study of Thermal and Some Mechanical Properties of Polymers Containing Schiff-Base Link

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Apstract

In this paper Schiff-base containing two hydroxyl groups on their side was prepared through the reaction of two mole from terephthaldehyde with one mole from 1,4- phenylene diamine. Then several polymeric material were prepared base on Schiff-base through the reaction with (maleic anhydride formaline , methylene diphenyl diisocyanate (MDI) , epoxy resin(based on bisphenol –A-), and polyfurfural alcohol.

The products were characterized by several technique, FTIR,TGA,and DSC .Also some mechanical properties were evaluated . The results showed that these polymers have high decomposition temperature and high chare residue**,** on the other hand good flexural ,impact strength were recorded of these polymers.

1-Introduction

Schiff-baseis one of the compounds carrying imine or azomethine(-C=N) functional group . This functional group produce by the condensation products of primary amines with carbonyl compounds and which was first reported by Hygo Schiff [1-3].

Schiff-base compounds have an important class of the most widely used organic compounds and have awide variety of application in many fields including analytical , biological and inorganic chemistry .Also have gained importance in medical and pharmaceutical fields due to abroad spectrum of biological activities like anti- inflammatory [4-6] ,analgesic [8],antimicrobial [9], anticonvulsant [10],anticancer [11].

Several reported have been done on the preparation of polymeric material containing Schiff-base linke.Khuhawar [12] was synthesis seven polymeric malarial containing Schiff-base link and study of their viscosity behavior ,also Amarasekara and etc...[13] was prepared some polymers derived from vanillin containing Schiff-base link and used it to removal of some metal ions.

On the other hand Akite and etc.. [14] also prepared some polymers derived from terephthaldelyde and glyoxal and study some thermal stability of these polymers while Mahzan and their works [15] prepared some polymers and their thermal stability study .In this study several new polymers containing schiff-base unite were prepared and study of some mechanical and thermal properties.

2-Experementals:

2-1-Materials

Terephtaldehyde, 1,4-diamino benzene, Absbluteethanol ,Furfuralalcohole, Acetone and phosphoric acid were supplied from (Merck componany) while formaline solution (35%), chlorform, sulphuric Acid , Maleic anhydride,sodium hydroxide, methanol and MDI were supplied from (Fluka-company).

These compounds were used with out purification except of furfural alcohol was redistilled.

2-2-Instruments

1-FTIR spectral of the prepared polymers were recorded as KBr-disk by using FTIR instrument Model (shimadza-84005) .

2-Thermo gravimetric analysis (TGA)

Thermal stability parameter of these polymers were evaluated by TGA – Techique model (50-shimadza).using atmospheric N_2 gas with flow rate of (30 ml/min) and heating rate 50 c/min .

3-Differential scanning calorimetry (DSC).

DSC model Q 20 TA was used to study the thermal behavior of these polymers by using inert atmosphere .

4-Flexural strength was performed by using Tinus Olenutm fitted with three point binding fixture at cross-head of 5mm/min and the test was done according to ASTM D 790.Izode impact strength was determine by using zwick model impact tester type machine (5102),equipped with a hummer (zwickco.germary) and the specimen were conforming according to ASTM (D256).

These two instruments presence in the Basra university /scientific college / chemistry department.

2-3-Synthesis:

2-3-1-synthesis of Schiff-base compound

A solution of terephthaldehyde (0.15 g ,1.118 mol)in ethanol (5 ml) , 4drops of glacial acetic acid were added ,then 1,4-phenylenediamine (0.241 g , 2.23 mole)in ethanol (10 ml) was added and The mixture was refluxed for 15 hrs . At room temperature with stirring .The yellow solution was left to dry at room temperature , the precipitate was washed with excess of methanol filterate and dried . An slightly yellow solid was obtained yield (75%),m.p .

2-3-2-synthesis of polymers:

2-3-2-1- synthesis of polymer (1)

This polymer was prepared in reaction of equimolar of schiff-base compound and maleic Anhydridein DMF solvent . The mixture was heated at temperature of (120-130 C^0) with stirring for about (3-4 hrs.) then the solution was left with stirring for (24 hrs.) at room temperature ,the precipitate was obtained by the addition of methanol, filtrate ,dried .

2-3-2-2-Synthesis of phenolic resin(polymer2)

A solution of Schiff-base (1.2 g , 3.8 m mole) in 5 ml ethanol ,was added slowly to the formalin solution (20 ml 35%) at 45 ^{0}C and the PH of the reaction mixture was adjust to 9-10 by added asolution of 10%. Sodium hydroxide .At the end of the addition the mixture was left (3hrs.) at (65-70 ^{0}C) with good stirring . Then the product was cooled to room temperature, nuterilized by adding 10% Solution of phosphoric acid .The product was washed several times with distilled wailer to removed unreached formalinand dry under vacuum to obtained brown viscous product which was curing at 100 ^{0}C for 3 h , 2 h at 120 ^{0}C and finally at 150 ^{0}C for one h. The final product was characterized as above for polymer (1).

2-3-2-3- Synthesis of polyurethane (polymer 3)

This polymer was prepared by the reaction of Schiff-base compound with MDI(1.1 g , 3.5 m mole) of Schiff-base compound dissolved in 5ml DMF, then 2 drops of trietlyl amine was added with stirrer ,after this (0.875 g , 3.5 m mole) of MDI in 5 ml DMF was added to the solution ,the mixture was heated at 79 c^0 with good stirring for about 1 h.then the product was precipitate by addition of methanol, filtrate and dried .The product was characterized by FTIR ,TGA and DSC techniques .

