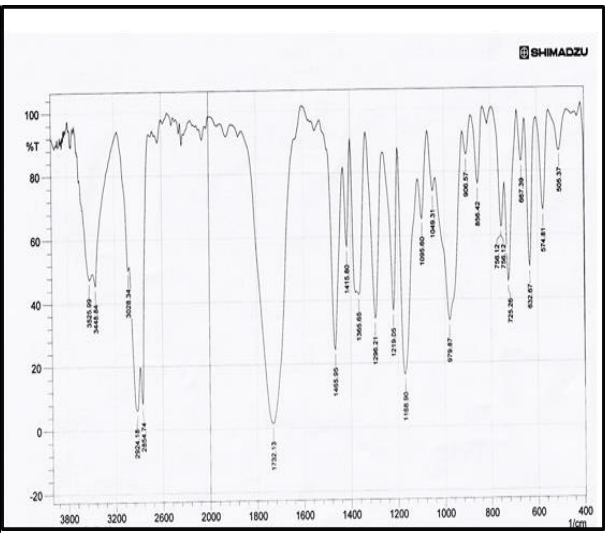


Fig 2 infrared spectra for copolymer P2

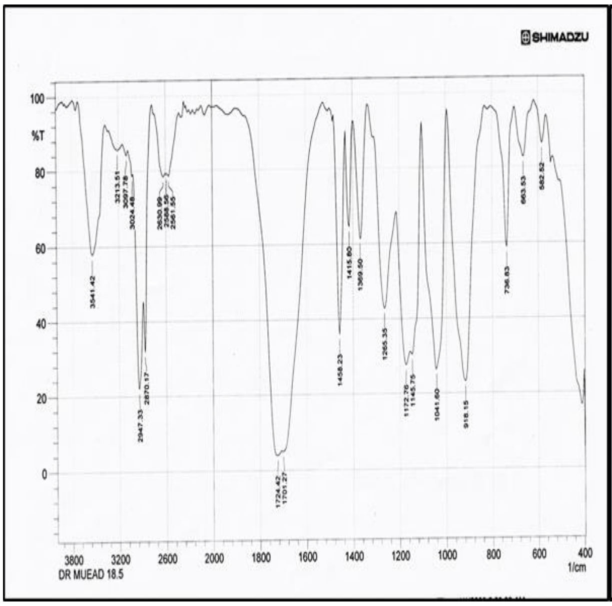


Fig 3 infrared spectra for copolymer P3

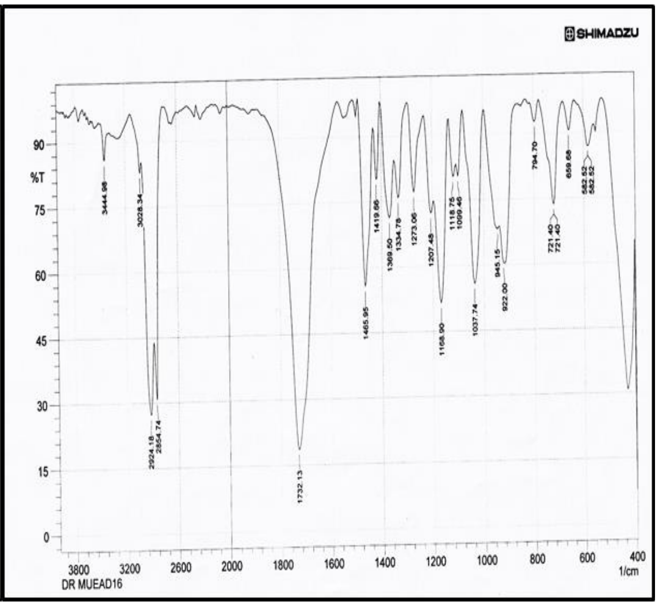
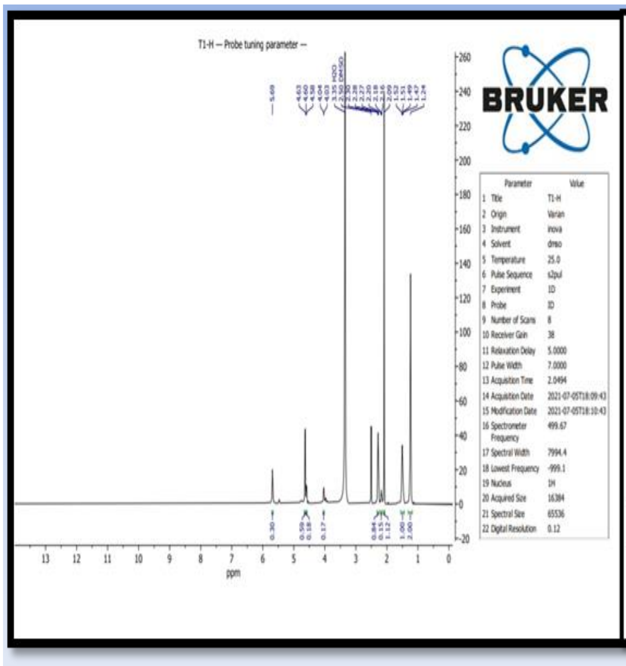


