Synthesis and Characterization of New Condensation Polymers Based on New Aromatic di-ethers

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Abstract

This research includes synthesis and identification of new polymers that are expected having industrial applications in paint ships and dyes. These polymers were prepared from cheap and available materials such as glycerol and catechol, hydroquinone and resorcinol and using cheap catalyst in good yields.

The resulting compounds were identified by FT-IR, ^{1}H-NMR, ^{13}C-NMR, CHN, and DSC techniques. Some physical properties of these compounds were studied.

Keywords: condensation polymerization, di-hydroxy benzene, glycerol.

الخلاصة

ويشمل هذا البحث تخليق وتحديد البوليميرات الجديدة التي يتوقع وجود تطبيقات صناعية في طلاء السفن والأصباغ. تم تحضير هذه البوليمرات من مواد رخيصة ومتوفرة مثل الكليسيرول والكاتيكول والهيدروكينون والريسورسنول واستخدام مواد مساعدة رخيصة للحصول على منتوج بنسب جيدة

تم تحديد المركبات الناتجة عن تقنيات FT–IR , ^{1}H–NMR , ^{13}C–NMR , CHN, DSC . تم دراسة بعض الخصائص الفيزيائية لهذه المركبات .

الكلمات المفتاحية: بلمرة التكاثف، ثنائي هيدروكسي البنزين، الكليسيرول.

Introduction

Hydroxy aromatic compounds such as catechol, resorcinol, and hydroquinone were used widely as industrial solvents. 1,2- Dihydroxy benzene is also widely used to produce food additive agents, hair dyes, and antioxidants [Dellinger, *et al*, 2001; Milligan, and Haggblom, 1998; Hays, *et al*, 2005]. Theses phenolic compounds were found in the effluents of industries such as textile, paper and pulp, steel, petrochemical, petroleum refinery, rubber, dye, plastic, pharmaceutical, cosmetic, etc. Also, they are found in the wastewater of conversion processes of synthetic coal fuel [Kumar, & Kumar, 2003; Schweigert, 2001].

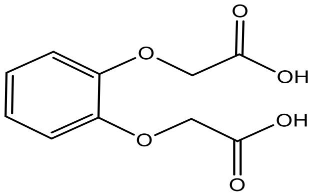
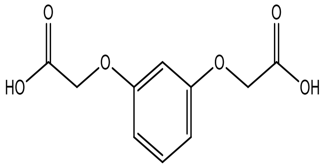
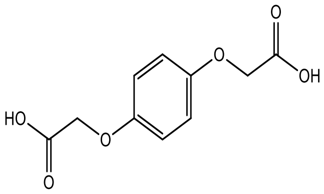
Here, we have prepared three new polymers by condensation polymerization process. Dihydroxy benzene compounds were used as a starting materials, which converted into dicarboxylic aromatic compounds. Finally, these derivatives used to prepare the target polymer molecules.

Synthesis of Ec, Er and Eh [Gabriela, *et al* 1997]

Compounds Ec, Er and Eh were prepared according to below procedure:

Dissolve 2 g of KOH in 4 mL of water in a 50 mL round bottom flask, 0.5 gm of (catechol, hydroquinone, or resorcinol) was added to the round bottom flask. The mixture was stirred until a homogeneous solution resulted. Fit the flask with a reflux condenser and heat to a gentle boil. Add 6 mL of a 50% aqueous solution (g/mL) of chloroacetic acid dropwise and boil the solution for 10 minutes. Cool the reaction mixture to room temperature and acidify the solution with dropwise addition of concentrated HCl, monitor the pH with pH paper. Cool the mixture in ice bath and filter the precipitate by vacuum filtration. Recrystallize the crude solid from boiling water to afford compounds Ec, Er and Eh. The reaction was followed using TLC technique using (Ethyl acetate: acetone (1:1)) (scheme 1, table 1).

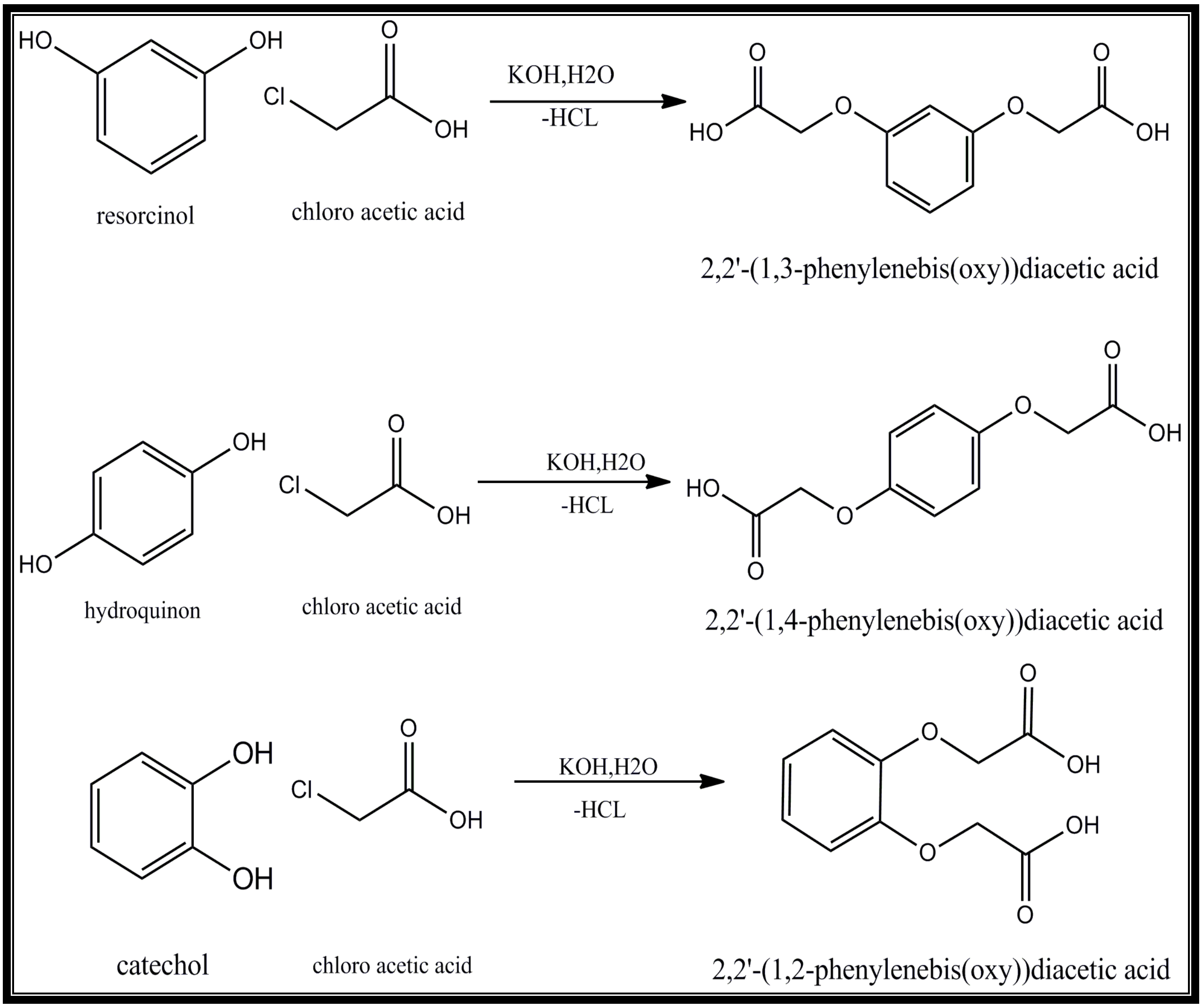
Table (1) Physical Properties of Ec, Er and Eh

No. comp.	compound	M.Wt	M.P °C	Product %	R_f
EC		**226**	**128-130**	**94**	***0.73***
Er		**226**	**132-134**	**88**	***0.866***
Eh		**226**	**119-120**	**82**	**0.827**

Synthesis of Polymers 1, 2, 3 [Marwan, 1981]

(0.1 mol) of glycerol with (0.1 mol) of compound (Ec, Eh, Er) were mixed. The mixture then heated gently until to 150-180 °C, then the temperature is raised gradually to 200 - 250 °C until the bubbles disappeared. The pure polymers output by washing with diethyl ether

Results and discussion



Schem1. Synthesis of ethers Ec, Er and Eh

The prepared compounds (Ec, Eh, Er) were identified using FT-IR spectroscopy, as well as through the spectrum ^{1}HNMR and ^{13}CNMR.

FT-IR spectra [Silverstein, *et al*,2005] (figures 1,2, and 3) showed absorption between (3433-3417) cm $^{-1}$ belonging to vibration (OH), and the package absorption between (3072-3026) cm $^{-1}$ attributed to the aromatics (CH). Absorption between (2951-2914) cm $^{-1}$ attributed to the (CH) aliphatic, and the absorption between (1737-1722) cm $^{-1}$ back to bond (C=O) ether. Also, the absorption between (1624-1645) cm $^{-1}$ back to the bond (C=C) in the aromatic rings, package absorption between (1114-1172) cm $^{-1}$ to (C-O). Table (2) shows infrared data of these compounds and the results of elemental analysis (CHN) shown in table (4).

