



Preparation and Investigation of Various Monomers and Studying of The Behavior (Thermal, Physical, Spectral, Chromatography)

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ABSTRACT

Various monomers of hetero cycles were synthesized in this work through reaction of amine-heterocycles derivatives in azotation reaction by coupling with other compounds bearing of function groups, or reactions of Schiff bases compounds with aromatic aldehydes then cyclization of imine group in (-CH=N-) to yield cyclic compounds as a monomer. The structure of the newly monomers were identified by using (TLC) and some techniques ((FT.IR, ¹H.NMR, Chromatography Analysis, DSC-Measurement)), melting points then studying ((chromatography behavior, thermal measurements for stability of monomers, studying of physical characterization and other analytical studies like solubility in various solvents)).

Keywords: oxadiazol, thiadiazole, thiazole, polymer.

Received 01.04.2016

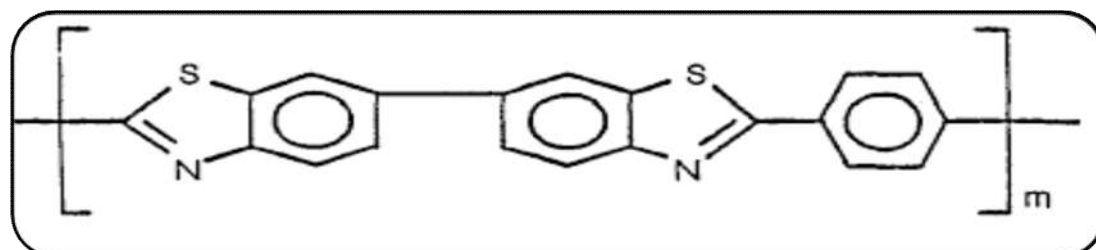
Revised 13.05.2016

Accepted 10.07.2016

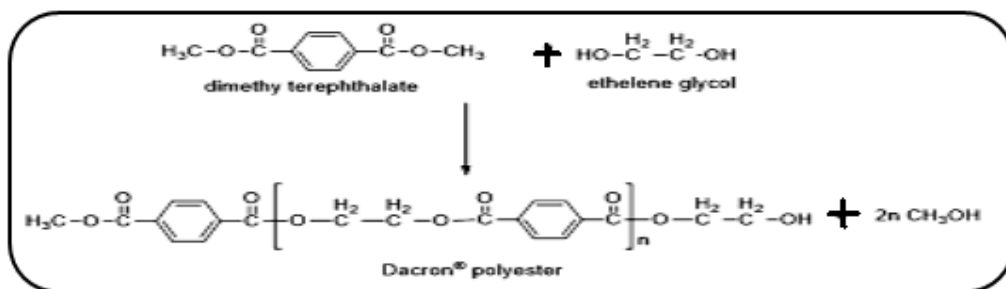
INTRODUCTION

Recently the design and synthesis of monomers or polymers compounds have attracted much attention from authors from chemists. These compounds have potential applications in the most of fields of industrial chemistry, which have important biological properties and synthetic compounds which used in many literature and past papers, especially in several fields like in medicinal chemistry with drugs, other applications in pharmaceutical field and synthetic chemistry field or other fields such as industrial polymers [1-5].

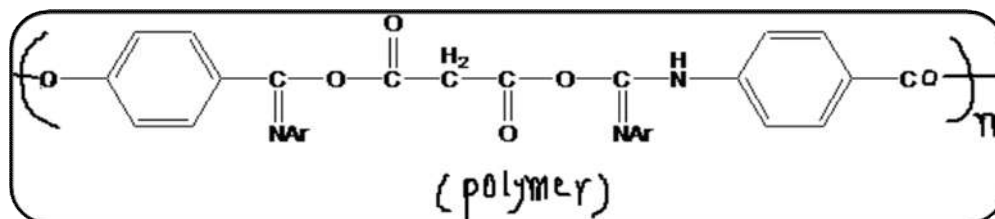
Hetero cycles give out different derivatives in monomers and polymers. Presence of thiazolidine, oxadiazole or thiadiazole in various monomers undergo different types of polymers.



Important natural polymers include bio-molecules like the proteins, which are polymers of amino acids, and the nucleic acids, which are polymers of nucleotides—complex molecules composed of nitrogen-containing bases, sugars, and phosphoric acid and several [5-10] inorganic polymers also are found in nature, containing diamond and graphite. Both are composed of carbon. In diamond, carbon atoms are linked in a three-dimensional network that gives the material its hardness. In graphite, used as a lubricant and in pencil “leads,” the carbon atoms link in planes that can slide across one another.



Most commonly, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms [10-13]. A simple example of ester bond in polymer :



Experimental & Materials

Melting points were recorded on Gallenkamp melting point apparatus and were uncorrected. FT-IR spectra were recorded by using (FT-IR 8300 Shimadzu) in the range (400-4000) cm^{-1} as KBr discs. ^1H -NMR-spectra in DMSO-solvent were carried out in Canada, and DSC - Thermal Analysis, chromatographic Analysis in Canada, physical and analytical studies in Baghdad university.

Methodology

Synthesis of Monomer [1]:

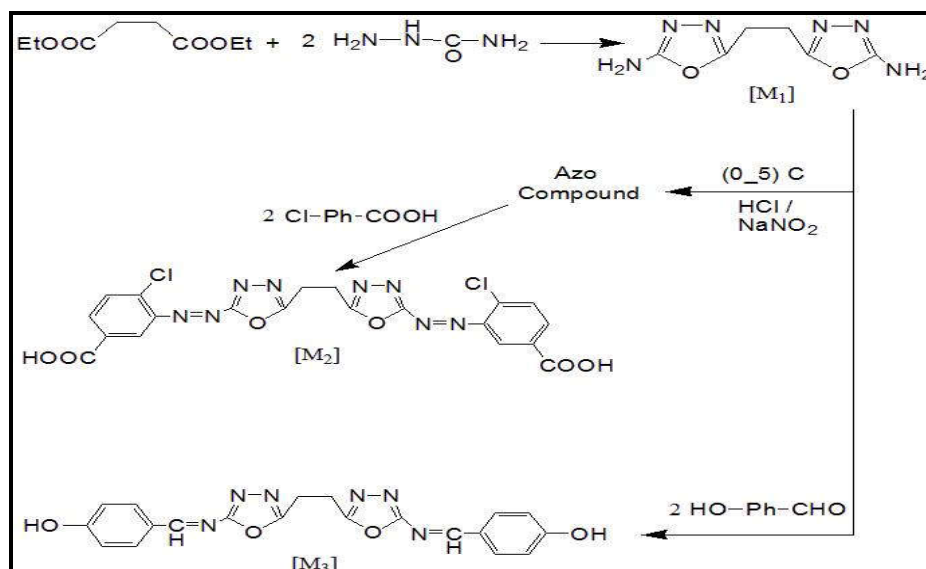
(0.01mole) Of diethyl succinate was refluxed with (0.02mole) of semicarbazide for (5hrs) in presence of (POCl_3) in absolute ethanol as a solvent according to studies [16, 17], to yield precipitation which filtered and dried then re crystallized to yield Monomer [1]

Synthesis of Monomer [2]:

(0.01mole) Of monomer [2] was dissolved in (2ml) of hydrochloric acid, then solution of sodium nitrite was added at (0-5) $^{\circ}\text{C}$, after that coupling reaction with 4-chloro benzoic acid according to studies^(16,17), after 48 hrs gave precipitation which filtered and dried then re crystallized to yield Monomer [2].