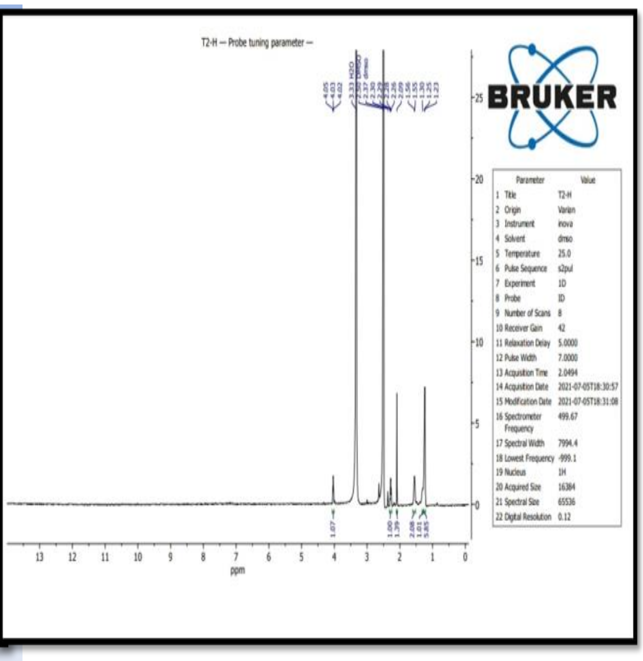
Fig 4 infrared spectra for copolymer P4

The copolymers were measured NMR spectroscopy in dimethyl sulfoxide (DMSO d6) as solvent. The copolymer **P1** show signal at 4.5 ppm and 2 ppm for protons methylene group (-CH2 -), the tow protons for (-CH=CH-) has shown signal at 5.6ppm because shielding chemical shift by oxygen atom neighbor[24][25]. The terminal protons as (OH) and (H) was showed tow bands at 2.18 ppm and 4 ppm respectively. While P3 copolymer was showed strong band at 1.5 ppm for protons methylene group and 2.22 ppm for protons cyclo hexane group [26]. P4 copolymers assigned strong band at 1.2 ppm for methylene group (-CH2 -) 10 and 4.79 ppm for proton al- cohol group. While

H terminal at 4.89 ppm, six protons for cyclo hexane were showed at 2.1 ppm and 1.8 ppm[27][28][29].

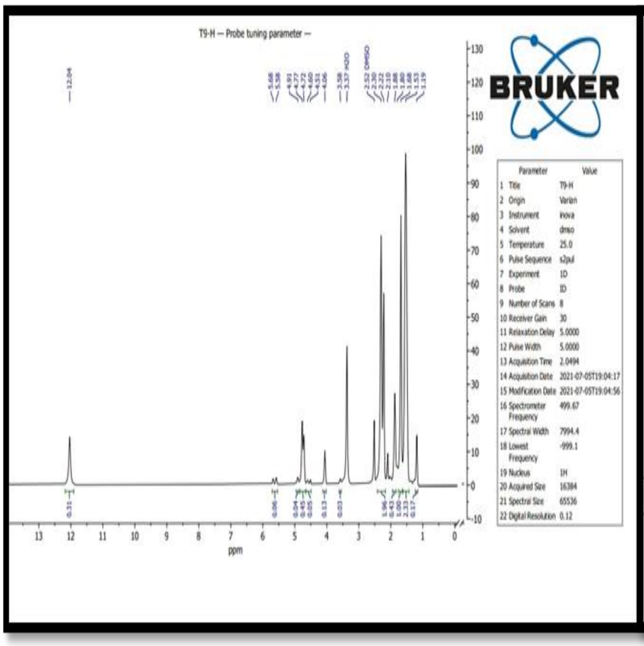


Parameter	Value
1 Title	T1-H
2 Origin	Varian
3 Instrument	inova
4 Solvent	dmso
5 Temperature	25.0
6 Pulse Sequence	s2pul
7 Experiment	1D
8 Probe	ID
9 Number of Scans	8
10 Receiver Gain	38
11 Relaxation Delay	5.0000
12 Pulse Width	7.0000
13 Acquisition Time	2.0494
14 Acquisition Date	2021-07-05T18:09:43
15 Modification Date	2021-07-05T18:10:43
16 Spectrometer Frequency	499.67
17 Spectral Width	7994.4
18 Lowest Frequency	-999.1
19 Nucleus	1H
20 Acquired Size	16384
21 Spectral Size	65536
22 Digital Resolution	0.12