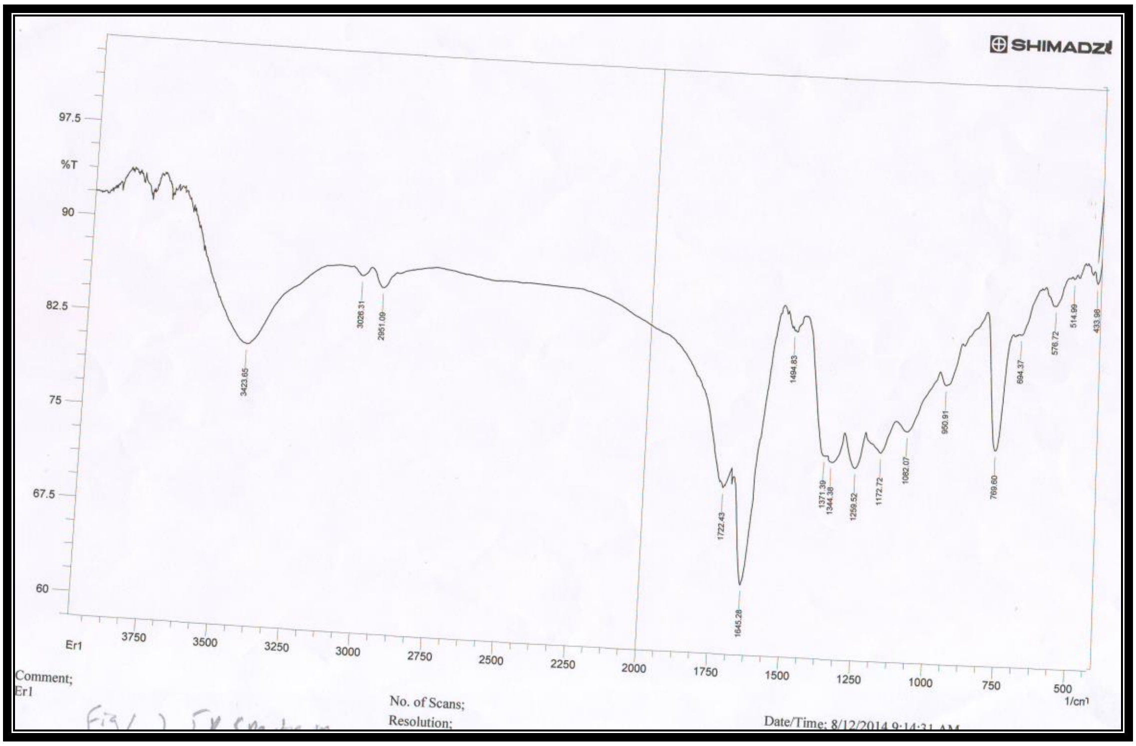


Fig. (1).FT-IR of compound(Er)

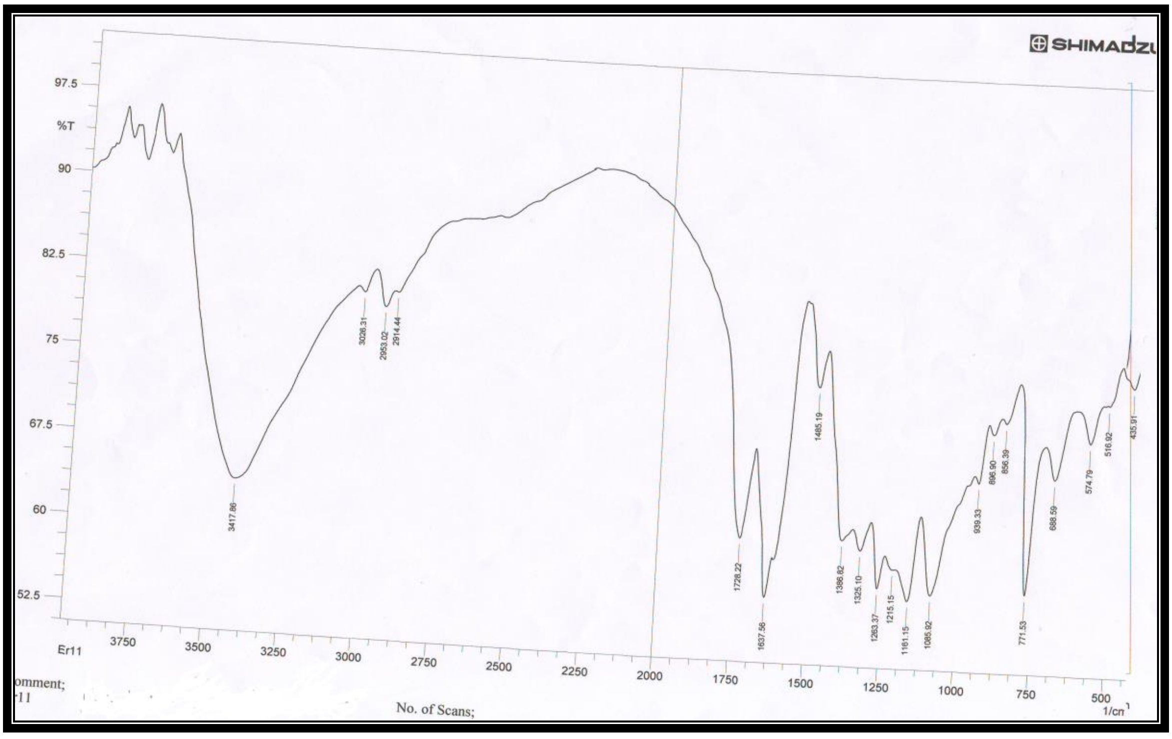


Fig. (2).FT-IR of compound(Er)

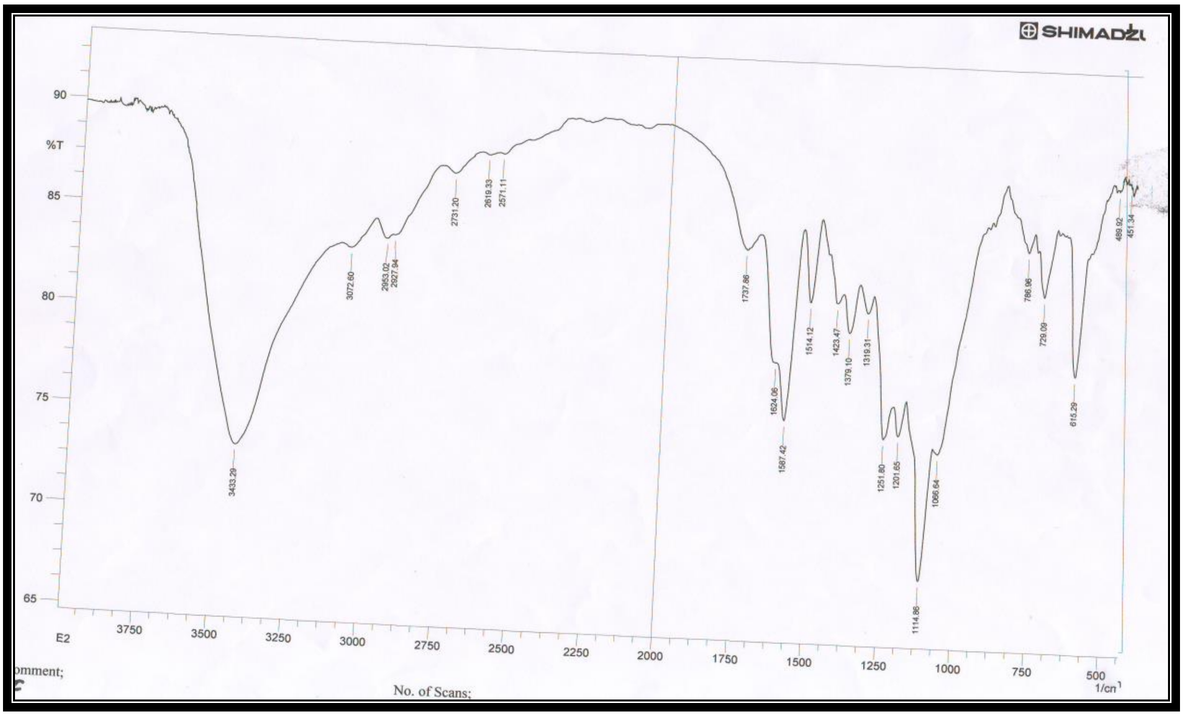


Fig. (3).FT-IR of compound(Ec)

^{1}HNMR spectra [Cremonini and Bonaga, 2012] of compounds Ec, Er and Eh shows shifted within range of (6.18-6.91ppm) to the frequency of protons (Ar-H). The peak at (8.07-8.5 ppm) due to the protons of (OH)-aliphatic. The frequency of protons between (3.97-4.25 PPm) is to protons (C-H) aliph, as shown in table (3). Figures (4, 5, and 6) show nuclear magnetic resonance spectra of these compounds. Also, ^{13}CNMR spectra shown in figures 7, 8, and 9 and the data in table 3.