Synthesis of Monomer [3]:

(0.01mole) Of monomer [1] was reacted with (0.02 mole) of 4-hydroxy benzaldehyde, with refluxing for 3 hrs in presence of drops from glacial acetic acid according to studies [15-17], after that gave precipitation which filtered and dried then re crystallized to yield Monomer [3].

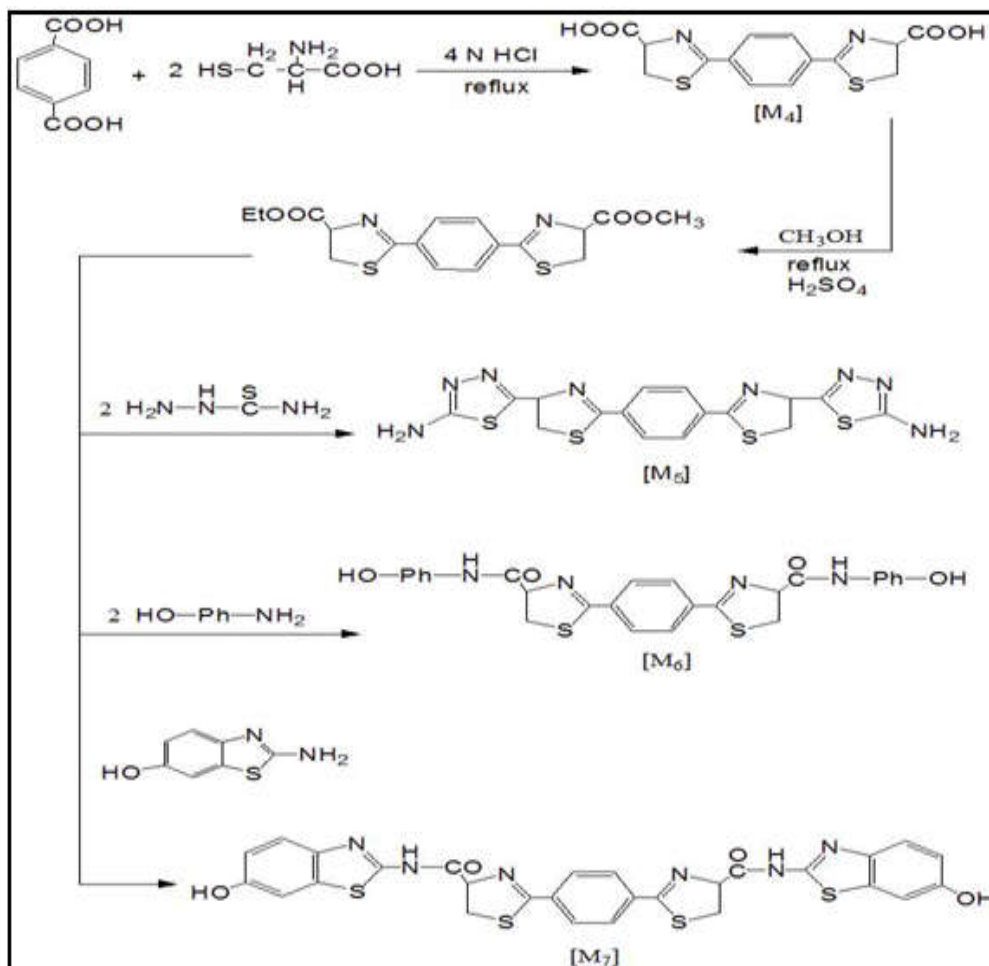


Synthesis of Monomer [4]:

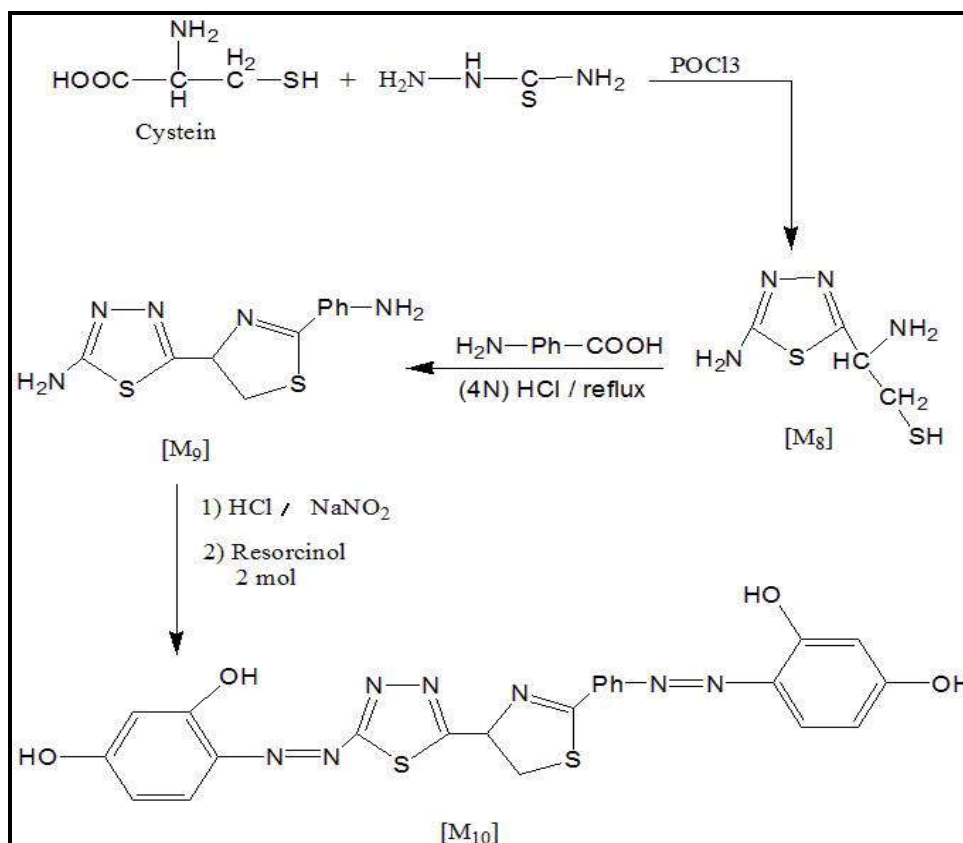
(0.01mole) Of triphthalic acid] was refluxed with (0.02 mole) of cystaien in (4N) of hydrochloric acid in presence of ethanol as a solvent , according to studies^(16,17) , then it gave precipitation which filtered and dried then re crystallized to yield Monomer [4] .