2-3-2-4- Synthesis of polymer 4

This polymer prepared by using the prepared Schiff-base as heat curing of epoxy resin ,so 3 g from Schiff-base was mixed with epoxy resin (based on bisphenol-A-) in the presence of 1% triphenyl phosphine as catalyst at temperature of about 120-125 ^{0}C for 3 hrs. Then post cure at 150 ^{0}C for 2 hrs. The product was characterized as above

2-3-2-5- Synthesis of (polymer 5)

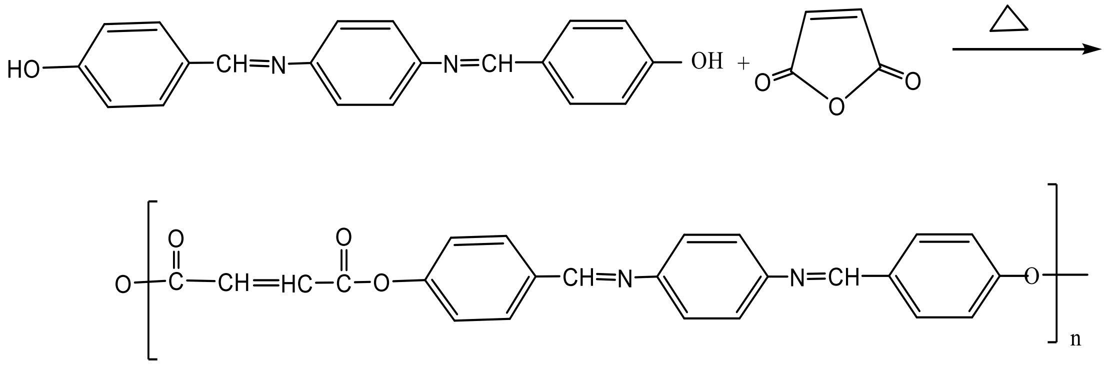
2 gm of furfural alcohol was heated at temperature of 100 ^{0}C in the presence of 2-3 drops of 2 m sulphuricacid . After 30 min the viscosity was increase (indicate polymerization point then 1 gm of Schiff-base was added with good mixing at the same temperature for about 30 min in order to get homogeneous mixture.The product was transfer to oven at temperature of 130 ^{0}C for about 3 h to complete copolymerization .The brown solid product was obtained and characterized .

3- Resultand Discussion:

3-1-Reaction scheme

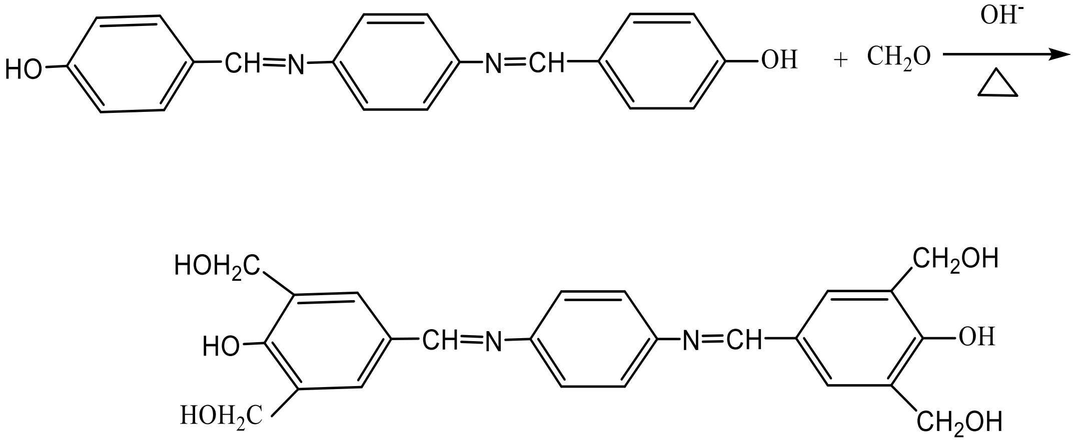
Some polymers were prepared in this study through the reaction of Schiff-base with several compounds as shown below.

A-



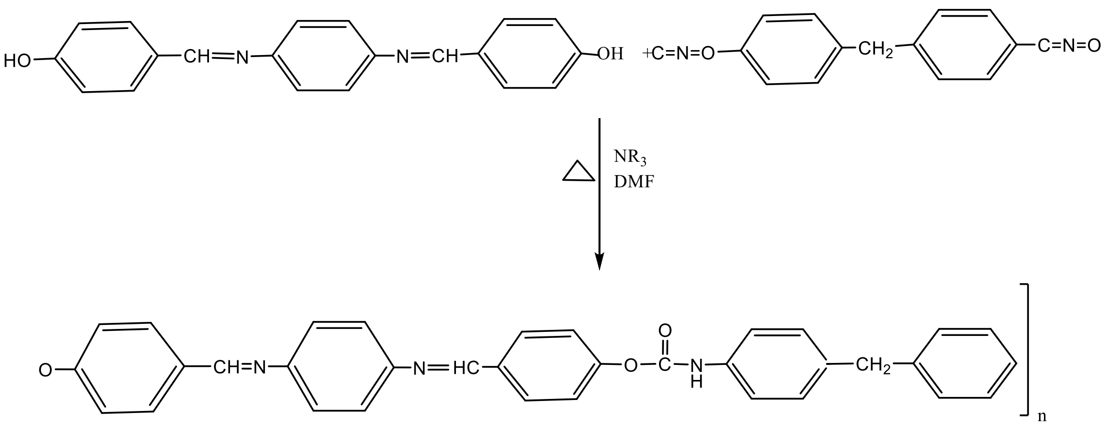
Scheme(1):Reuction with maleic anhydride (unsaturated poly ester)

B-



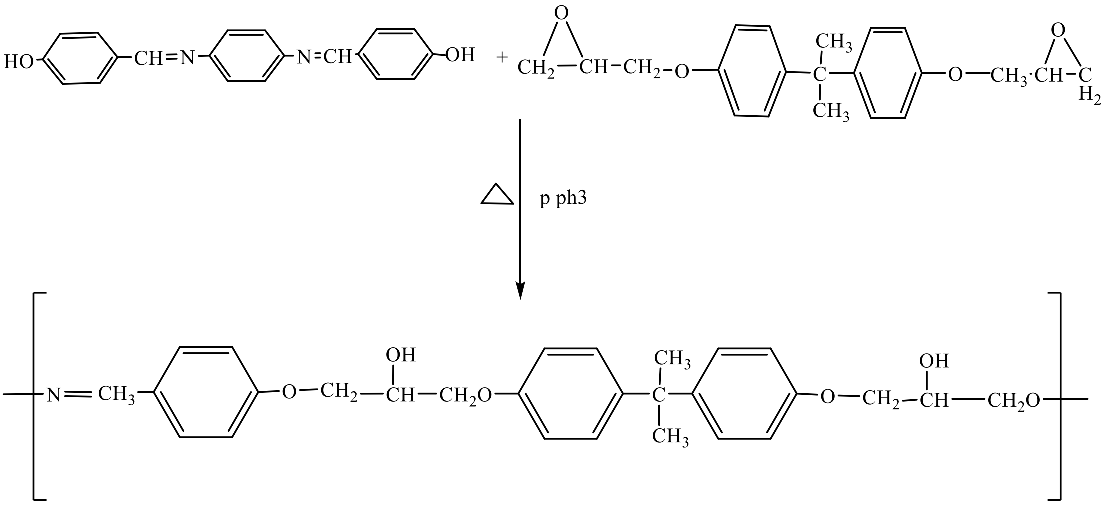
Scheme(2):Reaction with formaline in basic medium (phenolic resin)