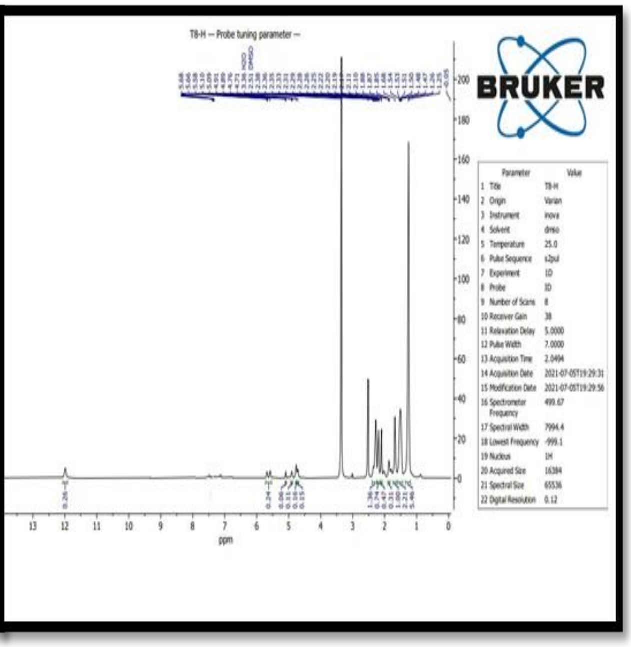


Parameter	Value
1 Title	T2-H
2 Origin	Varian
3 Instrument	inova
4 Solvent	dmso
5 Temperature	25.0
6 Pulse Sequence	s2pul
7 Experiment	1D
8 Probe	ID
9 Number of Scans	8
10 Receiver Gain	42
11 Relaxation Delay	5.0000
12 Pulse Width	7.0000
13 Acquisition Time	2.0494
14 Acquisition Date	2021-07-05T18:30:57
15 Modification Date	2021-07-05T18:31:08
16 Spectrometer Frequency	499.67
17 Spectral Width	7994.4
18 Lowest Frequency	-999.1
19 Nucleus	1H
20 Acquired Size	16384
21 Spectral Size	65536
22 Digital Resolution	0.12

Fig5 ^{1}H-NMR spectrum for copolymer P. Fig6 ^{1}H-NMR spectrum for copolymer P2



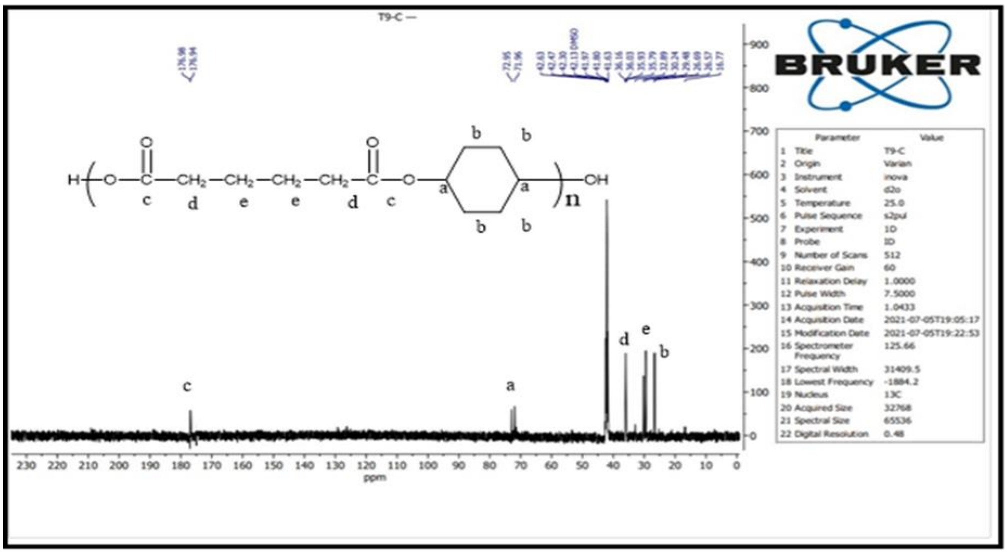
Parameter	Value
1 Title	T9-H
2 Origin	Varian
3 Instrument	inova
4 Solvent	dmso
5 Temperature	25.0
6 Pulse Sequence	s2pul
7 Experiment	1D
8 Probe	ID
9 Number of Scans	8
10 Receiver Gain	30
11 Relaxation Delay	5.0000
12 Pulse Width	5.0000
13 Acquisition Time	2.0494
14 Acquisition Date	2021-07-05T19:04:17
15 Modification Date	2021-07-05T19:04:56
16 Spectrometer Frequency	499.67
17 Spectral Width	7994.4
18 Lowest Frequency	-999.1
19 Nucleus	1H
20 Acquired Size	16384
21 Spectral Size	65536
22 Digital Resolution	0.12



Parameter	Value
1 Title	T8-H
2 Origin	Varian
3 Instrument	inova
4 Solvent	dmso
5 Temperature	25.0
6 Pulse Sequence	s2pul
7 Experiment	1D
8 Probe	ID
9 Number of Scans	8
10 Receiver Gain	38
11 Relaxation Delay	5.0000
12 Pulse Width	7.0000
13 Acquisition Time	2.0494
14 Acquisition Date	2021-07-05T19:29:31
15 Modification Date	2021-07-05T19:29:56
16 Spectrometer Frequency	499.67
17 Spectral Width	7994.4
18 Lowest Frequency	-999.1
19 Nucleus	1H
20 Acquired Size	16384
21 Spectral Size	65536
22 Digital Resolution	0.12

Fig7 ^{1}H-NMR spectrum for copolymer P3   Fig8 ^{1}H-NMR spectrum for copolymer P4