Synthesis of Monomers [5,6,7]:

Monomer [4] was refluxed in presence of ethanol as a solvent and (8 ml) of H₂SO₄, to produce ester compound which reacted with one of (0.02 mole) from [thiosemicarbazide , p-hydroxy aniline , hydroxy-2-aminobenzo thiazole] in refluxing for (5-7) hrs, according to studies [16, 17], then it gave precipitation which filtered and dried then re crystallized to yield Monomer [5, 6, 7] .

**Synthesis of Monomers [8,9,10]:**

(0.01mole) Of cystaien was refluxed with (0.01mole) of thiosemicarbazide for (5hrs) in presence of (POCl₃) in absolute ethanol as a solvent ,to yield precipitation which filtered and dried then re crystallized to yield Monomer [8], which refluxed in ethanol in presence of (4N) of hydrochloric acid to give monomer [9] , which dissolved in (2ml) of hydrochloric acid ,then solution of sodium nitrite was added at (0-5) C ,after that coupling reaction with resorcinol according to studies [16, 17], after 48 hrs gave precipitation which filtered and dried then re crystallized to yield Monomer [10] .



RESULTS AND DISCUSSION

In the present work of our work, we synthesized Monomers [1- 10] and will identified them by spectral methods like (FT.IR , H.NMR) and studying some of thermal and analytical measurements with chemical applications like (DSC - Analysis , Solubility in different solvents , chromatography behavior) :

Spectral Studying

The FT.IR-spectrum showed an absorption bands at (1720 -1730) cm^{-1} in monomers [M₂ , M₄ ,] due to the carbonyl of carboxyl (15, 16) group (-COO-), which disappeared and other bands are appeared at {(3230- 3300) cm^{-1} for (NH) amide of groups , and amine (NH₂) at(3220, 3390) cm^{-1} for amine group(16,17) in Monomers [M₁ ,M₅,M₆ , M₈ ,M₉] respectively .While Monomers [M₂ and M₁₀] appeared bands at (1486 , 1490) cm^{-1} for azo groups (-N=N-) , and other bands in Table (1) , and some Figures (1 -4).

Table (1): FT.IR- data (cm^{-1}) of Monomers [M₁ - M₁₀] .

Monomers	I.R.(KBr) ((Only Important Groups))
[M ₁]	(NH ₂): 3300 , 3282 , (C=N) endo cycle :1608
[M ₂]	(CO-O-)of carboxyl group: 1720, (C=N) endo cycle: 1606, (OH) of carboxyl group: 2600-3150 , (-N=N-): 1486
[M ₃]	(OH): 3440, (C=N) endo cycle: 1605, (CH=N) imine: 1630.
[M ₄]	(CO-O-)of carboxyl group: 1725, (C=N) endo cycle: 1610, (OH) of carboxyl group: 2610-3170 , (C-S): 680 .
[M ₅]	(NH ₂): 3220, 3290, (C-S): 690, (C=N) endo cycle: 1612 .
[M ₆]	(CO-NH) Amide: 3200, (C=N) endo cycle: 1605, (OH):3400 , (-CO) amide:1698.
[M ₇]	(CO-NH) Amide: 3260, (C=N) endo cycle: 1611, (OH):3430 , (-CO) amide:1678.
[M ₈]	(NH ₂):3310, 3350 , (SH) : 2340 , (C=N) endo cycle: 1610.
[M ₉]	(NH ₂): 3240, 3289 , (C=N) endo cycle: 1608
[M ₁₀]	(OH): 3420, (C=N) endo cycle :1616, (N=N) Azo: 1490 , (C-S): 672

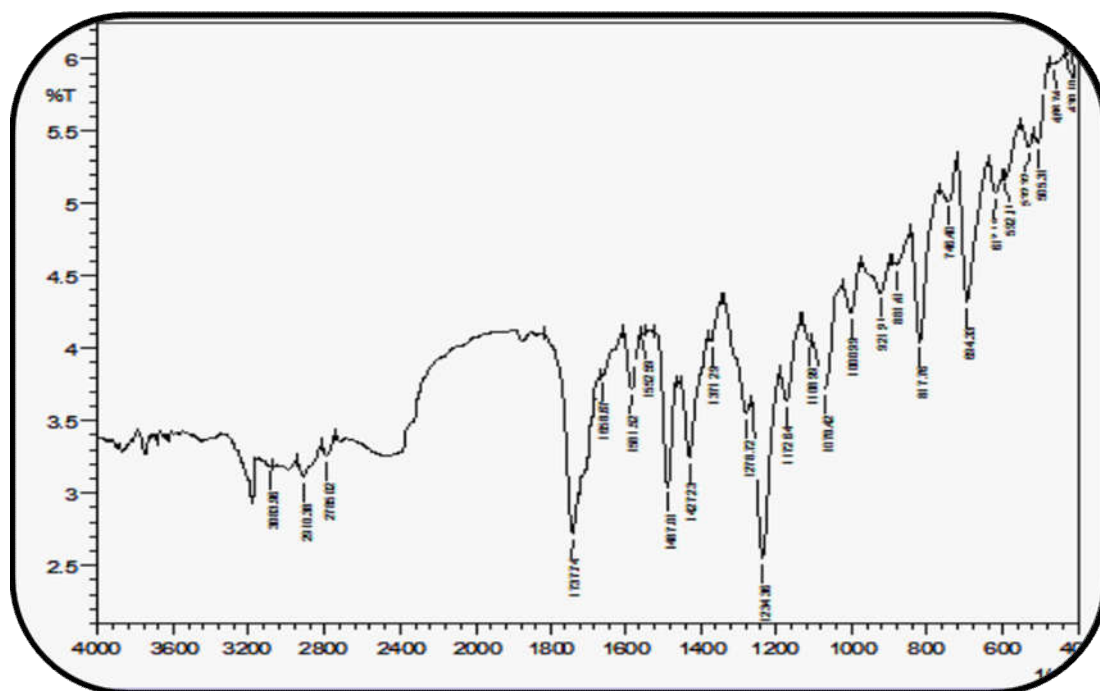


Fig (1) :FT-IR of Monomer [M2]