C-



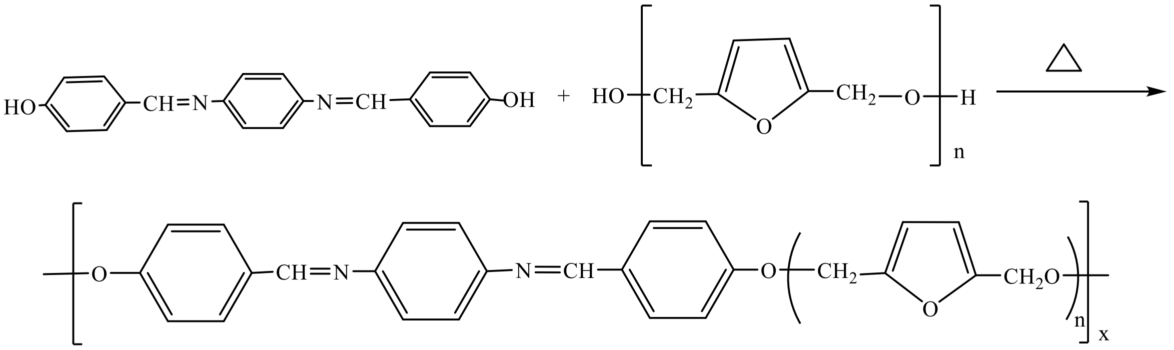
Scheme(3):Reaction with MDI in the presence of triethyl amine catalyst

D -



Scheme(4):Reaction with Epoxy resin in the presence of triphenyl phosphine catalyst

E-



Scheme(5):Reaction with PFA (copolymer with PFA)

These polymer are solid ,not soluble in most organic solvent , which was characterized by FTIR and give a significant band . In the case of polymer(1) the figure (2), show bands at 1707 cm^{-1} due to the carbonyl group and bands at 3088and 3132 cm^{-1} due to stretching vibration of olifenic hydrogen, Another broad bands in the range (3200-3400)cm^{-1} due to hydroxyl group formed through the reaction.Figure (3) show the FTIR spectrum of polymer (2) , significant band at 1014 and 1122 cm^{-1} due to C-O-C ,and band at 1599 cm^{-1} due to the aromatic C=C and bands at 2889,2974 cm^{-1} due to – CH_2 – Stretching vibration , also broad band at 3292, 3360cm^{-1} due to hydroxyl group, in the case of the polymer(3) figure(4) show the band at 1701 cm^{-1} due to the carbonyl group present in the urethane linkage.another band at 1598 cm^{-1} due to the -C=C-in the benzene ring and band at 1082 cm^{-1} Due to C-O-C group .

3-2-Thermal study

Thermal study of the prepared polymers were evaluated by TGA and DSC technique. In the case of TGA ,thermo grams of these polymers are shown in figures (5-8) ,and from these thermo grams ,several thermal parameter were evaluated and listed in table (1).From the result ,the trends of these polymers According to the activation energy and rate of decomposition are : Polymer 5 > polymer 2 > polymer 1 > polymer 3 > polymer

4 . In general these polymers have high char content > 45 % due to the high aromatic fused structure in the networks structure and these may good agreement for use of these polymer as thermal insulation **.**

Table 1: Thermal parameters for the prepared polymers .

Polymer NO.	**Optimum decomposition temp C^0**		**Char % at 600 C^0**	**Rate of decomposition % / min**	**Activation energy KJ/Mole**	**Temp. of 50 % weight loss C^0**
	T0P 1	TOP2				
1	291	400	75	7.00	84.21	> 700 C^0
2	139	214	50	6.50	91.73	600
3	334	590	52	14.31	65.41	612
4	320	480	47	15.23	58.73	520
5	280	516	67	2.50	93.89	> 700 C^0

The DSC thermo grams of these polymers were shown in figures (9-12) . for polymer(1) glass transition tempreture (Tg) was around 250 ^{0}C it is high due to more cross link thought the reaction of Schiff-base with maleic anhydride and no endothermic peak due to melt of this polymer. While for polymer(2) there is a broad endothermic peaks in the range (123-150c^0) due to condensation reaction between unreactedmethylol group present in there structure which lead to formation of ether bridge and methylene bridgeWhile for polymer (3 and 4) the DSC thermo grams showed the glass transition temperature was 269 and 251 ^{0}C respectively ,this high Tg value also due to more cross link polymers was obtained .Finally for polymer (5) the Tg was 281 ^{0}C . Table (2) show the glass transition temperature for the preparedpolymers

Table 2 : Glass transition tempreture for the prepared polymers

Polymer No.	Tg
1	250 ^{0}C
2	-
3	269
4	251
5	281

3-3-Loss on ignition (LOI)

Loss on ignition was performed to test to measure amount of moisture or impurities loss when the sample was ignited .It also determines the presence of organic or other gas forming materials in the polymers .

The polymers was weighted and put into a crucible .The samples was then heated at 500 ^{0}C for 30 minutes .After the samples were taken out of the oven , they were immediately placed in desiccators .The samples were again weighted and (LOI) was measured according to initial weight minus final weight and divided by the initial weight in unit gram**.**

Table3 : show the result of this test

Polymer	LOI %
1	3.6
2	2.8
3	4.0
4	4.2
5	2.2

The result show good LOI for polymer (2 and 5) according to brown ( ),LOI mast be kept below 3 % .

3-4-Mechanical test

3-4-1- Flexural test

Flexural test were tested by the prepare the specimence with dimension of 75x75x2 mm and the span .to-thickness ratio was set at L/D =32 to 1 in all cases .The values were taken from an average of at last five specimens. The result shown in table(5).

Table 4: Flexural test results of the prepared polymers

Polymers No.	Flexural strength Mpa	Flexural modulus Gpa
1	11	2.71
2	16	3.23
3	10	1.96
4	25	4.75
5	21	4.03

The result shown that these polymers differed from each others in morphology structure and cross link density leading to variation in their value of flexural strength and modulus .

3-4-2 Izod impact strength .

The impact strength of the notched sample of the prepared polymers was determined by using having hammer mass which was deflected at 90 angle from the vertical and allowed to full and strike the samples .The rectangular specimens of 80x10x4 mm were taken according to ASTM D-256-88.The tests were carried out at room temperature and the values were taken from an average of atleast five specimens .The izod impact values are calculated as follows:

$$Is=\frac{u1-u2}{(w-a)t}\ (KJ/m^2)$$

Where ,u1:the impact energy (KJ); u2: the residual energy (KJ); w:the specimen

width (m); and a: the notch length (m) .