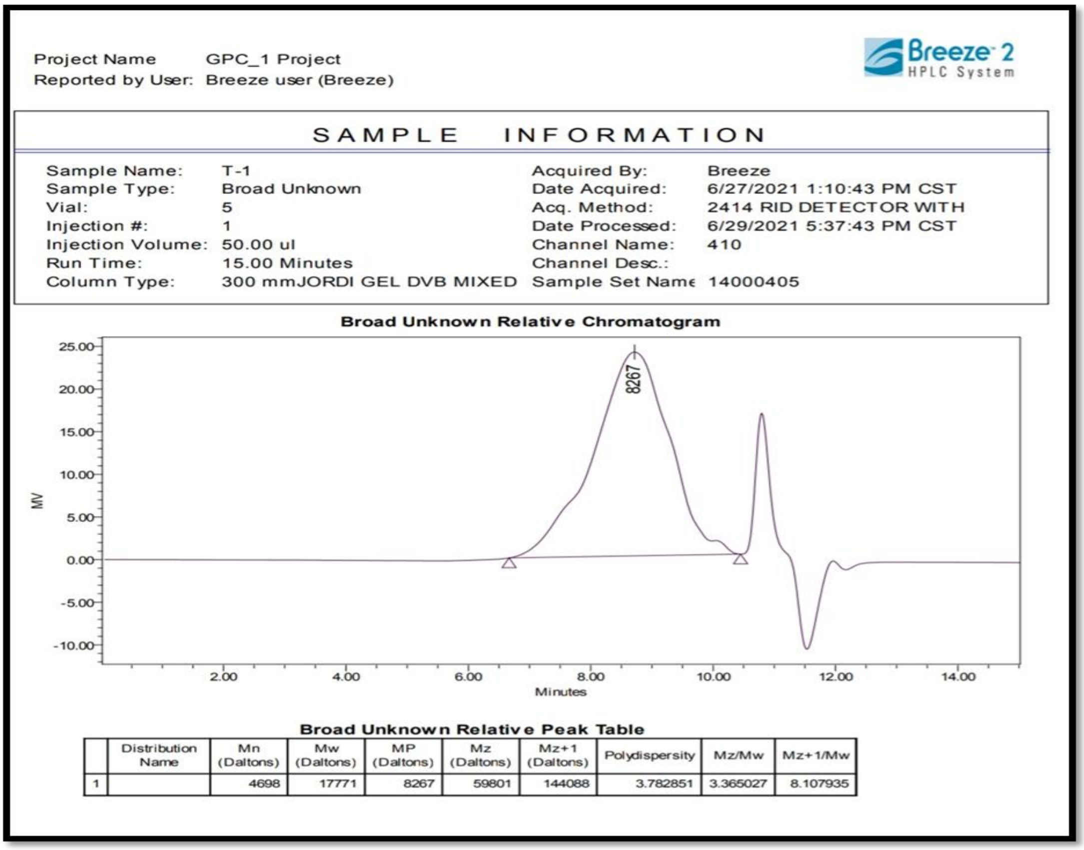
The synthesized polyester were characterized by ^{13}C-NMR spectra for copolymer **P3** only, **P3** Copolymer show signal at 176 ppm was attributed to carbonyl carbon (c)[30] while the methylene carbon at polymer chain was signal at 36ppm and 32ppm for(d) and (e)[31] .on the other the methylene carbon in cyclo hexane (b) show signal at 23 ppm .while carbon (a) at 71 ppm[32].



Parameter		Value
1	Title	T9-C
2	Origin	Varian
3	Instrument	inova
4	Solvent	d2o
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	ID
9	Number of Scans	512
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	7.5000
13	Acquisition Time	1.0433
14	Acquisition Date	2021-07-05T19:05:17
15	Modification Date	2021-07-05T19:22:53
16	Spectrometer Frequency	125.66
17	Spectral Width	31409.5
18	Lowest Frequency	-1884.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536
22	Digital Resolution	0.48

Fig 9 ^{13}C-NMR spectra for polymers P3

Gel permeation chromatography (GPC) is the only technique available to characterize the molecular weight distribution of polymers and separate mixtures into discrete fractions such as polymer, found copolymer **P1** has number average molecular weight (Mn) was 4698 g/mole ,weight average molecular weight (Mw) was 17771 g/mole and poly disparity index (PDI) 3.78. While copolymer **P2** has (Mn) was 5484g / mole, (Mw) was 11094 g/ mole and poly dispersity index (PDI) was 2.0. Copolymer **P3** has (Mn) was 523 g/mole ,(Mw) was 1076 g/ mole and poly dispersity index (PDI) was 1.6 also copolymer **P4** has (Mn) 2292 g /mole ,(Mw) was 7499 g/ mole and pol dispersity index (PDI)was 3.2.