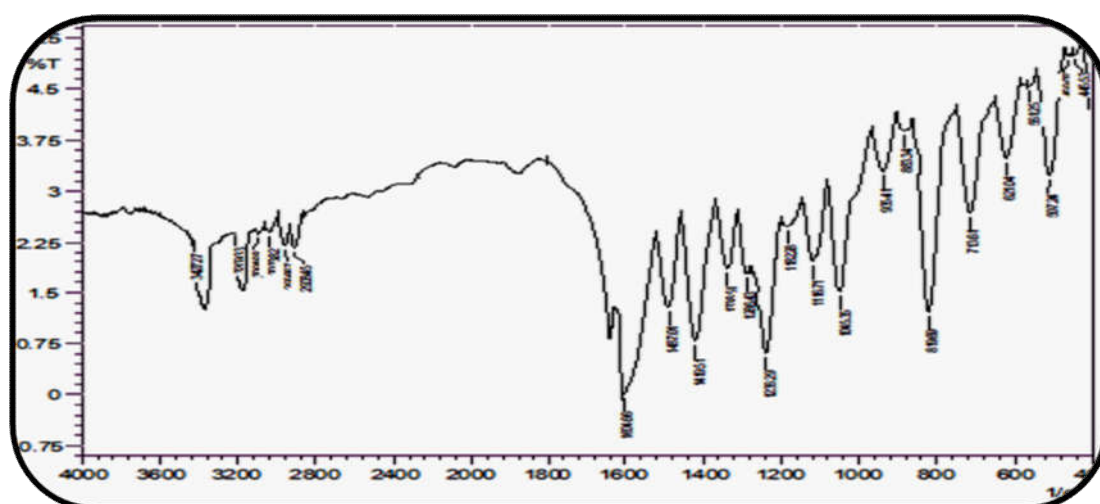


Fig (2) :FT-IR of Monomer [M6]

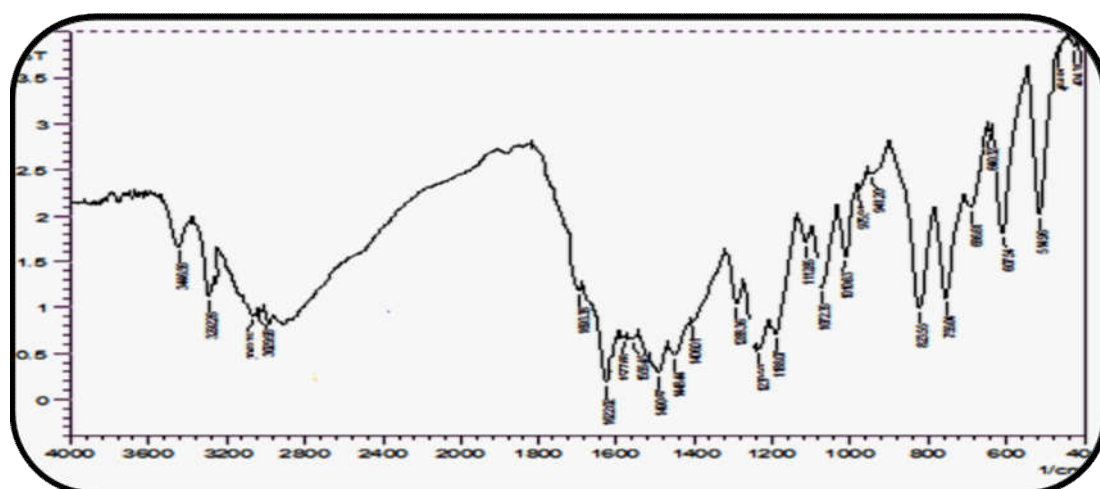


Fig (3) :FT-IR of Monomer [M7]

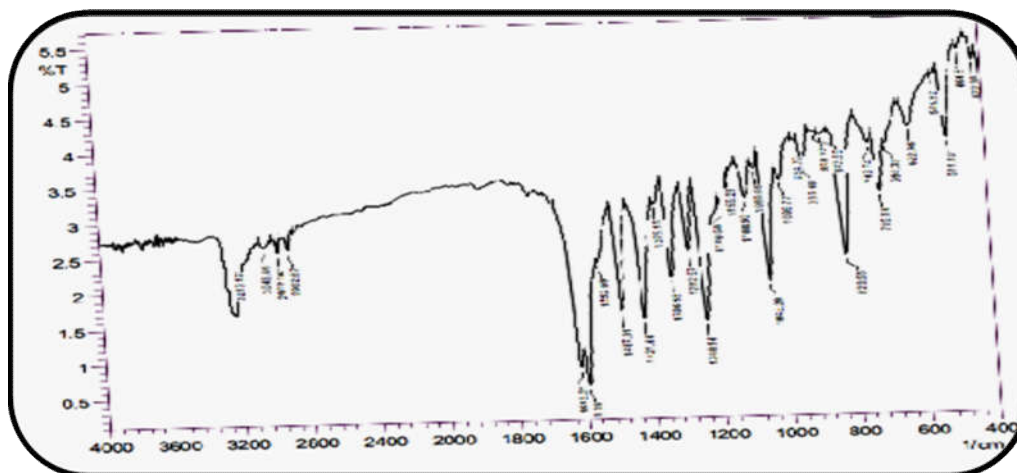


Fig (4) :FT-IR of Monomer [M10]

The ¹H-NMR- Spectra: showed signals at δ {δ (13.20 - 13.11) for proton of (COOH) carboxyl groups in monomers [2 , 4] respectively .

While monomers [1, 5, 8 , 9] showed signal at δ (5.24) for protons of (NH₂- amine , δ (5.51 -5.63) for NH₂ group } respectively .