Table (5)Impact strength value of the prepared polymers.

Polymers No.	**impact strength Kj/m^2**
1	1.32
2	2.71
3	1.03
4	3.11
5	2.87

The result shown that the value of impact strength of these polymer with the trend Polymer 4 > polymer 5 > polymer 2 > polymer 1> polymer 3 ,these may be due to the different of cross linking density or molecular weight distribution between these polymers .

Conclusion :

New Schiff-base was prepared in this study from the reaction of p-hydroxybenzaldehyde with 1,4-phenylene diamine and from this compounds five new polymeric material were prepared .These were characterized by FTIR,TGA,DSC and some mechanical properties .From the results obtained the following conclusion can be drown:

1- These polymers have high decomposition temperature and high char residue .
2- The DSC analysis of these polymers indicate high Tg value .
3- From mechanical properties study, these polymer have good flexural and impact strength.

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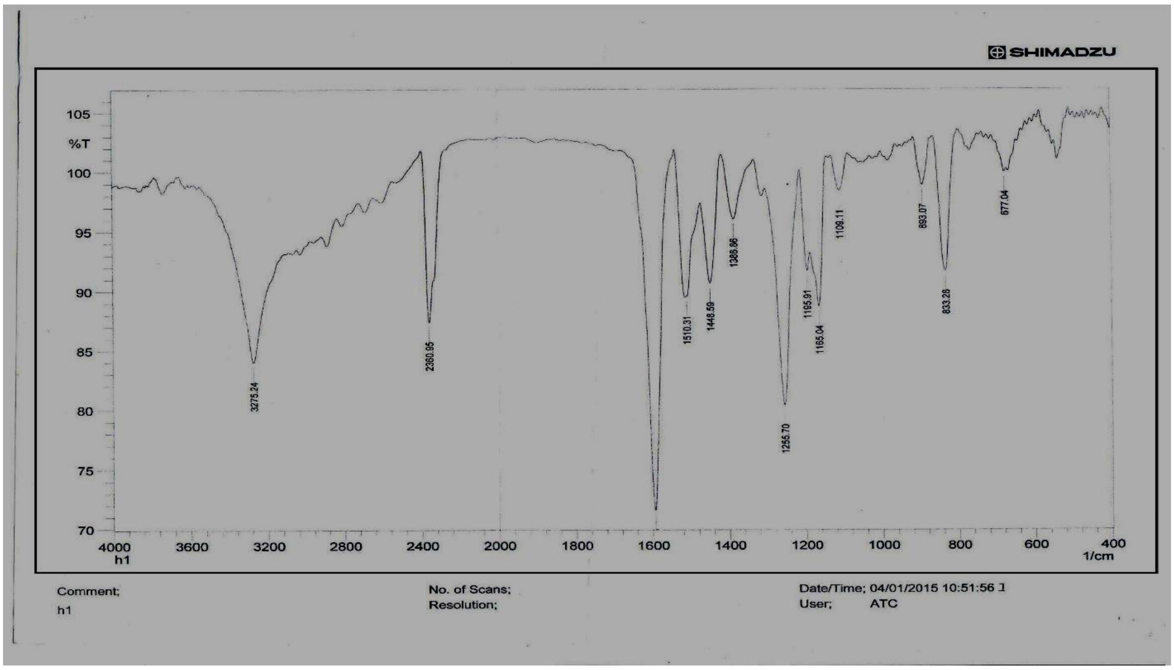