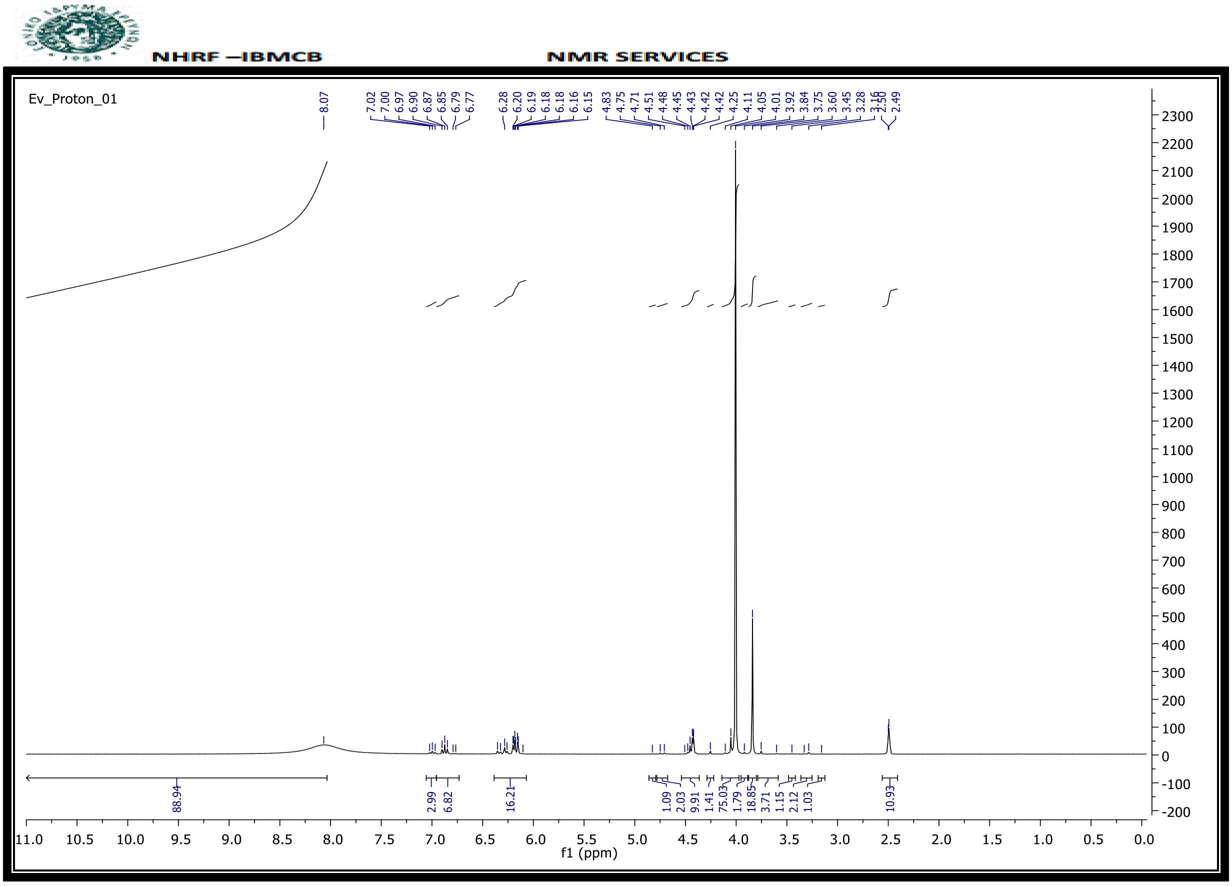


Fig. (4) ^{1}HNMR of compounds (Er)

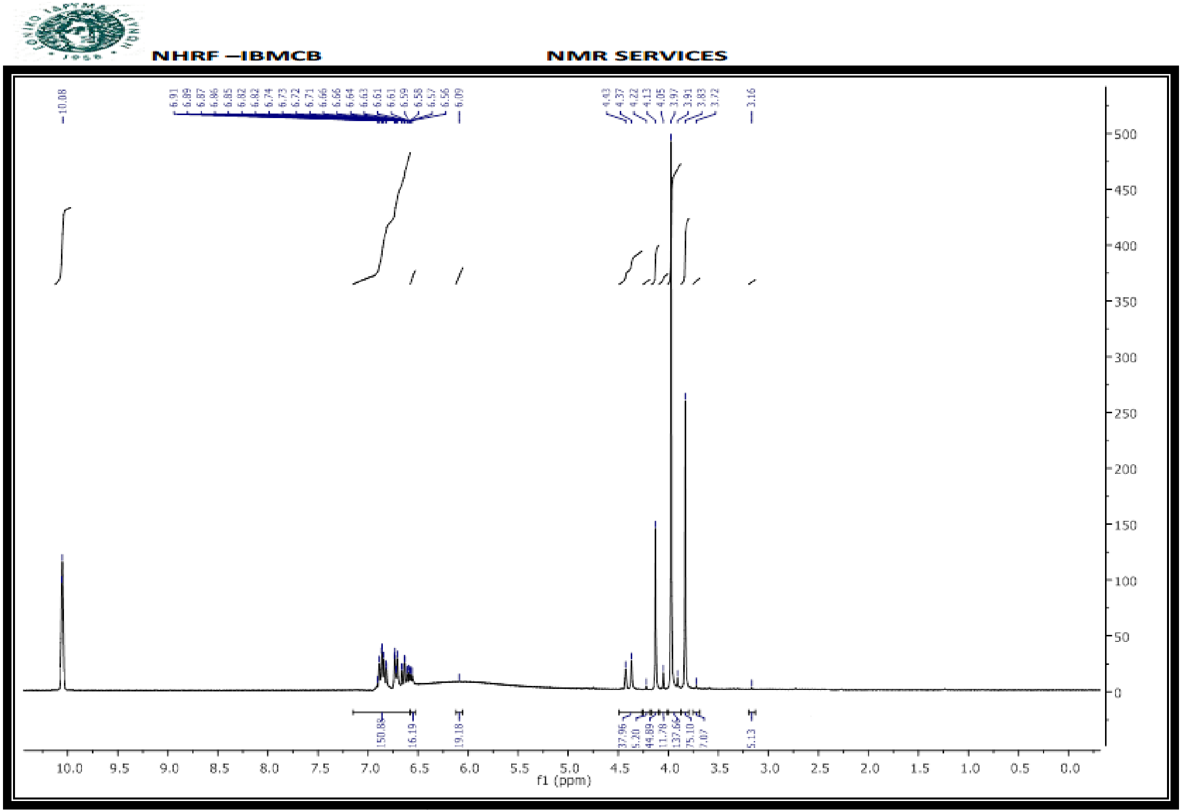


Fig. (5) ^{1}HNMR of compounds (Ec)

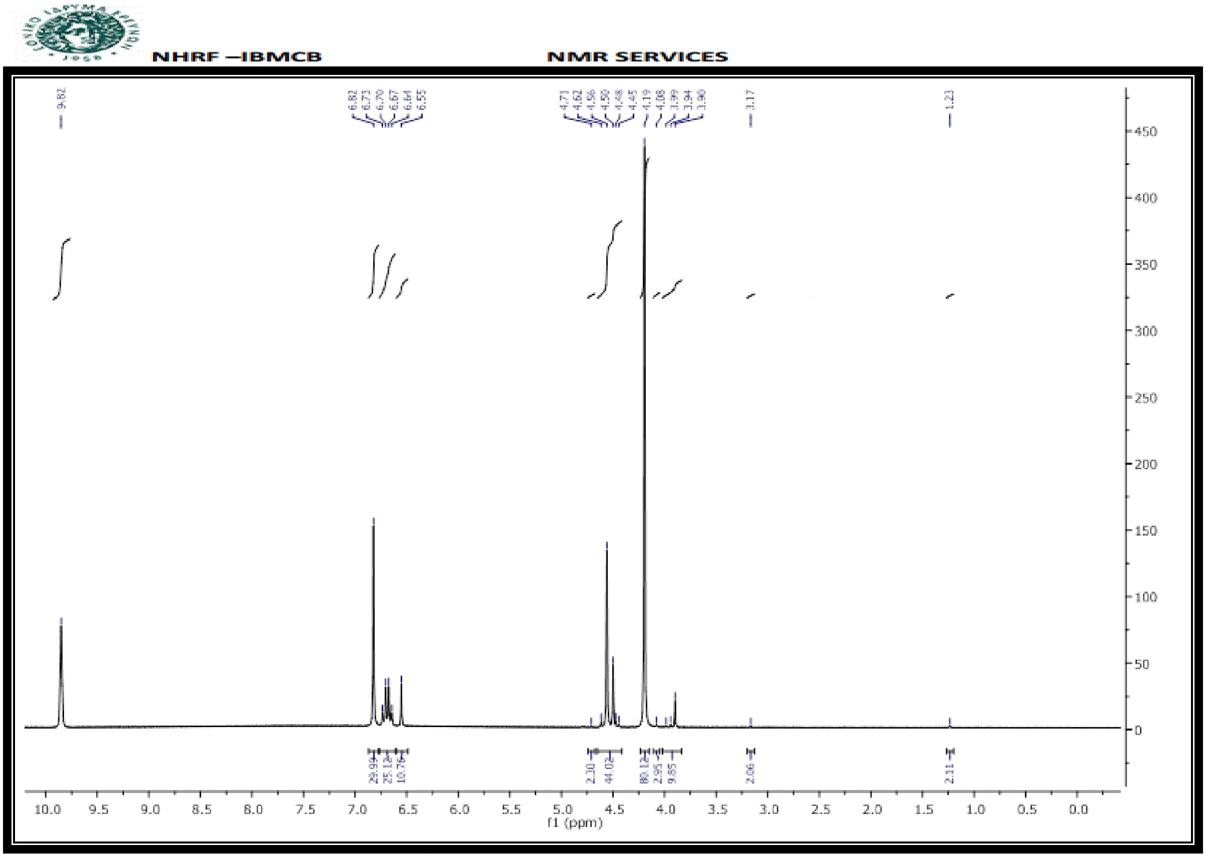


Fig. (6) ^{1}HNMR of compounds (Eh)