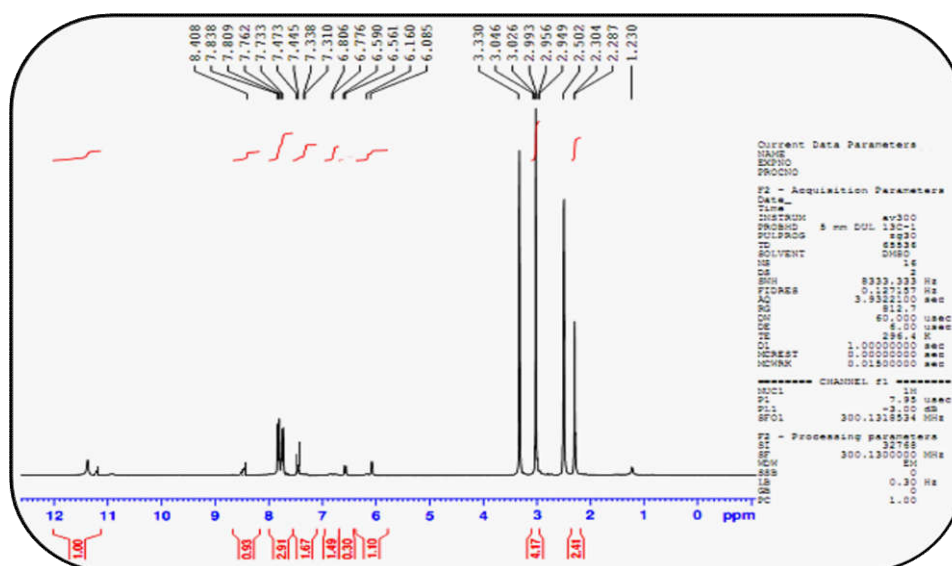
Monomers [M3 , M6 ,M7 , M10] showed signals at δ(11.42 – 11.09) for proton of (OH) phenol groups, respectively .

Monomer [M4] showed signal at δ(8.33) due to proton of Imine group (CH=N),.

Monomers [M6 ,M7] showed signals at δ(10.31 , 10.53) proton of amide (NH-CO-), and other signals in table (2) , and Figures (5-7) .

Table (2): H.NMR- data (δ - ppm) of Monomers [1-10]

Monomers	H.NMR ((Important Peaks))
[M1]	(NH ₂)proton of amine: 5.24 .
[M2]	(CO-OH) proton of carboxyl group: 13.20
[M3]	(OH)proton of phenol : 11.42 , (CH=N)proton of imine: 8.33 .
[M4]	(CO-OH)proton of carboxyl group: 13.11 .
[M5]	(NH ₂)proton of amine: 5.51 .
[M6]	(CO-NH)proton amide: 10.31 , (OH)phenol :11.09 .
[M7]	(CO-NH)proton amide: 10.53 , (OH)phenol :11.15 .
[M8]	(NH ₂) Two groups :5.70 , 5.26 ., (SH) : 12.13 .
[M9]	(NH ₂): 5.63 .
[M10]	(OH) phenol groups : 11.17 , 11.56 .



Fig(5): H.NMR of Monomer [M3]

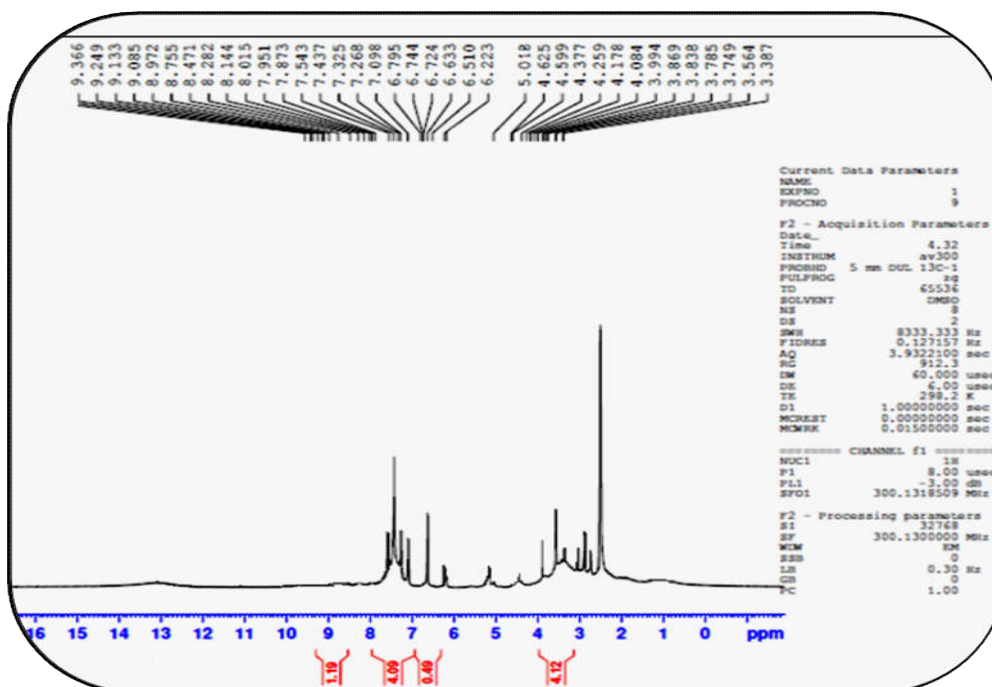


Fig (6) : H.NMR of Monomer [M5]

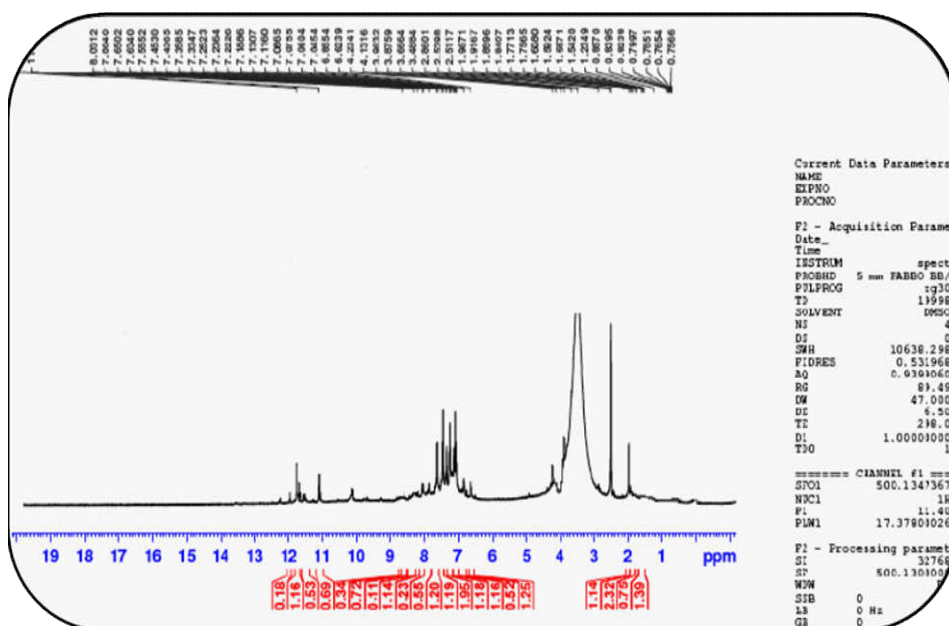
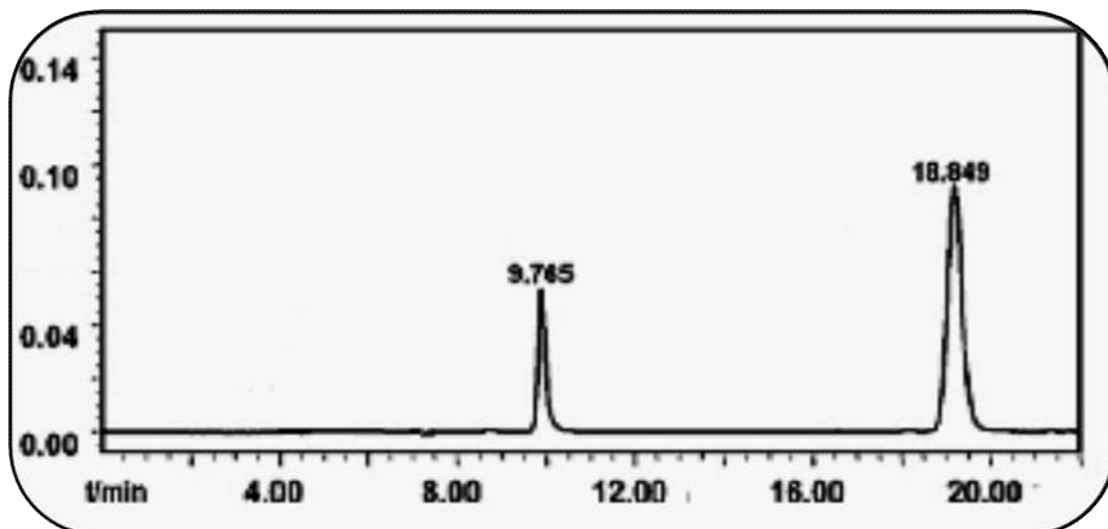