Figure (1) : FTIR spectrum of the prepared Schiff-base compound

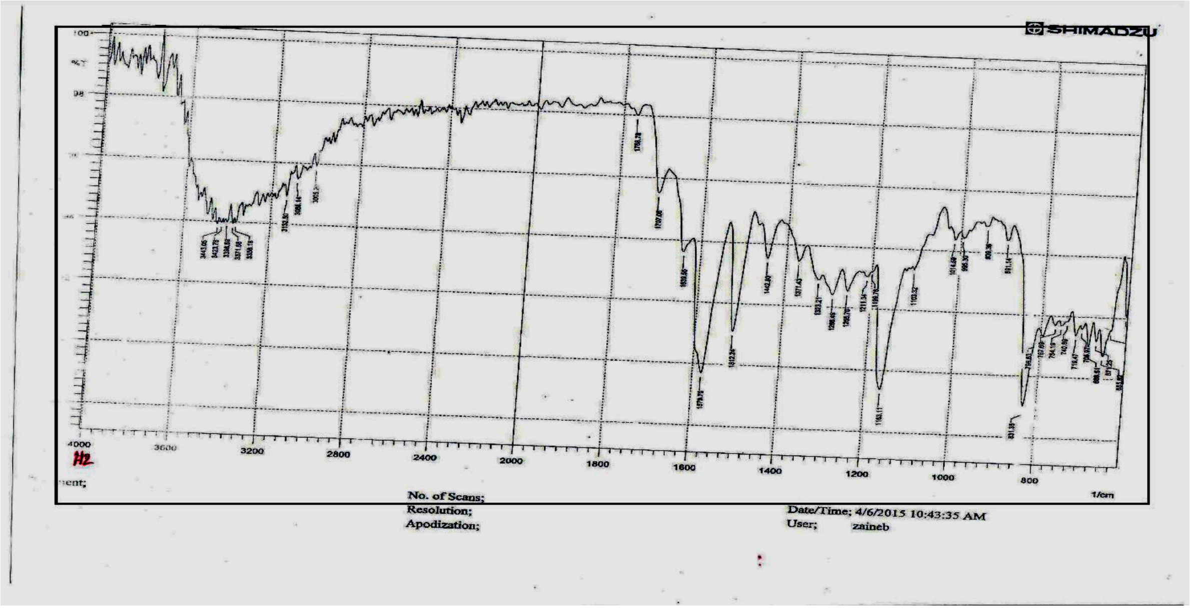

Figure (2) : FTIR spectrum of polymer -1-

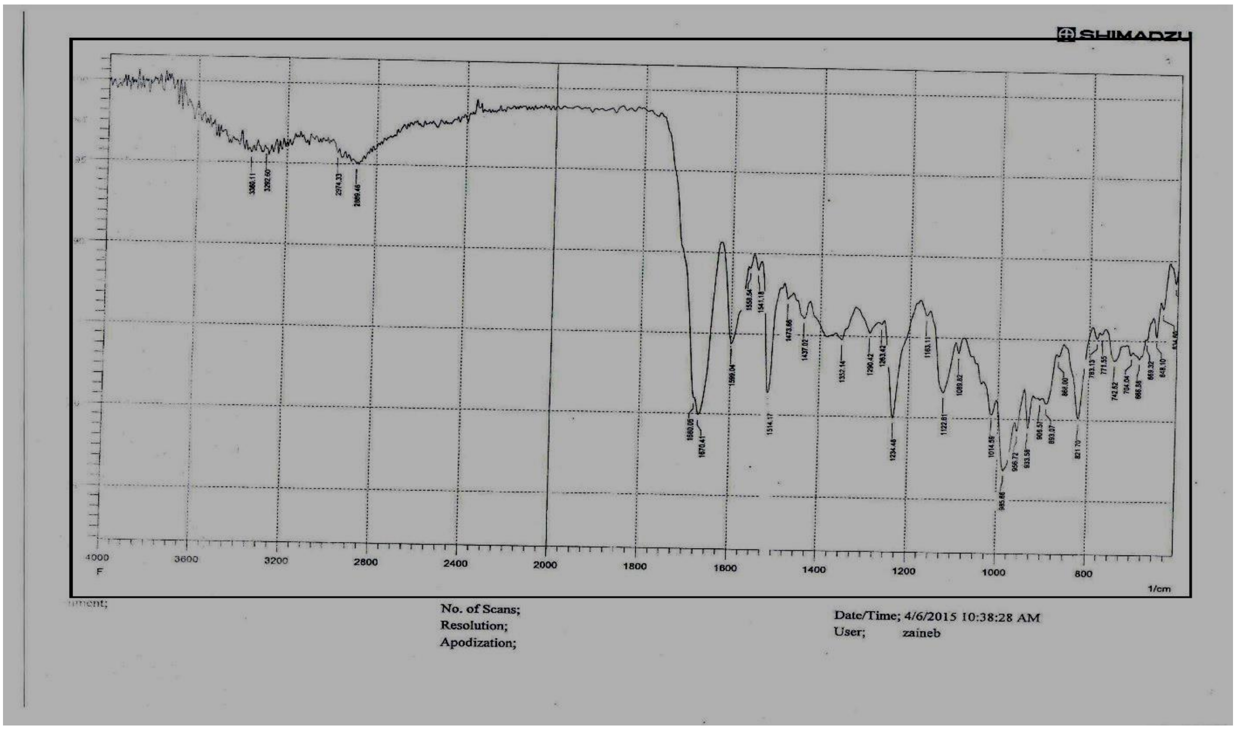

Figure (3) : FTIR spectrum of polymer -2-

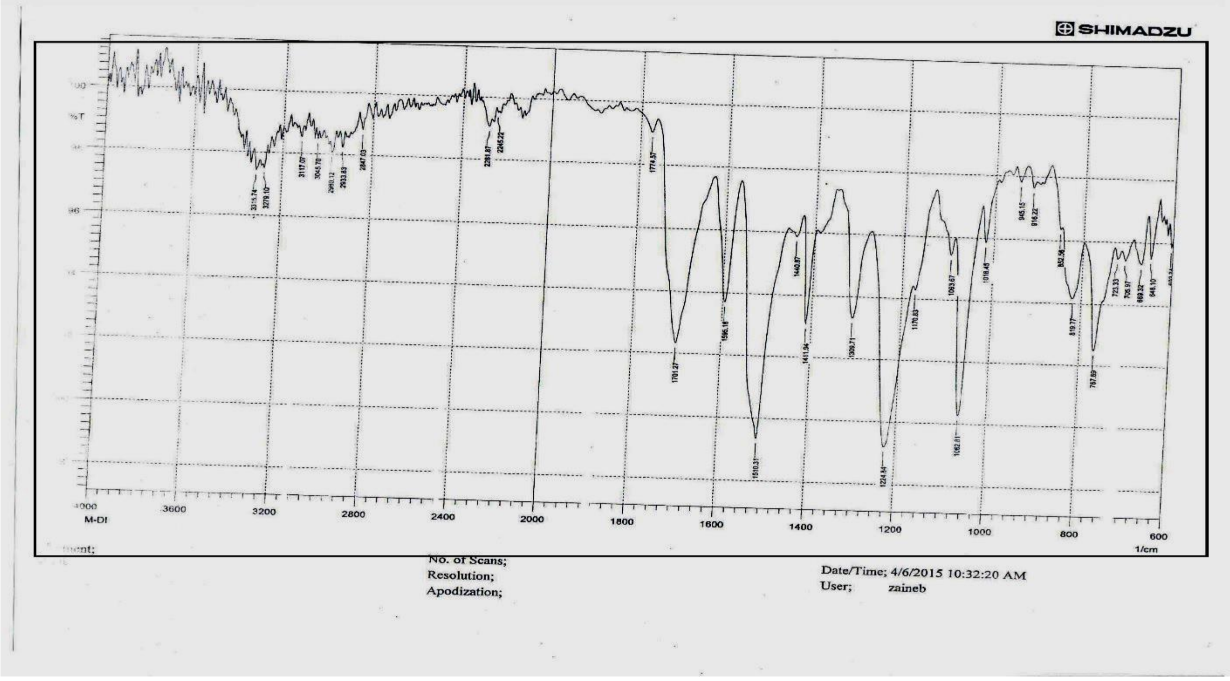