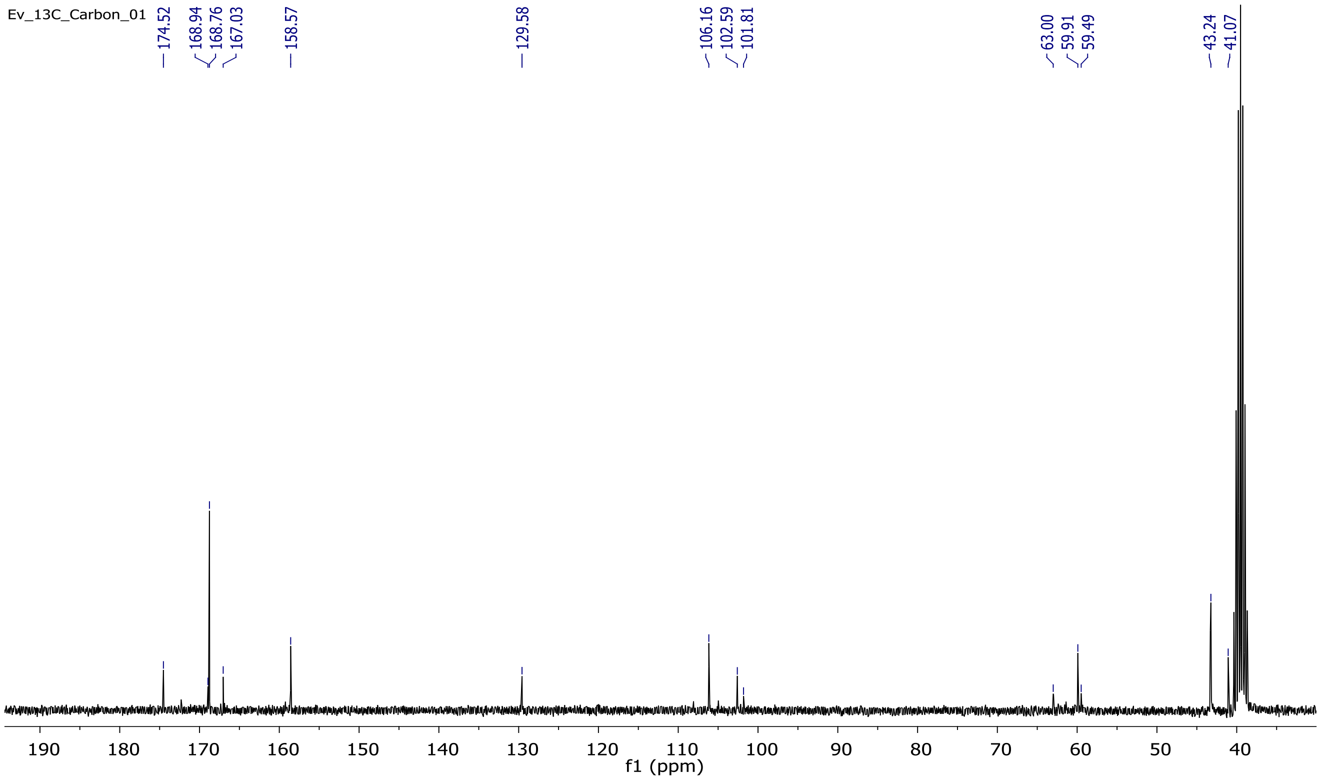


Fig. (7) ^{13}CNMR of compounds (Er)

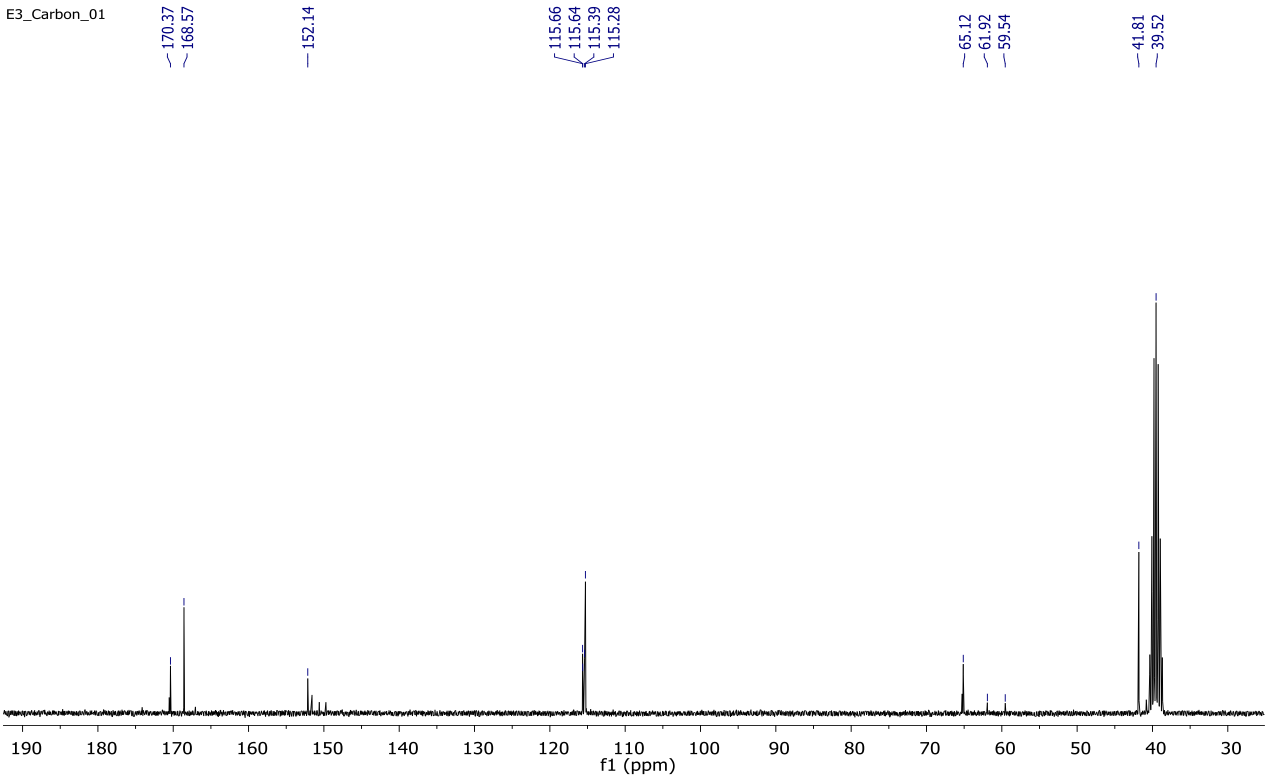


Fig. (8) ^{13}CNMR of compounds (Eh)