Project Name GPC_1 Project
Reported by User: Breeze user (Breeze)

SAMPLE INFORMATION

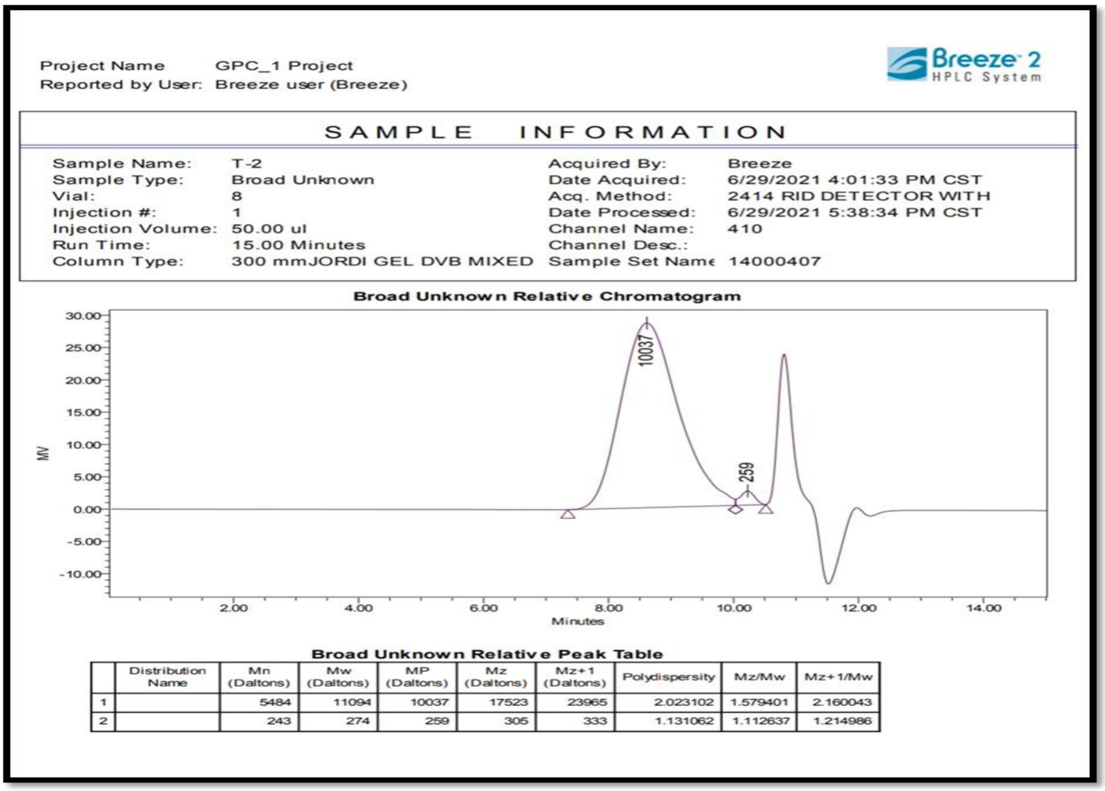
Sample Name: T-1
Sample Type: Broad Unknown
Vial: 5
Injection #: 1
Injection Volume: 50.00 ul
Run Time: 15.00 Minutes
Column Type: 300 mmJORDI GEL DVB MIXED
Acquired By: Breeze
Date Acquired: 6/27/2021 1:10:43 PM CST
Acq. Method: 2414 RID DETECTOR WITH
Date Processed: 6/29/2021 5:37:43 PM CST
Channel Name: 410
Channel Desc.:
Sample Set Name 14000405

Broad Unknown Relative Chromatogram

Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		4698	17771	8267	59801	144088	3.782851	3.365027	8.107935

Fig 10 GPC spectrum and data relative peak for copolymer P1



Project Name GPC_1 Project
Reported by User: Breeze user (Breeze)