Fig (7): H.NMR of Monomer [M7]

Analytical Studying :

Analysis of some monomers by Chromatography measurements:

Preparation of diluted solutions (concentration of 1ppm for vehicles) from monomers [M3 ,M5 ,M7 , M9 ,] after dissolved with ethanol , shaking continuous., injected models by using a syringe(Hamilton) with a capacity of 10ml individually and then injected the mixture, and then install the measurement conditions through the use of nitrogen a gas flow of 25ml/min bus speeds and injection temperature was 25C° degrees higher than the temperature separation column and then use a flame ionization detector is 50C° higher than the temperatures of the column either column temperature programmed gradual increase of of(90-160)C°, taking into consideration the maximum temperature to avoid damage to the column ., all data are shown in figures (8- 11).



Fig(8): Chromatogram of Monomer [M3]

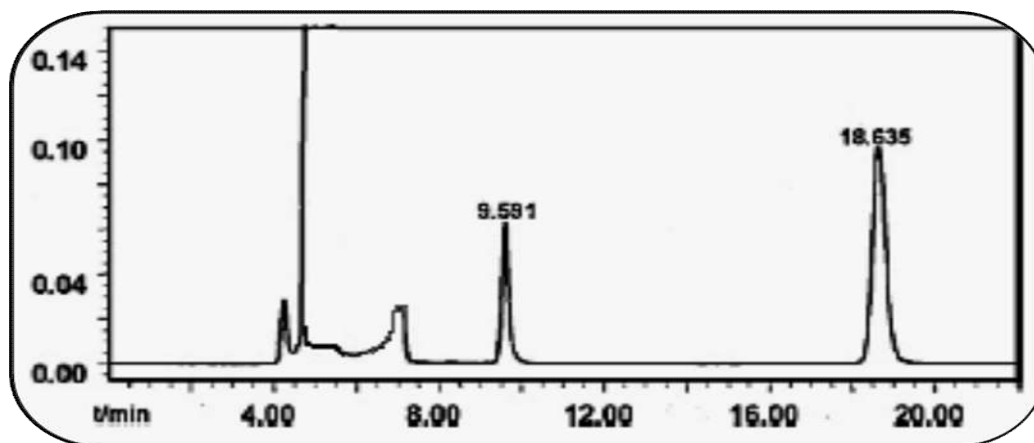


Fig (9): Chromatogram of Monomer [M5]

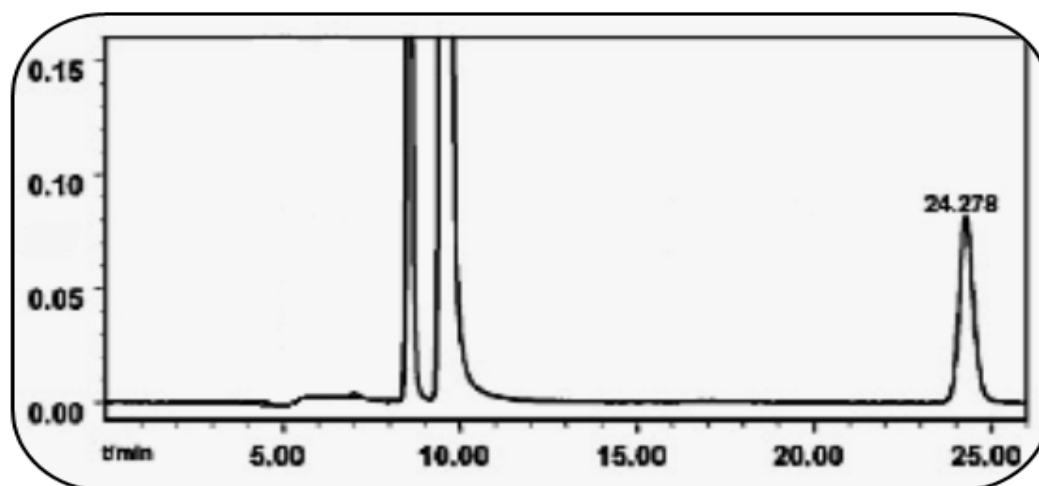


Fig (10): Chromatogram of Monomer [M7]