Figure (4) : FTIR spectrum of polymer -3-

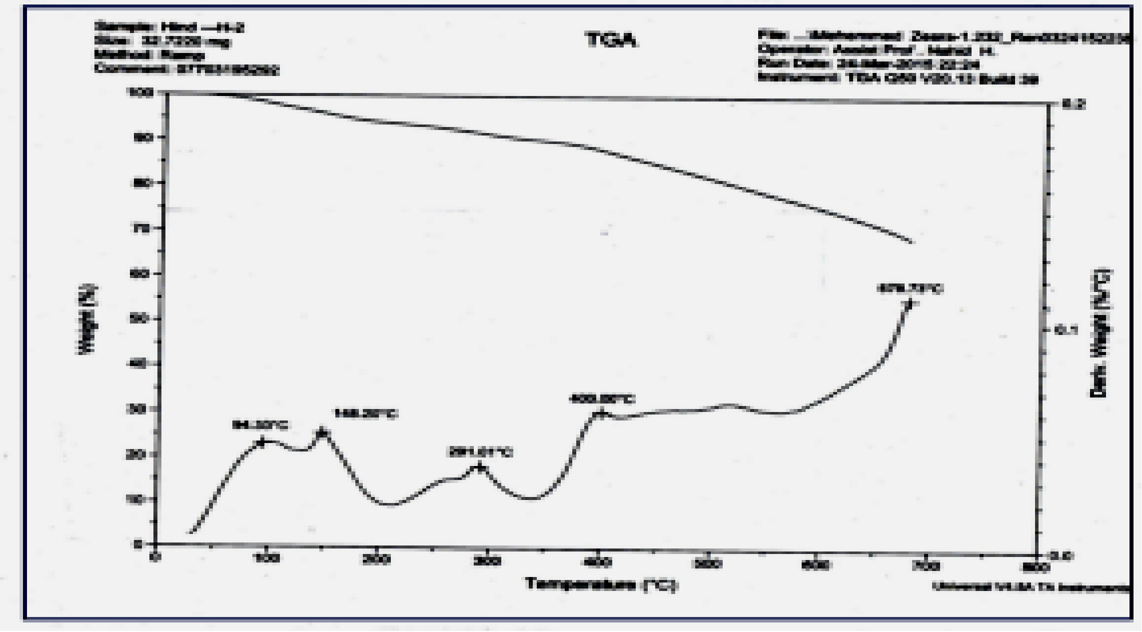

Figure (5   ) : TGA & DTG thermogram of polymer -1-

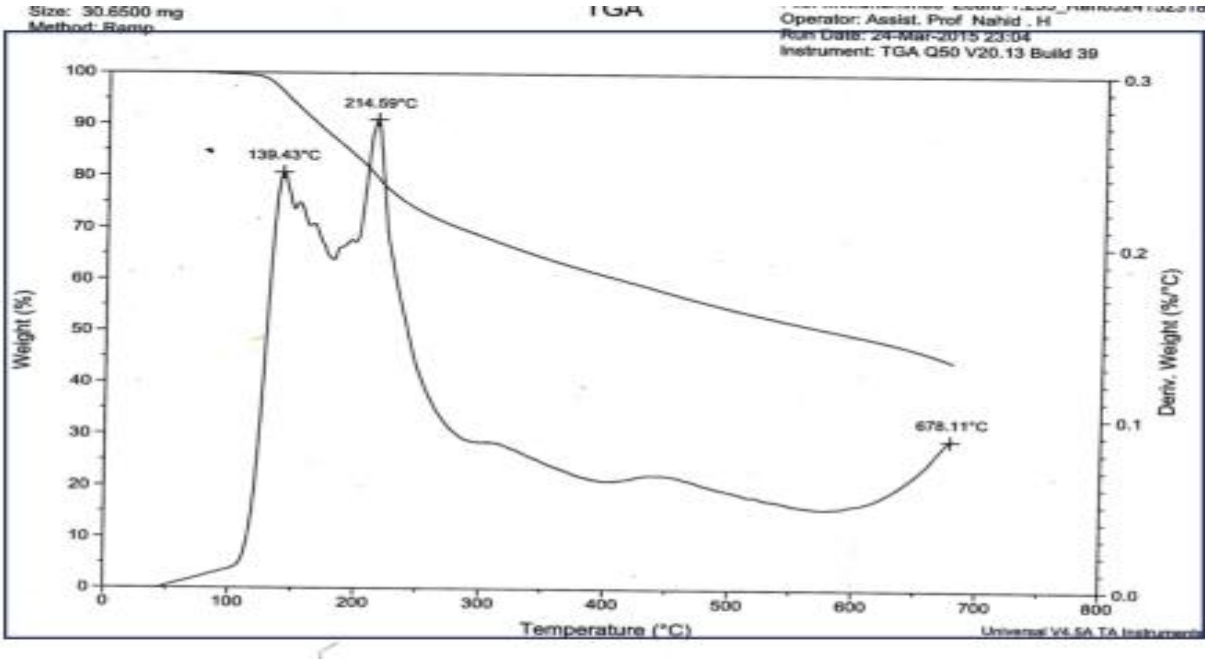

Figure (6   ) : TGA & DTG thermogram of polymer -2-