SAMPLE INFORMATION

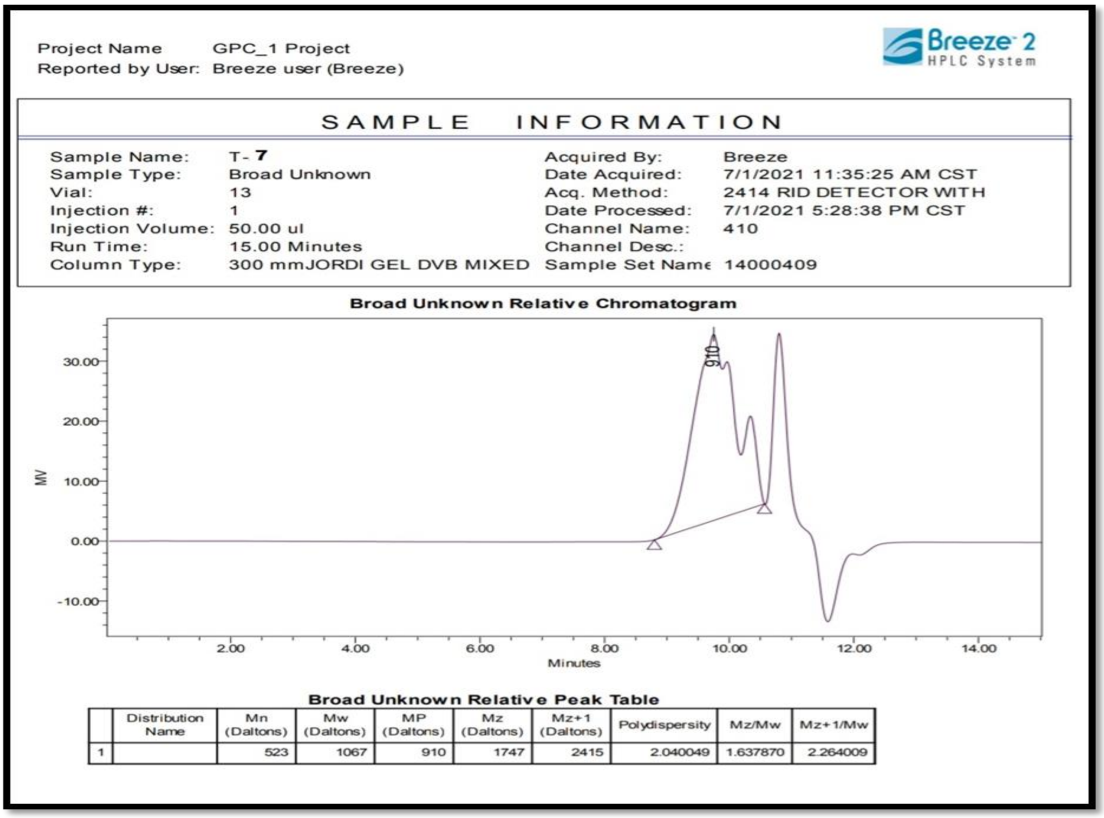
Sample Name: T-2
Sample Type: Broad Unknown
Vial: 8
Injection #: 1
Injection Volume: 50.00 ul
Run Time: 15.00 Minutes
Column Type: 300 mmJORDI GEL DVB MIXED
Acquired By: Breeze
Date Acquired: 6/29/2021 4:01:33 PM CST
Acq. Method: 2414 RID DETECTOR WITH
Date Processed: 6/29/2021 5:38:34 PM CST
Channel Name: 410
Channel Desc.:
Sample Set Name 14000407

Broad Unknown Relative Chromatogram

Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		5484	11094	10037	17523	23965	2.023102	1.579401	2.160043
2		243	274	259	305	333	1.131062	1.112637	1.214986

Fig11 Spectrum and data relative peak for copolymer P2



Project Name GPC_1 Project
Reported by User: Breeze user (Breeze)

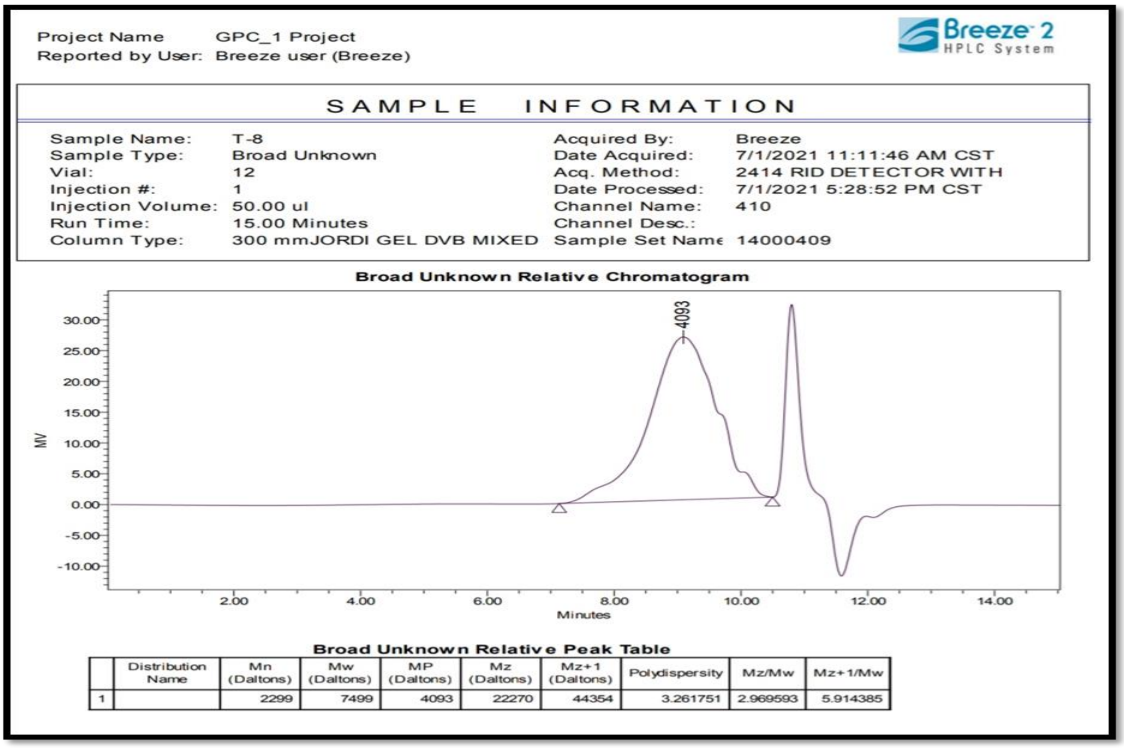
SAMPLE INFORMATION

Sample Name:	T- **7**	Acquired By:	Breeze
Sample Type:	Broad Unknown	Date Acquired:	7/1/2021 11:35:25 AM CST
Vial:	13	Acq. Method:	2414 RID DETECTOR WITH
Injection #:	1	Date Processed:	7/1/2021 5:28:38 PM CST
Injection Volume:	50.00 ul	Channel Name:	410
Run Time:	15.00 Minutes	Channel Desc.:	
Column Type:	300 mmJORDI GEL DVB MIXED	Sample Set Name	14000409

Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		523	1067	910	1747	2415	2.040049	1.637870	2.264009

Fig 13 GPC spectrum and data relative peak for copolymer P3



Project Name GPC_1 Project
Reported by User: Breeze user (Breeze)

SAMPLE INFORMATION

Sample Name:	T-8	Acquired By:	Breeze
Sample Type:	Broad Unknown	Date Acquired:	7/1/2021 11:11:46 AM CST
Vial:	12	Acq. Method:	2414 RID DETECTOR WITH
Injection #:	1	Date Processed:	7/1/2021 5:28:52 PM CST
Injection Volume:	50.00 ul	Channel Name:	410
Run Time:	15.00 Minutes	Channel Desc.:	
Column Type:	300 mmJORDI GEL DVB MIXED	Sample Set Name	14000409

Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		2299	7499	4093	22270	44354	3.261751	2.969593	5.914385

Fig 14 GPC spectrum and data relative peak for copolymer P4

5-Conclosion

In this work, new long chain linear polyester were prepared by using toluene as solvent and *p*-toluene sulfuric acid as catalyst. Four copolymers named (decan 1,10-dioic acid - co - cis buten 2,4-dioate)(**P1**), (Dodecane 1, 10-dioic acid -co-1,10- decan dioate)(**P2**), (1,4-cyclo hexane -co- 1,4-butane di carboxylate) (**P3**) and(1, 4-cyclohexan-co -1,10-decan carboxylate)(**P4**).

This copolymers characterization by using many technique such as (FTIR) spectroscopy,(^{1}HNMR) spectroscopy and ^{13}C-NMR spectroscopy for copolymer P3.the results of molecular weight distribution analysis were showed higher weight average molecular weight (Mw) was 17771 g/mole for copolymer **P1,** and higher number average molecular weight (Mn) was 5484g / mole for copolymer **P2**, while poly disparity was 3.78 for copolymer **P1**,but the lower poly disparity was 1.2 for copolymer **P3**, the reason effect can be attributed to the length of repeating unit and cyclo hexane ring in copolymer **P3** and **P4**.

We concludes from the above the copolymers containing an aliphatic ring **P3** and **P4** have less molecular weight, that can be explained by steric hindrance of the ring, also the copolymer **P3** has less molecular weight and less value of PDI ,it shows the lengths of polymeric chains are almost equal than of the other copolymers.

References

[1] Ulery, B. D., Nair, L. S., & Laurencin, C. T. [2011]. Biomedical applications of biodegradable polymers. Journal of polymer science Part B: polymer physics, 49(12), pp.832-864.

[2] Seyednejad, H., Ghassemi, A. H., van Nostrum, C. F., Vermonden, T., & Hennink, W. E. [2011]. Functional aliphatic polyesters for biomedical and pharmaceutical applications. Journal of Controlled release, 152(1), pp. 168-176

[3]Fisher, H. L. (1941). Collected Papers of Wallace Hume Carothers on High Polymeric Substances (Mark, H.; Whitby, GS; eds.)

[4] Stempfle, F., Quinzler, D., Heckler, I., & Mecking, S. [2011]. Long-chain linear C19 and C23 monomers and polycondensates from unsaturated fatty acid esters. Macromolecules, 44(11), pp.4159-4166.

[5] Li, Y., Wang, C., Wang, G., & Qu, Z. [2008]. Application of the long-chain linear polyester in plastification of PVC. Journal of Wuhan University of Technology-Mater. Sci. Ed., 23(1), pp.100-104.

[6] Lee, B., Niu, Z., Wang, J., Slebodnick, C., & Craig, S. L. [2015]. Relative mechanical strengths of weak bonds in sonochemical polymer mechanochemistry. Journal of the American Chemical Society, 137(33), pp.10826-10832.

[7] Xixi, W., Lu, D., Suyun, J., & Bogeng, L. [2019]. Synthesis and Application in the Polycondensation of Long-Chain Aliphatic Dicarboxylic Acids. Progress in Chemistry, 31(1), 70.

[8] Kinkelin, E., Spindler, J., & Pössenecker, G. [2001]. U.S. Patent No. 6,255,443. Washington, DC: U.S. Patent and Trademark Office.

[9] Hernández, J. J., Rueda, D. R., García-Gutiérrez, M. C., Nogales, A., Ezquerra, T. A., Soccio, M., & Munari, A. [2010]. Structure and morphology of thin films of linear aliphatic polyesters prepared by spin-coating. Langmuir, 26(13), pp.10731-10737.

[10] Stempfle, F., Ritter, B. S., Mülhaupt, R., & Mecking, S. [2014]. Long-chain aliphatic polyesters from plant oils for injection molding, film extrusion and electrospinning. Green Chemistry, 16(4), pp.2008-2014.