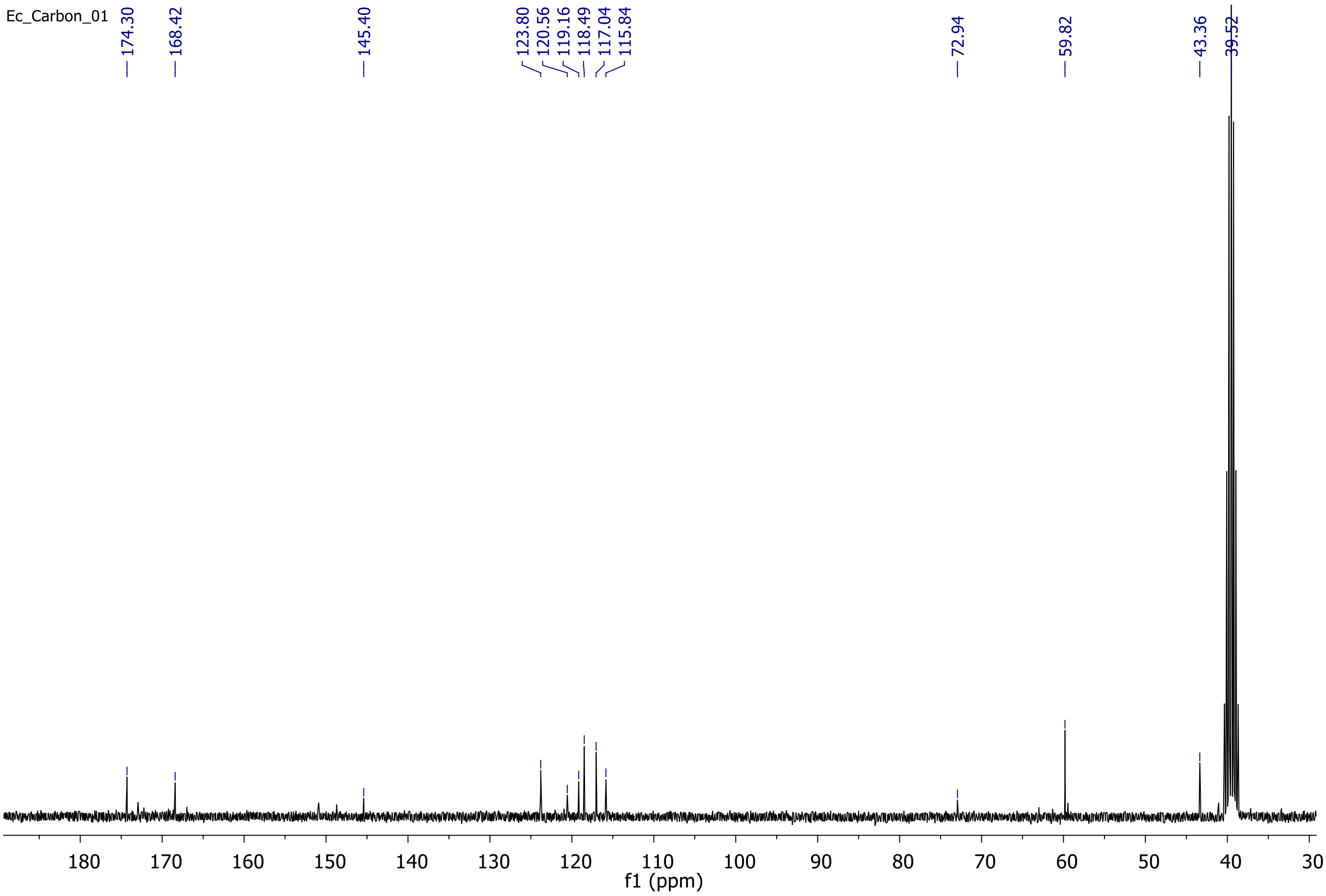


Fig. (9) ^{13}CNMR of compounds (Ec)

Table (2) FT-IR data of compounds (Ec, Eh ,Er)

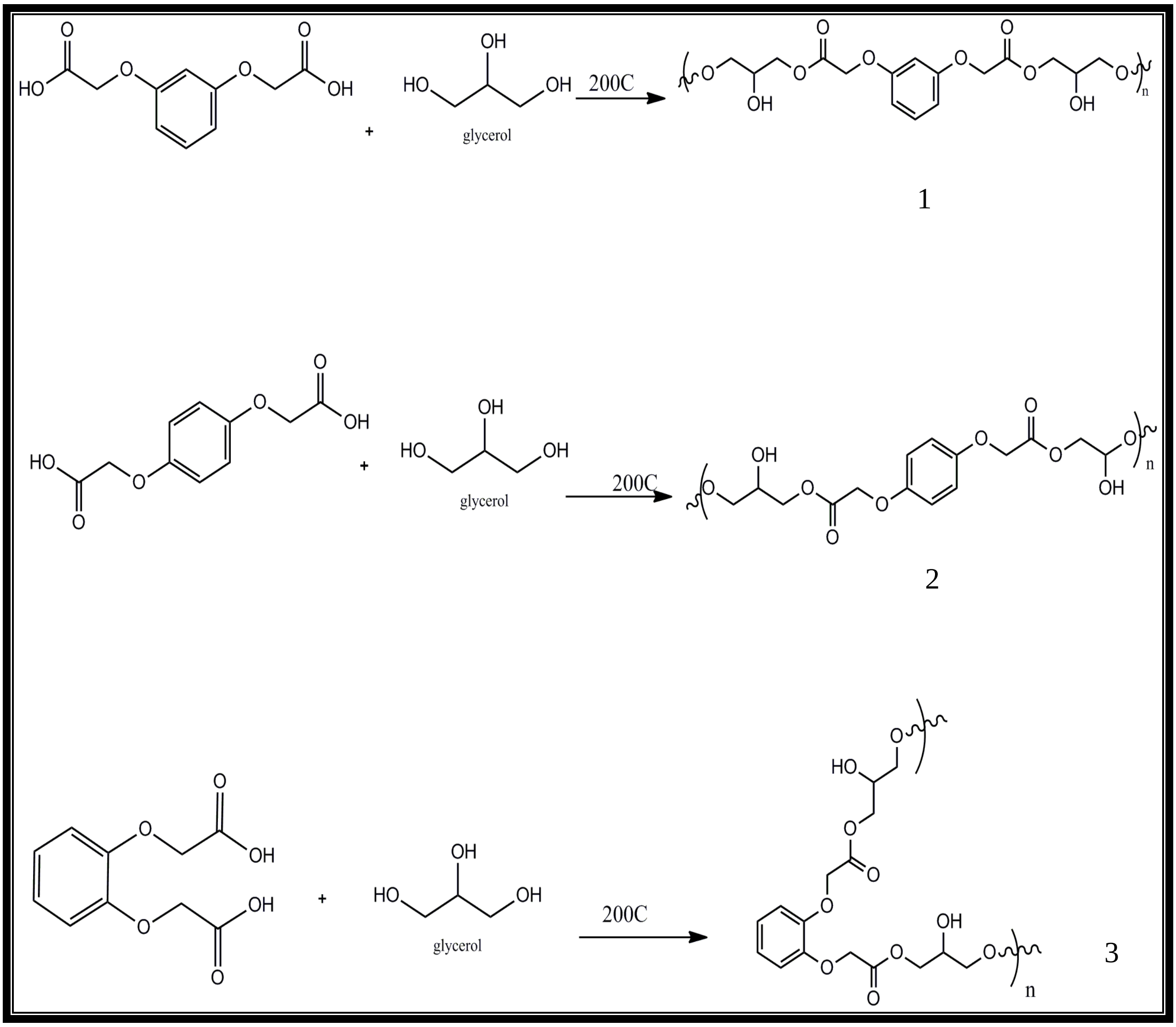
comp No	υ(O-H) cm^{-1}	υ (C-H)$_{Ar.}$ cm^{-1}	υ(C-H)$_{al.}$ cm^{-1}	υ(C=O)$_{alc}$ cm^{-1}	υ (C=C) Ar. cm^{-1}	υ (C-O) cm^{-1}	υ(C-C) ring cm^{-1}
Ec	3433.29	3072.6	2927.9	1737.86	1624.06	1114.8	729
Eh	3423.65	3026.31	2951.0	1722.4	1645.2	1172.7	769.6
Er	3417.8	3026	2914.4	1728.2	1637.5	1161.15	771

Table (3) ^{1}HNMR and ^{13}CNMR data of compounds (Ec, Eh, Er)

Comp No	**Chemical Shift Proton (ppm)**			**Chemical Shift ^{13}CNMR (ppm)**		
	C-Hal	C-H Ar	OH al	C-C ring	C-O Ar	C=O
Ec	4.25	6.79 6.18-6.20	8.07	117.04-123.80	158.57 145.40	174.30 168.42
Eh	3.97	6.56-6.91	9.95	115.66-115.28	152.14	168.42-170.37
Er	4.19	6.70	8.5	101.81 106.16 129.58	158.57	168.57

Table (4) C.H.N data of compound (Ec, Eh, Er)

comp . No.	***C%***		***H%***		***N%***	
	Cal.	***Fou.***	***Cal.***	***Fou.***	***Cal.***	***Fou.***
Ec	***53.09***	***52.78***	***4.42***	***3.99***	-	-
Eh	***53.09***	***52.53***	***4.42***	***3.95***	-	-
Er	***53.09***	***52.61***	***4.42***	***3.89***	-	-



1

2

3

Scheme 2. Synthesis of polymers 1, 2, 3

The prepared compounds (1,2, and 3) were identified using FT-IR spectroscopy, as well as through the ^{1}HNMR spectra.

FT-IR Spectra showed infrared absorptions between (3406-3385) cm^{-1} belonging to vibration (OH) The package absorption between (2937-3100) cm^{-1} attributed to the aromatics (CH) and the package absorptions between (2887-2937) cm $^{-1}$ attributed to the aliphatic (CH). Package absorption between (1743-1749) cm $^{-1}$ to (C = O) ether, and package absorption between (1606-1608) cm $^{-1}$ to the aromatics (C=C), Absorption between (1091-1196) cm $^{-1}$ to (C-O) as shown in table (5) and figures 10, 11, and 12.