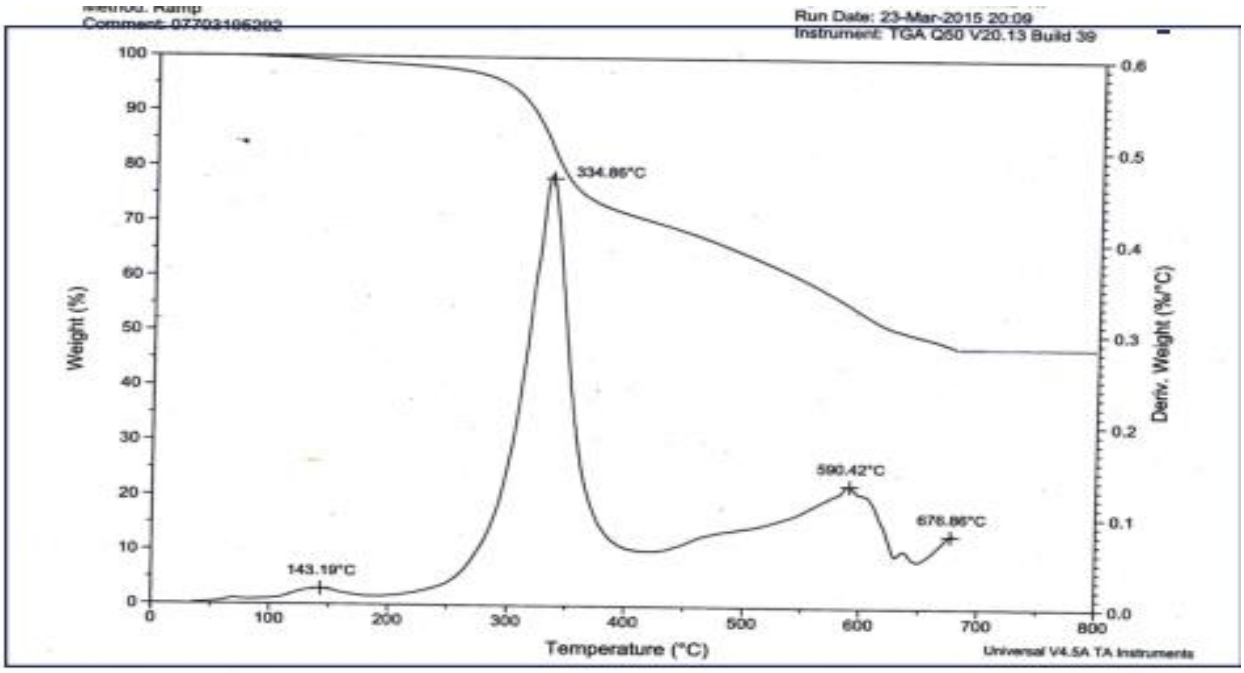

Figure (7) : TGA & DTG thermogram of polymer -3-

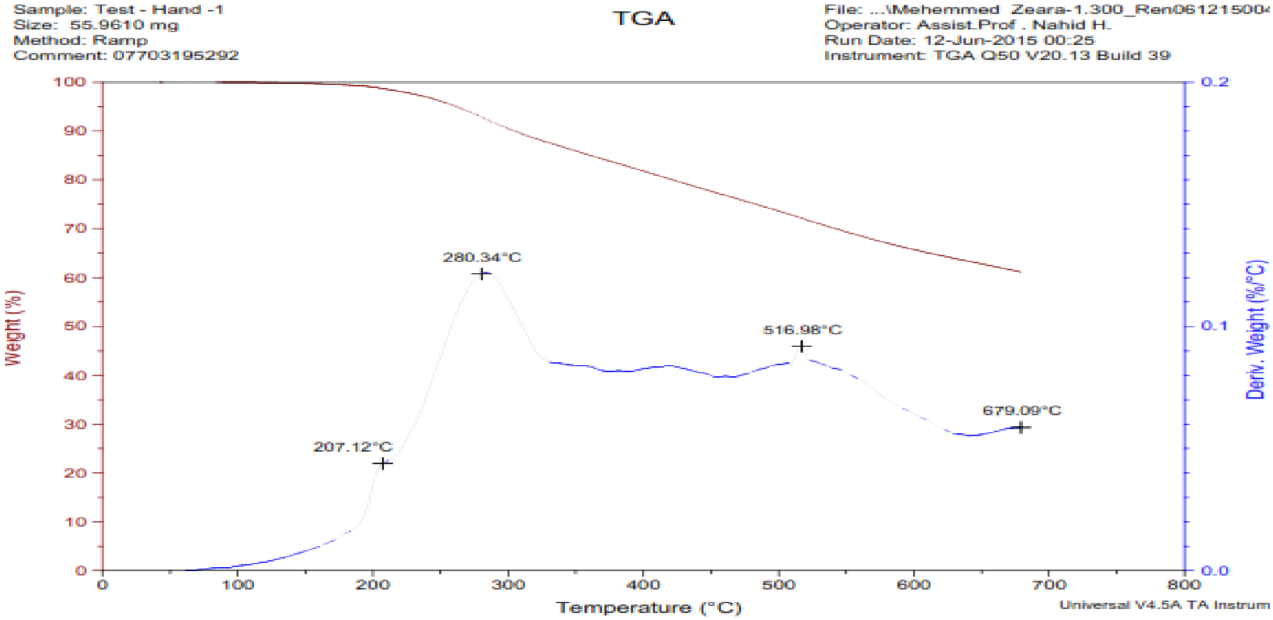

Figure (8) : TGA & DTG thermogram of polymer -5-

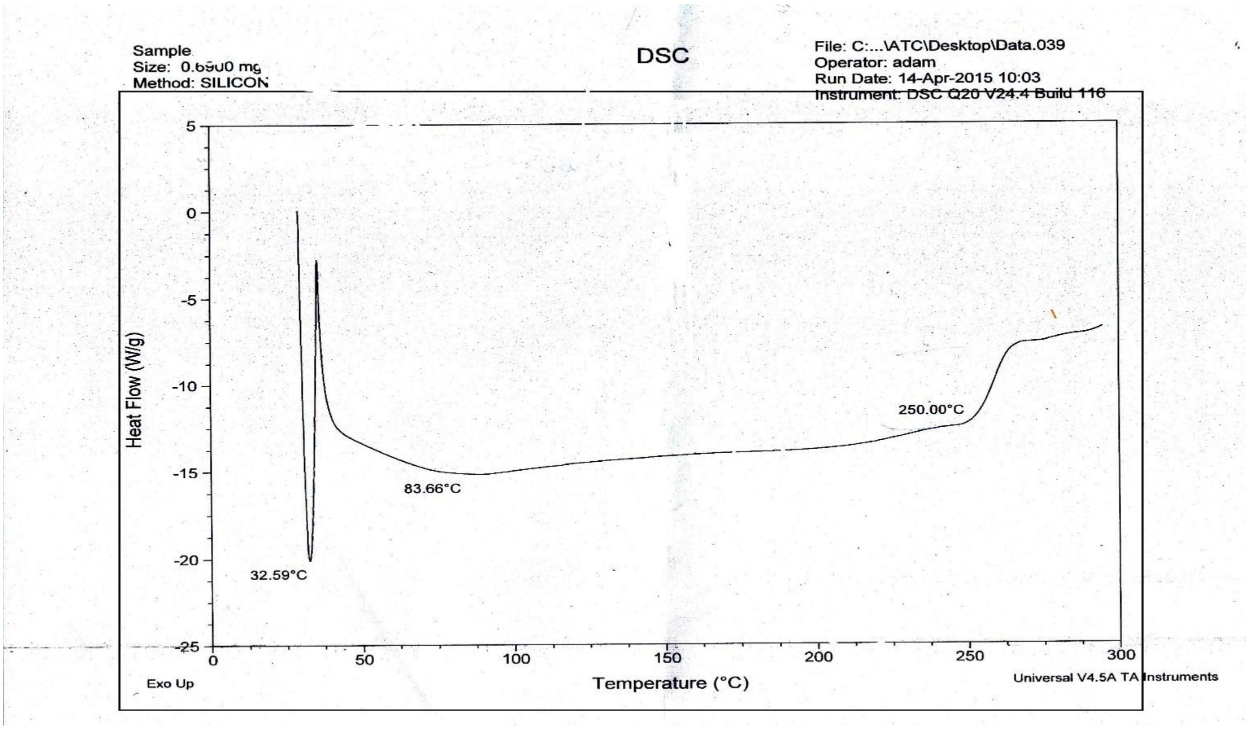

Figure (9) : DSC thermogram of polymer -1-