[11] Jalal,M,A., Khalaf,M.N., &Hussein,M.A., [2021]"Effect of variation in polymer structure on eddies suppression of Basra light crude oil turbulent flow" Egyption. Journal of chemistry.64.(7) pp.3362-3378.

[12] Trzaskowski, J., Quinzler, D., Bährle, C., & Mecking, S. [2011]. Aliphatic long- chain C20 polyesters from olefin metathesis. Macromolecular rapid communications, 32(17), pp.1352-1356.

[13] Mandelkern, L. [1967]. ‘’The effect of molecular weight on the crystallization and melting of long- chain molecules. In Journal of Polymer Science Part C: Polymer Symposia (18, (1), pp. 51-55). New York: Wiley Subscription Services, Inc., A Wiley Company.

[14] Katoh, T., Ogawa, Y., Ohta, Y., & Yokozawa, T. [2021]. Synthesis of polyester by means of polycondensation of diol ester and dicarboxylic acid ester through ester–ester exchange reaction. Journal of Polymer Science, 59(9), pp.787-797.

[15] Noroozi Pesyan, N. [2017]. Synthesis of polyol esters by p-toluenesulfonic acid catalyst as synthetic lubricant oils. Asian Journal of Green Chemistry, 1(1), pp.41-45.

[16] Amarasekara, A. S., Ha, U., & Okorie, N. C. [2018]. Renewable polymers: Synthesis and characterization of poly (levulinic acid–pentaerythritol). Journal of Polymer Science Part A: Polymer Chemistry, 56(9), pp.955-958.

[17] Sun, L., Zhu, L., Xue, W., & Zeng, Z. [2020]. Kinetics of p-toluene-sulfonic acid catalyzed direct esterification of pentaerythritol with acrylic acid for pentaerythritol diacrylate production. Chemical engineering communications, 207(3), pp.331-338.

[18] Fakirov, S., & Denchev, Z. [1999]. Sequential reordering in condensation copolymers. Trans reactions in condensation polymers, 319.

[19] Rogers, M. E., & Long, T. E. (Eds.). [2003]. Synthetic methods in step-growth polymers. John Wiley & Sons.

[20] Žagar, E., & Grdadolnik, J. [2003]. An infrared spectroscopic study of H-bond network in hyperbranched polyester polyol. Journal of Molecular Structure, 658(3),pp.143-152.

[21] Ali,K,M. [2022]:Preparation and characterization of some polymers and their use as pour point depressant and viscosity index improves for Iraqi base oils.M.Sc. Thesis, Chemistry Department,Collage of Science,University of basrah.

[22] Buckholtz, G. A., & Gawalt, E. S. [2012]. Effect of alkyl chain length on carboxylic acid SAMs on Ti-6Al-4V. Materials, 5(7), pp1206-1218.

[23] Katon, J. E., & Sommer, A. J. [1992]. IR micro spectroscopy. Analytical Chemistry, 64(19), pp. 931-940.

[24] Otsuka, Y., Utsunomiya, Y., Umeda, D., Yonemochi, E., Kawano, Y., & Hanawa, T. [2020]. Effect of Polymers and Storage Relative Humidity on Amorphous Rebamipide and Its Solid Dispersion Transformation: Multiple Spectra Chemometrics of Powder X-Ray Diffraction and Near-Infrared Spectroscopy. Pharmaceuticals, 13(7), 147.

[25] Thomas, J., BRUNO, S., & PARIS, D. [2020]. “Handbook of basic table for chemical analysis”4th Ed., Data-driven Methods and Interpretation. CRC Press.

[26] Mahir.A.J., [2021]: Synthesis, Characterization and Evaluation of some Polymers as Drag Reducing Agents for Basra Crude Oil, PHD .thesis, chemistry department, Collage of science. University of Basrah.

[27] Murano, M. [1972]. Studies on Monomer Sequences in Polyesters Having Asymmetric Monomers. Polymer Journal, 3(6), pp.663-669.

[28] Koo, J. M., Hwang, S. Y., Yoon, W. J., Lee, Y. G., Kim, S. H., & Im, S. S. [2015]. Structural and thermal properties of poly (1, 4-cyclohexane dimethylene terephthalate) containing isosorbide. Polymer Chemistry, 6(39), pp.6973-6986.

[29] Fleming, I., & Williams, D. H. [1966]. Spectroscopic methods in organic chemistry (pp. 160-160). New York: McGraw-hill.

[30] Akitt, J.W., & Mann, B.E. [2000]. NMR and Chemistry: An introduction to modern NMR spectroscopy: An introduction to modern NMR spectroscopy, Fourth Edition (4th ed.). CRC Press. https://doi.org/10.1201/9781315274690

[31] Moszner, N., Zeuner, F., & Rheinberger, V. [1997]. Polymerization of cyclic monomers, 4. Synthesis and radical polymerization of bi- and trifunctional 2- vinylcyclopropanes. Macromolecular rapid communications, 18(9), pp775-780.

[32] Maity, S., & Ghosh, S. [2010]. An asymmetric route to 2, 3-epoxy-syn-1, 4-cyclohexane diol derivatives using ring closing metathesis (RCM). Journal of chemical sciences, 122(6), pp.791-800.