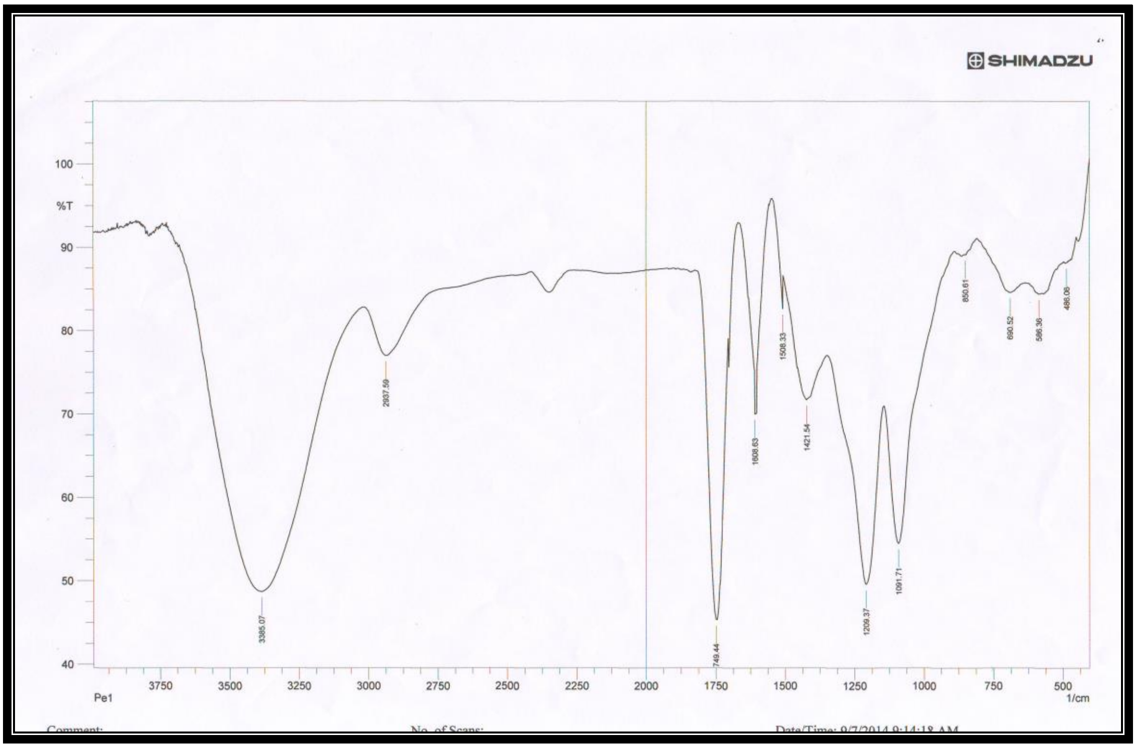


Fig. (10) FT-IR of compounds (1)

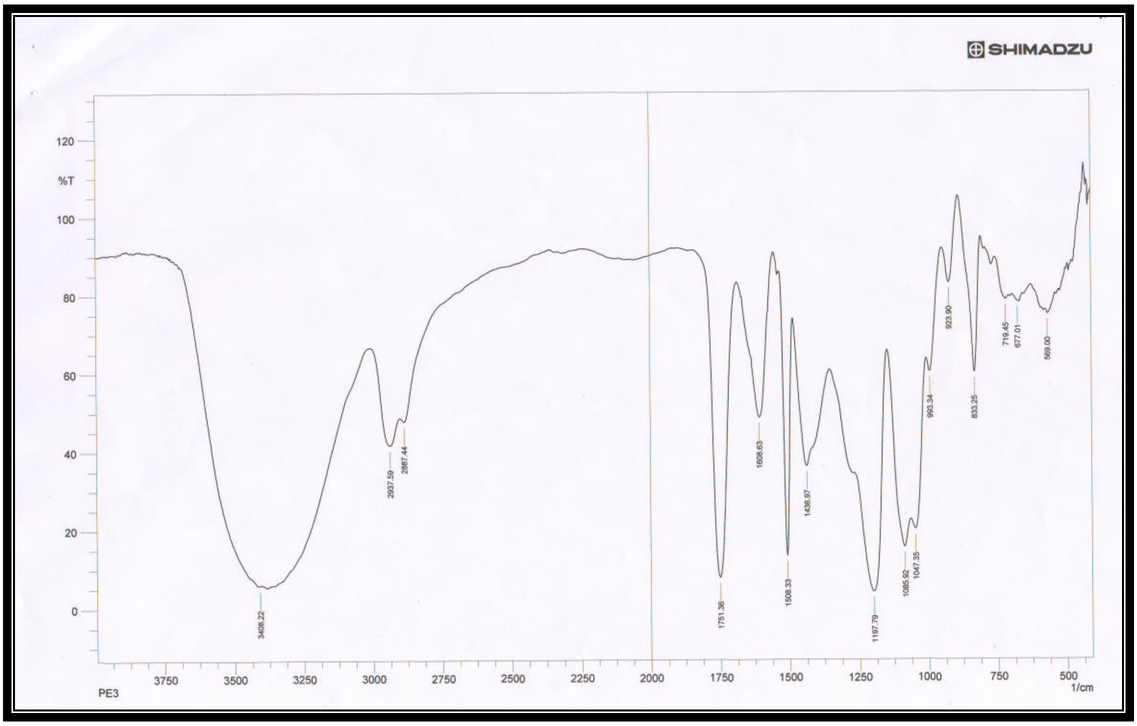


Fig. (11) FT-IR of compounds (2)

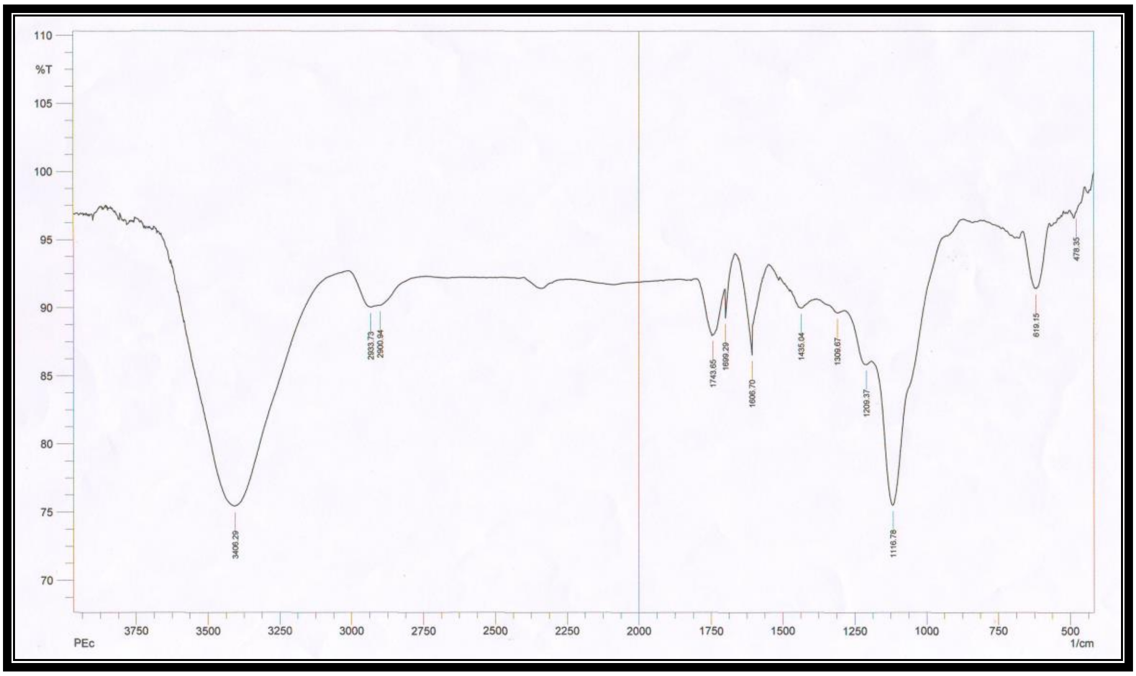


Fig. (12) FT-IR of compounds (3)

Figures 13, 14, and 15 shows the ^{1}HNMR spectra of compounds 1,2, and 3 shifted within the range (6.18-6.91ppm) , which back to the frequency of protons (Ar-H). Peaks at (8.07-8.5 ppm) due to the frequency protons of aliph-(OH) between (3.97-4.25PPm)) protons of aliph-(O-CH_2) (Table 5). Figure 16, shows the ^{13}CNMR spectrum of polymer (2) (table 5).