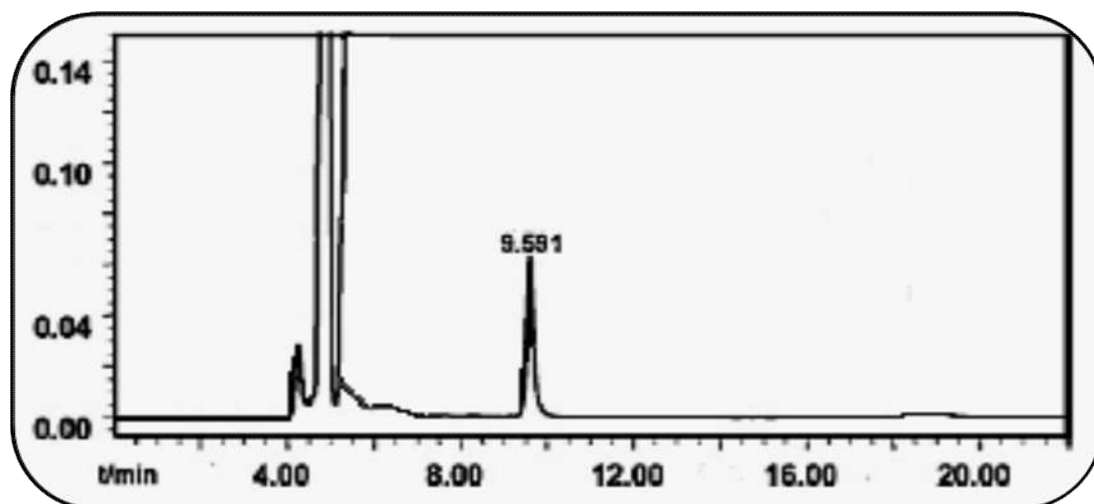
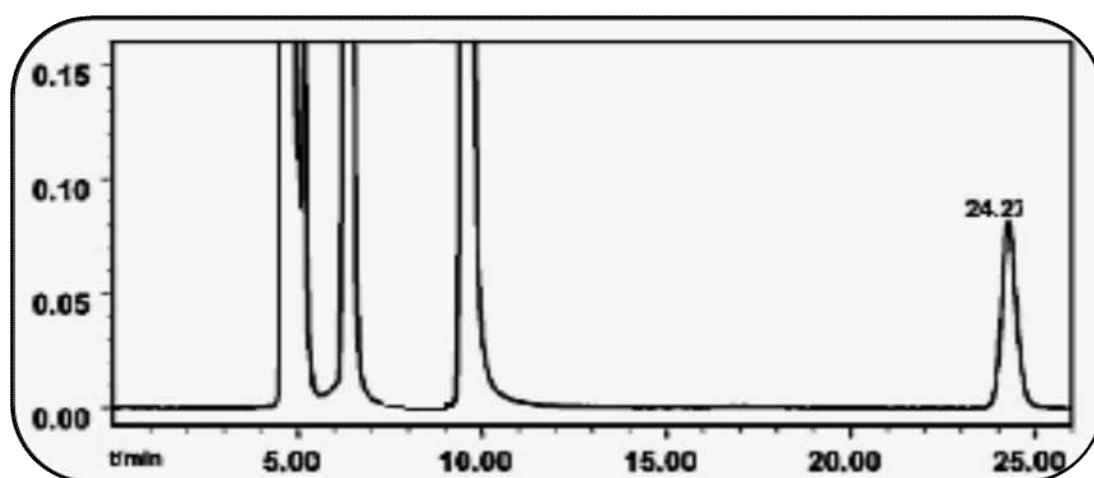


Fig (11): Chromatogram of Monomer [M9]



Fig(12): Chromatogram of Monomer [M10]

For the past three decades, there have been several methods developed and Reported in the literature for compounds analysis. The trend is to develop multi-compounds analysis methods which are simple and easy to separation.

The use of hetero cycles in monomers covered a wide area application in industry and analytical field like chromatography .

From the results ,all monomers separated according to molecular weight and interaction between them in column through separation in chromatography column.

Analytical Studying - Effect of Solvent :

The interaction of monomers were tested in various solvents according to polarity type of solvents , the results are summarized in Table (3).

Table (3) : Solubility of Compounds in Various Solvents.

Compounds	Solvents					
	C ₂ H ₅ OH	CH ₃ OH	Toluine	CHCl ₃	CCl ₄	Hexane
[M1]	+	+	-	-	-	-
[M2]	+	+	-	-	-	-
[M3]	+	+	-	-	-	-
[M4]	+	+	-	-	-	-
[M5]	+	+	-	-	-	-
[M6]	+	+	-	-	-	-
[M7]	+	+	-	-	-	-
[M8]	+	+	-	-	-	-
[M9]	+	+	-	-	-	-
[M10]	+	+	-	-	-	-

The solubility of prepared Monomers depend on type of functional group and terminal groups (polarity of group) in monomers which cause interaction such as : (OH - group , NH₂- group , COOH group , SH - group) or any other active functional groups.

Thermal Studying (DSC - Measurements) :

DSC - measurements of some monomers measured for stability of hetero cycles- monomers in some figures (13 - 17) ,DSC- Curves showed high stability [15, 18] toward high temperature:

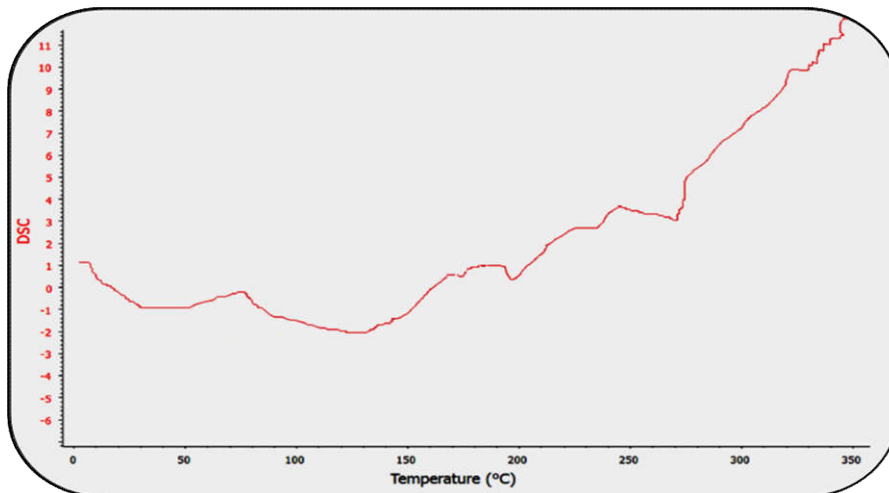


Fig (13) : DSC of Monomer [2]