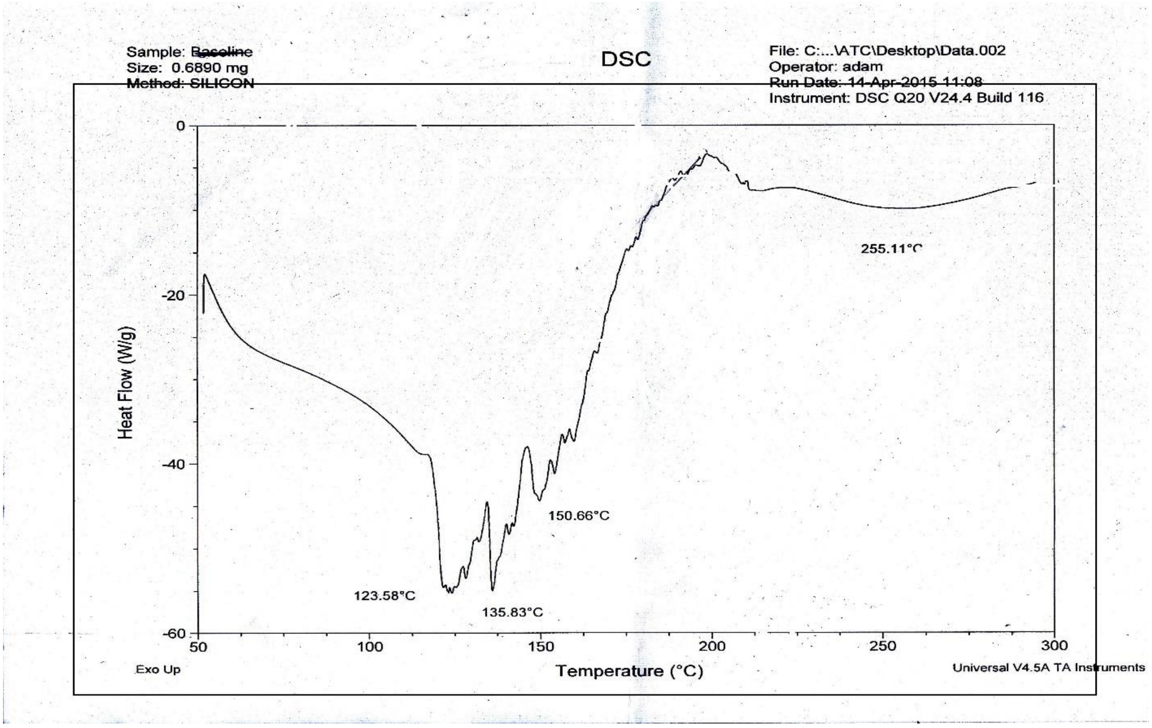

Figure (10) : DSC thermogram of polymer -2-

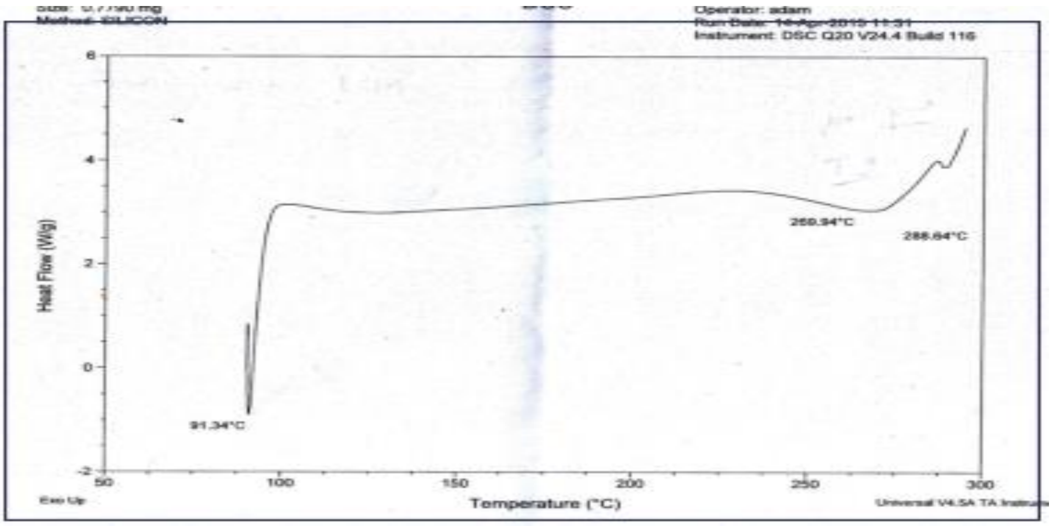

Figure (11) : DSC thermogram of polymer -3-

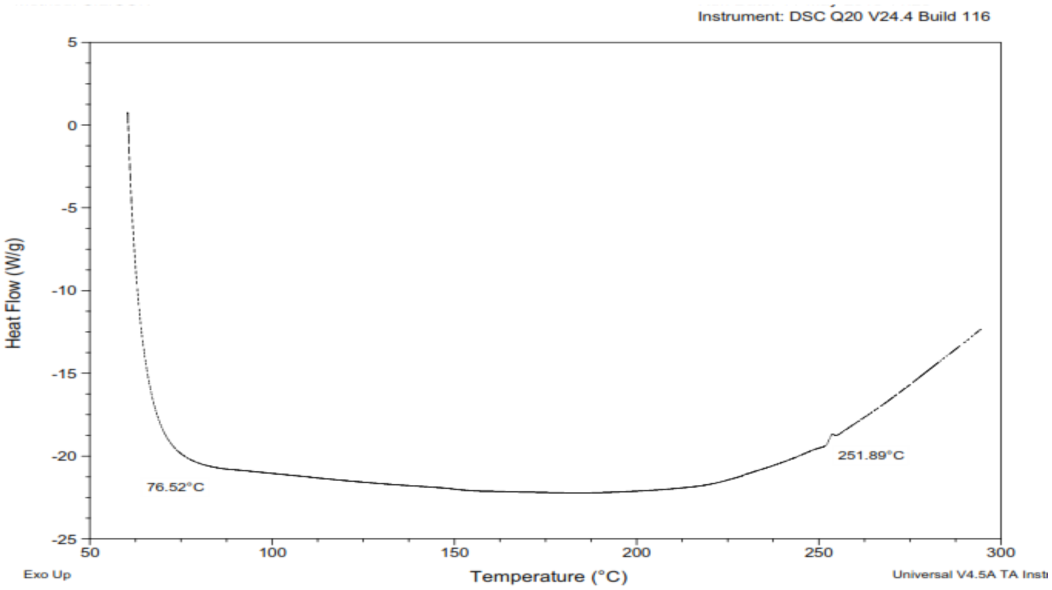

Figure (12) : DSC thermogram of polymer -4-