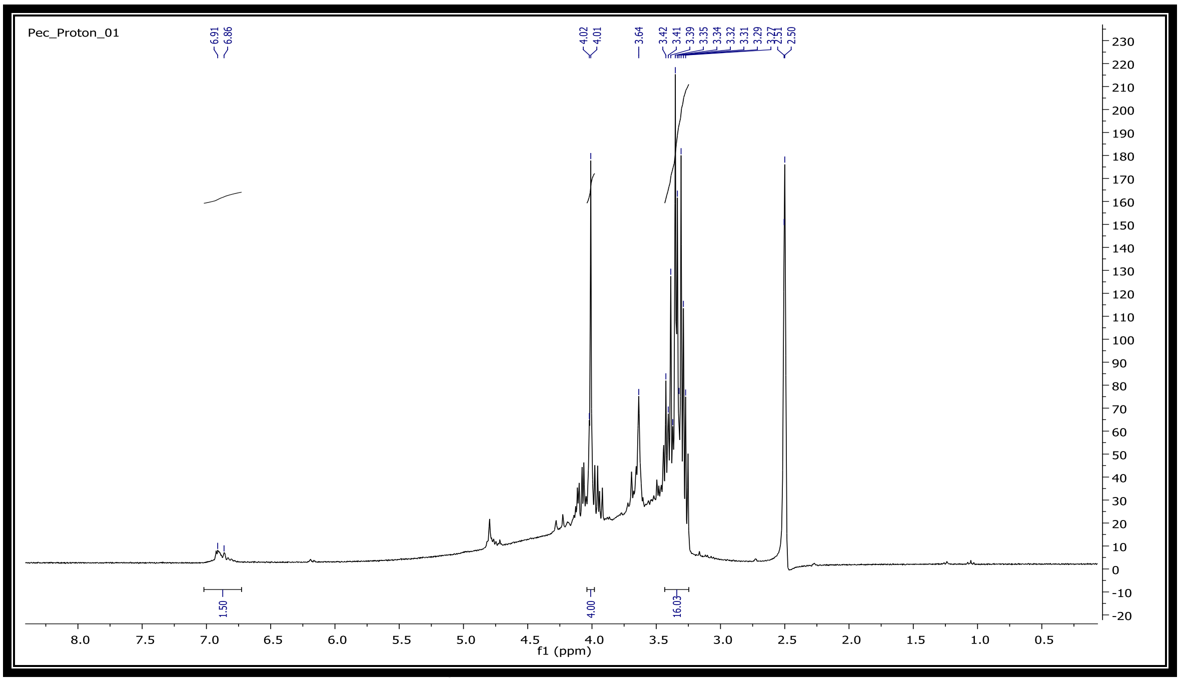


Fig. (13) ^{1}HNMR of compounds (1)

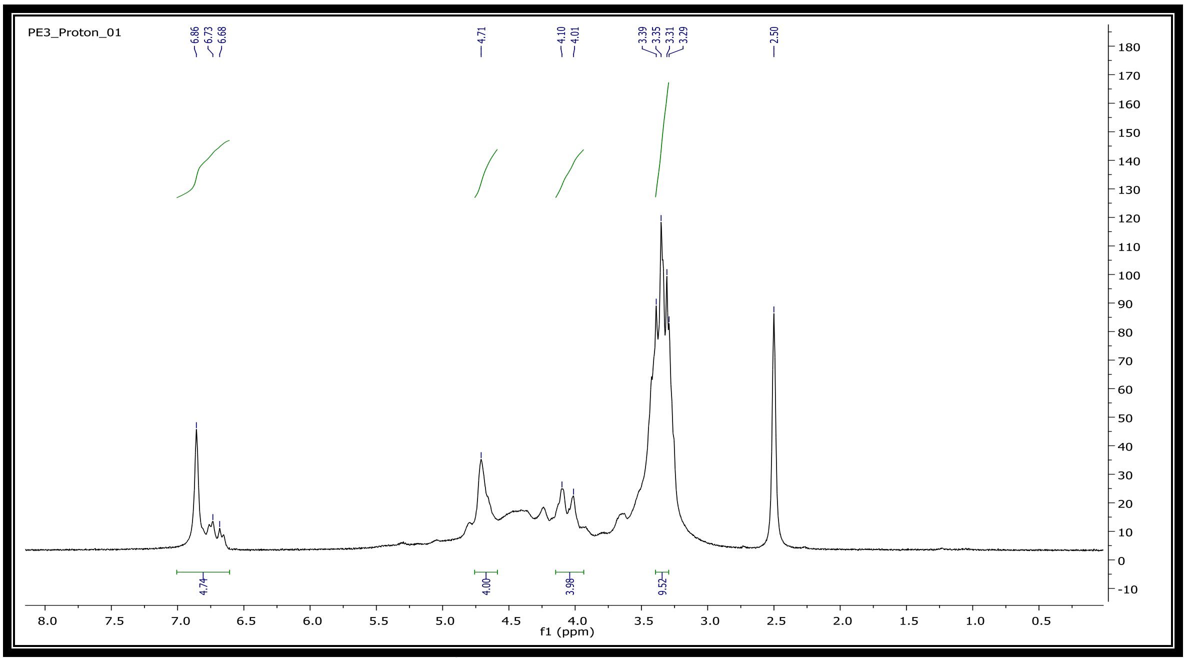


Fig. (14) ^{1}HNMR of compounds (2)

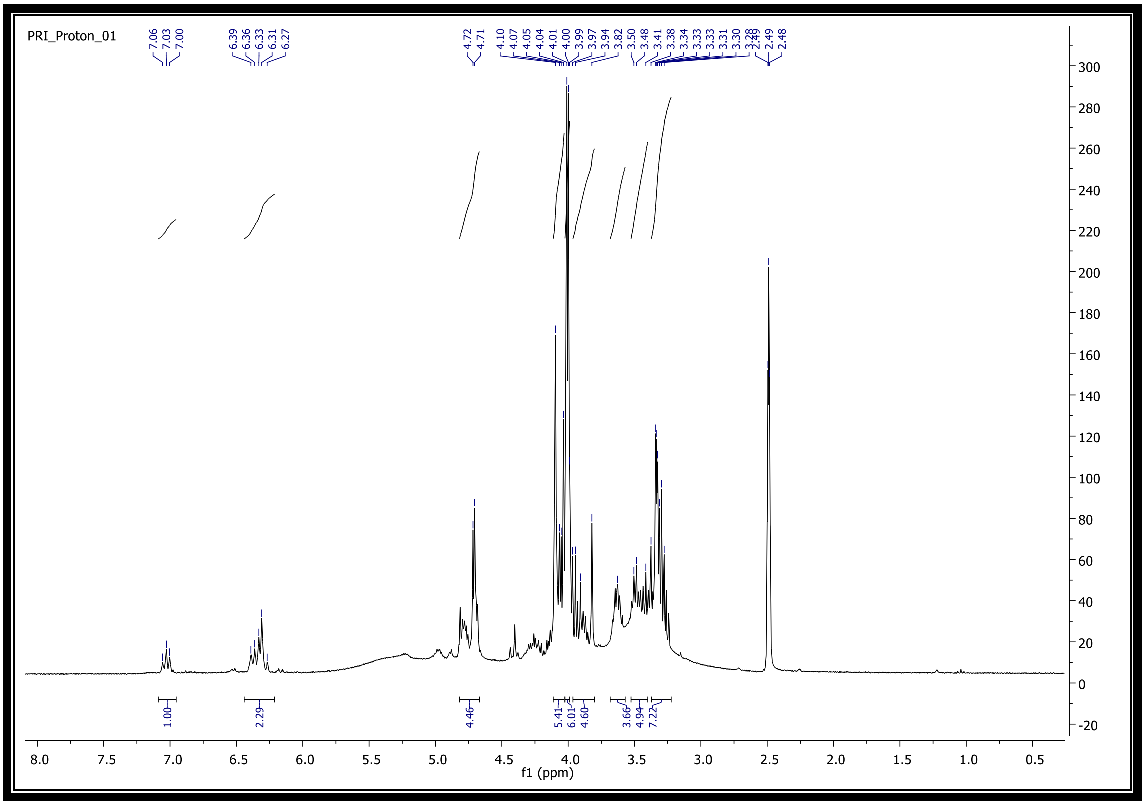


Fig. (15) ^{1}HNMR of compounds (3)

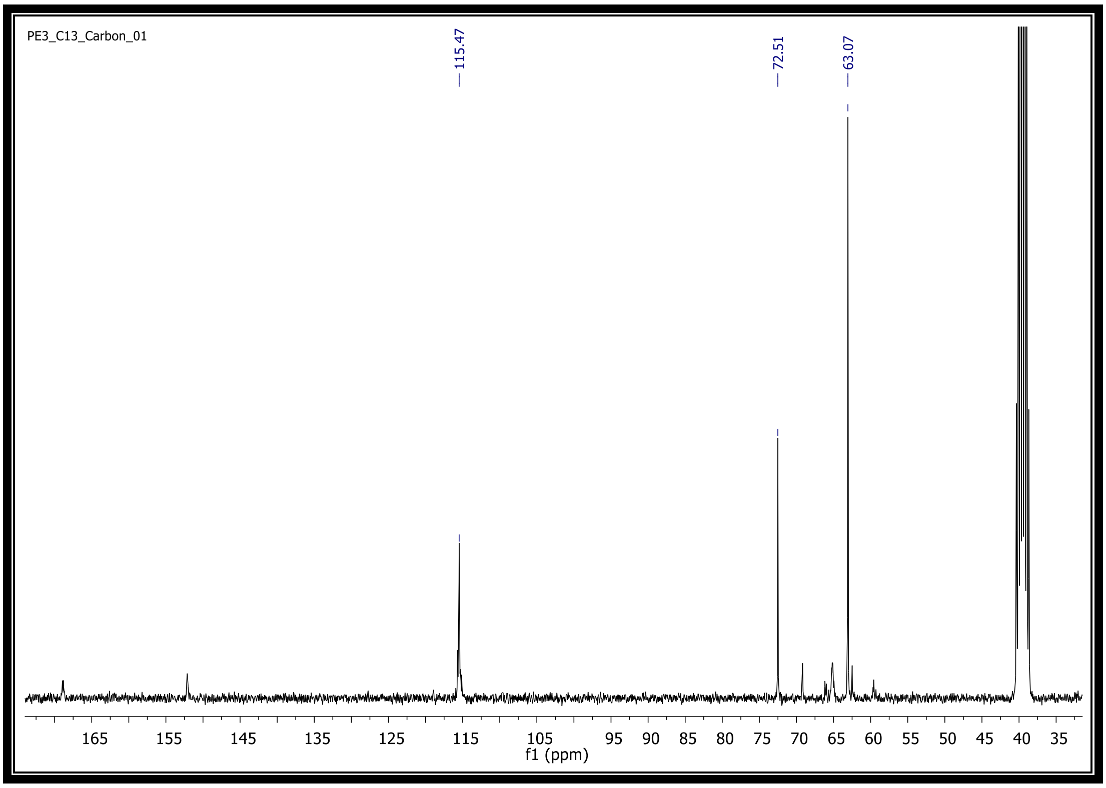
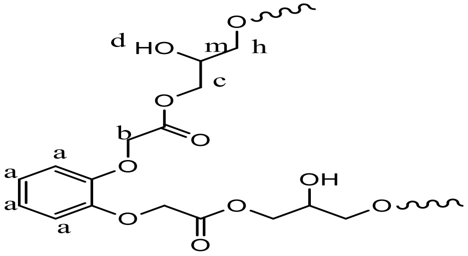