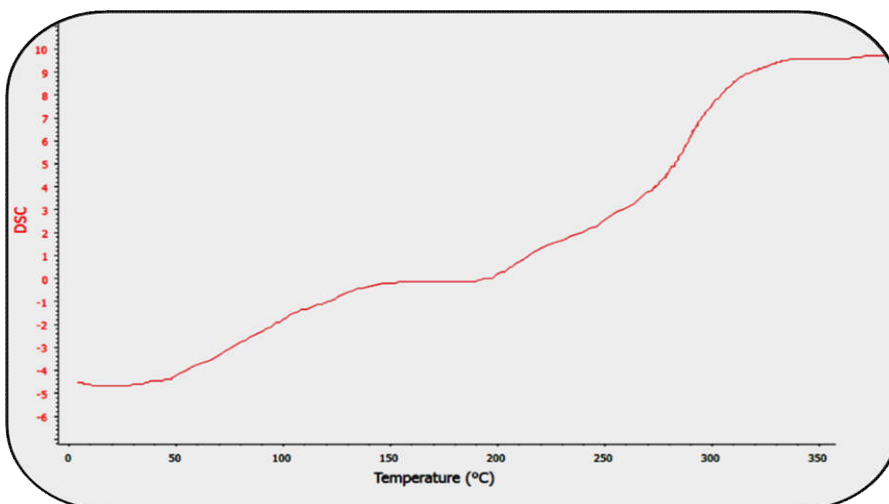


Fig (14) : DSC of Monomer [3]

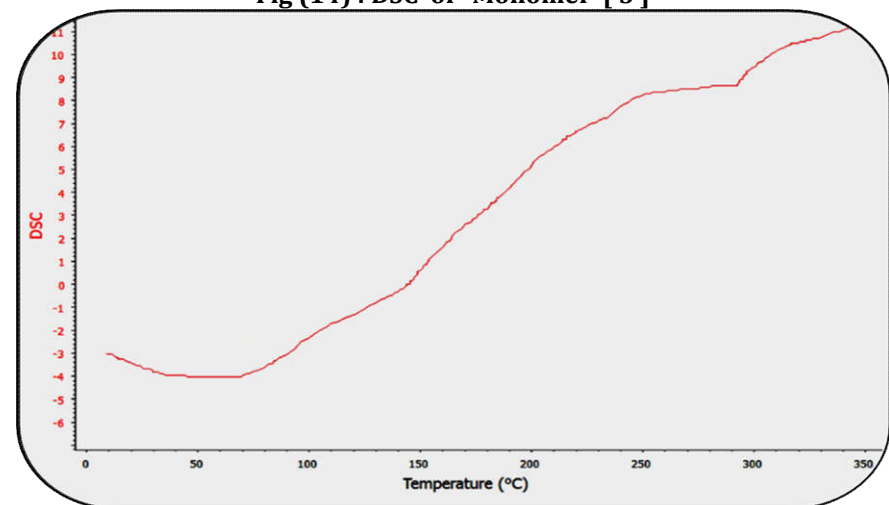


Fig (15) : DSC of Monomer [6]

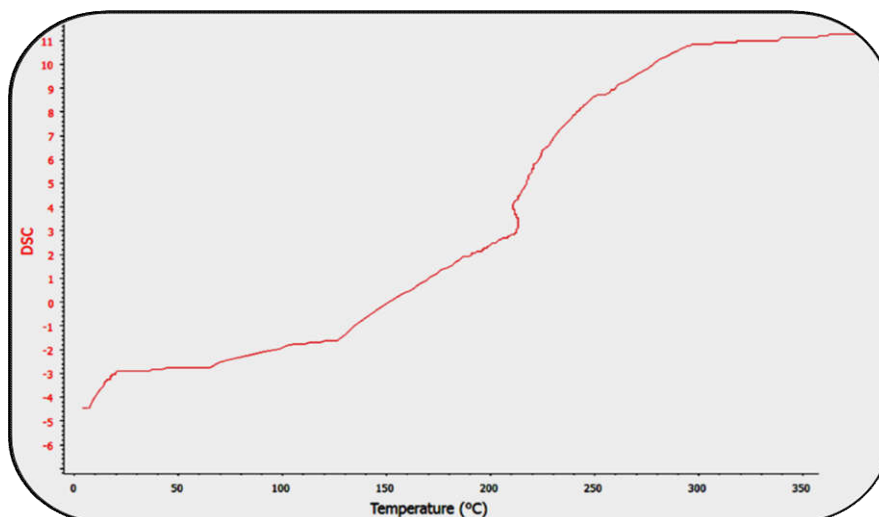


Fig (16) : DSC of Monomer [7]

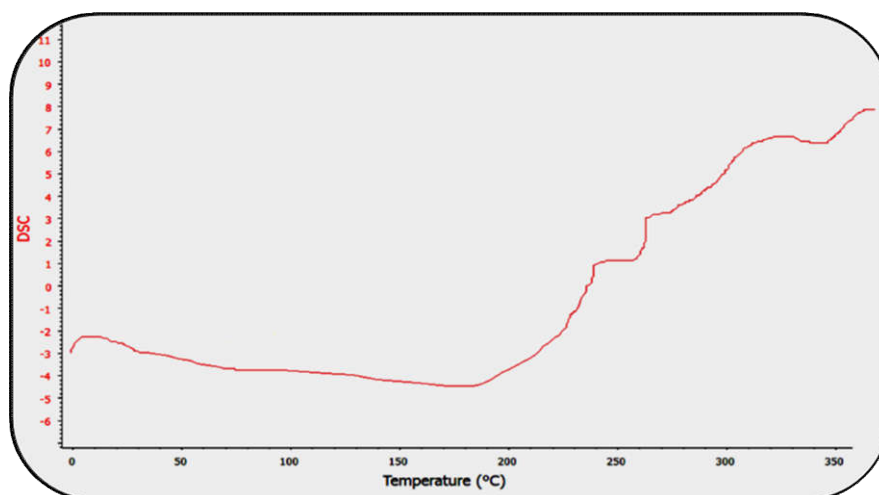


Fig (17) : DSC of Monomer [10]

Other Physical Properties :

Some physical and chemical properties like R_f of TLC- Technique for following the reactions solvent which are used in TLC – Plate , and products from reactions % , all data are summarized in Table (4):

Table(4): Some Physical and Chemical Properties for Monomers [M1–M10]

Monomers	Products %	R_f	Solvents of (TLC)
[M1]	80	0.82	Ethanol : Benzene
[M2]	78	0.64	Ethanol : Benzene
[M3]	84	0.60	Ethanol : Benzene
[M4]	82	0.80	Ethanol : Benzene
[M5]	74	0.78	Ethanol : Benzene
[M6]	78	0.68	Ethanol : Benzene
[M7]	80	0.80	Ethanol : Benzene
[M8]	72	0.68	Ethanol : Benzene
[M9]	70	0.70	Ethanol : Benzene
[M10]	76	0.65	Ethanol : Benzene

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CITATION OF THIS ARTICLE

Nagham M A , Hayfaa J S ,Huda S H, Noor D J, Fatima A W, Nemah S M.Preparation and Investigation of Various Monomers and Studying of The Behavior (Thermal ,Physical , Spectral , Chromatography). Bull. Env. Pharmacol. Life Sci., Vol 5 [9] August 2016: 37-48