Table (5) IR data of polymers 1, 2, and 3.

comp No	v(O-H) cm^{-1}	v (C-H)$_{Ar.}$ cm^{-1}	v(C-H)$_{al.}$ cm^{-1}	v(C=O)$_{alc}$ cm^{-1}	v (C=C) Ar. cm^{-1}	v (C-O) cm^{-1}	v(C-C) ring cm^{-1}
1	3406.29	3100	2900.9	1743.6	1606.7	1116.7	619.1
2	3408.22	3050	2937.59	1751.3	1608.3	1197.7	719
3	3385.07	3100	2937.5	1749.4	1608.6	1091.7	850

Table (6) ^{1}HNMR data of polymers 1, 2, and 3.

No . Comp	Compound Structure	Position	Proton(PPm)	^{13}C (PPm)
1		a b c d h m	6.86-6.91 4.71-7.79 3.44-3.63 3.28-3.38 3.40-3.44 4.0-4.02	

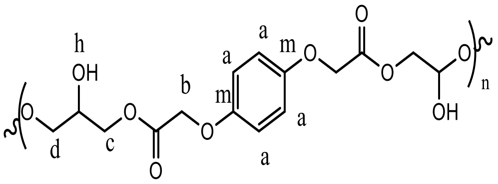
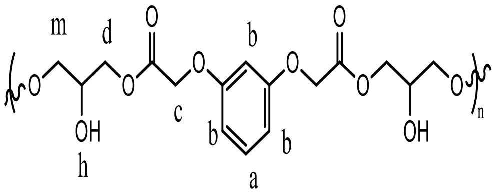
2		a b c d h m	6.86-6.68 4.71-4.01 4.71-4.01 3.35-3.31 3.35-3.31	115.47 63.07 65 72.51 - 153
3		a b c d h m	7.04 6.41-6.20 4.70 4.08 3.39-3.35 4.05	

Figure 17 shows the thermal analysis conducted Type Differential Scanning Calorimetry (DSC) for polymer 1 and described the degree of the glass transition (Tg = 110˚C).

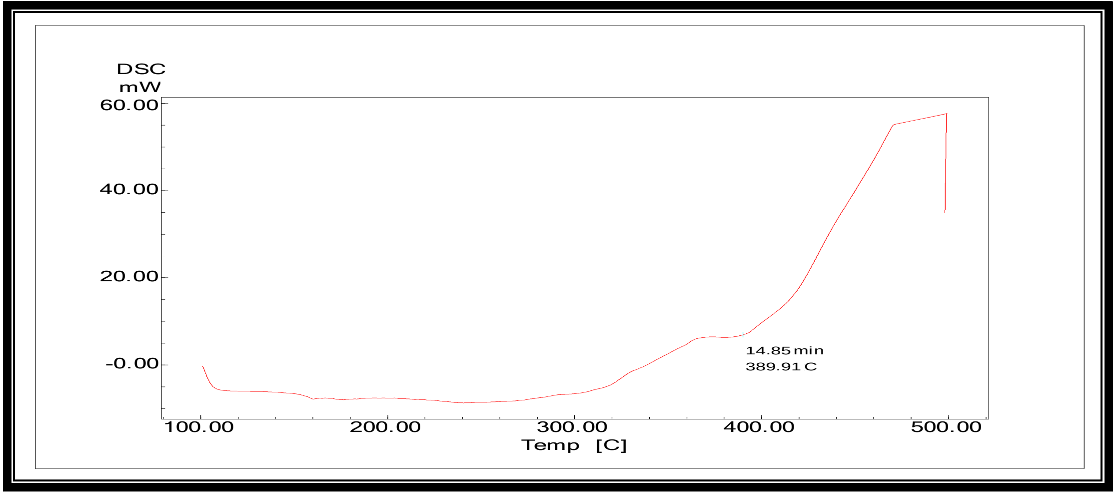


Fig. (17). DSC of polymer 1

Thermal analysis was conducted Type Differential Scanning Calorimetry (DSC) for polymer 2 and described as in figure (18), where the degree of the glass transition is (Tg = 319˚C)

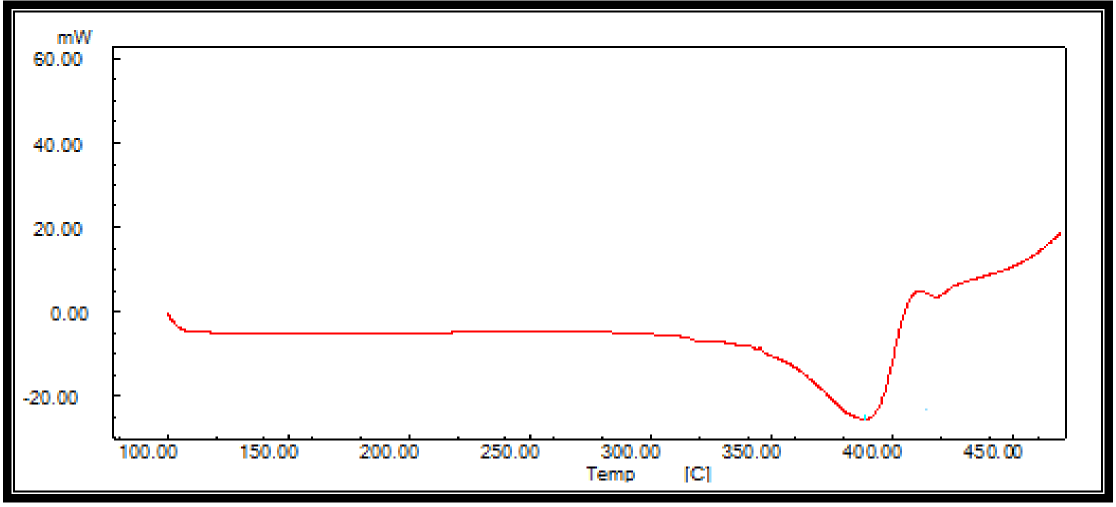
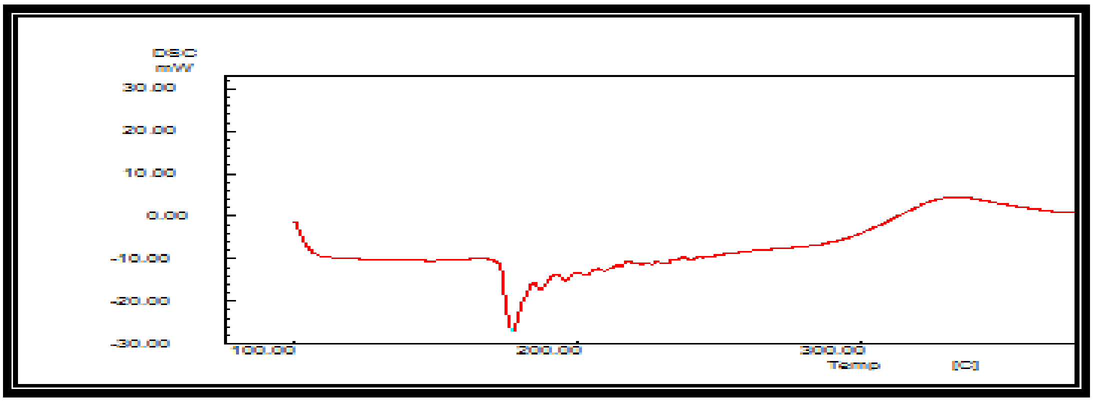


Fig. (18). DSC of polymer 2

Thermal analysis was conducted Type Differential Scanning Calorimetry (DSC) for this polymer P_3 and described as in figure (19), where the degree of the glass transition is (Tg = 110˚C).



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