

SYNTHESIS, CHARACTERIZATION AND POLYMERIZATION OF N-SUBSTITUTED MALEIMIDYL ACRYLATES

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Abstract

Four N-(hydroxy phenyl) maleamic acids were prepared in high yields (90-95)% via reaction of maleic anhydride with ortho, meta and para amino phenols.

Dehydration of the prepared maleamic acids via treatment with acetic anhydride and pyridine produced the corresponding N-(hydroxy phenyl) maleimides in good yields (70-80)%.

Esterification of the prepared imides with acryloyl chloride in the presence of triethyl amine gave the corresponding maleimidyl acrylates which in turn were polymerized free radically to produce new polyacrylates.

The prepared compounds were characterized by FTIR, U.V and ¹HNMR spectroscopy while thermal stability of the prepared polymers were investigated by (TG) and (DTA) thermal analysis.

Introduction

Polyacrylates in general are colorless transparent polymers which have in addition to their tough rubber like extensibility, excellent chemical resistance and especially outstanding aging properties^(1,2).

Because of their low softening temperatures the polyacrylates are particularly suited to film-forming applications.

Also polyacrylates are used in many other applications including fiber optics, molding, adhesives, artificial leather and some of them find versatile applications in pharmacological field as polymer supports or drug binders^(3,4).

In the search for polymers having better hardness, less cold flow and higher softening points, the target of the present work is directed toward synthesis of new thermally stable polyacrylates via synthesis of new acrylic monomers having maleimidyl groups in their side chain.

Polymerization of these monomers produces new polyacrylates containing maleimidyl groups in their structural units, which exhibit the polymers good thermal stability since insertion of N-substituted maleimide units into some polymer chains is greatly improved their heat resistance and chemical stability⁽⁵⁻⁶⁾.

Experimental

1. Instruments

Melting points were determined on Gallen Kamp capillary melting point apparatus and were uncorrected.

FTIR spectra were recorded on a shimadzu FTIR-8400 Fourier Transform Infrared spectrophotometer.

UV spectra were recorded on a shimadzu UV-VIS recorder spectrophotometer U.V-160.

¹HNMR spectra were run on a Bruker 300 MHZ spectrometer at room temperature using TMS as internal reference and CDCl₃ as solvent.

C.H.N analysis were determined on Perkin-Elmer 240 Elemental Analyzer.

Softening points were determined on thermal Micro scope Reichert Thermovar with Reichert-Jung Temperature controller.

Intrinsic viscosities were determined with Automatic viscometer Tafesa Ubbelohde viscometer.

Thermal analysis (TG and DTA) diagrams were recorded on a NETZSCH Geratebau GmbH seib model STA409.

2. Chemicals

Maleic anhydride, Amino phenols and Acryloyl chloride.

All chemicals employed were of analytical reagent grade and were used without further purification.

1. Preparation of N-(hydroxy phenyl) maleamic acids [1-4]

Maleic anhydride was allowed to react with ortho, meta and p-amino phenols in dry acetone according to literatures^(7,8).

The prepared maleamic acids were purified by dissolving in 5% solution of NaHCO₃ followed by precipitation from dilute hydrochloric acid.

Table (1) lists melting points, percent yields, U.V absorptions and major FTIR absorptions of the prepared amic acids.

2. Preparation of N(hydroxy phenyl) Maleimides [5-8]

The titled imides were prepared by using acetic anhydride as dehydrating agent in the presence of pyridine according to literature⁽⁹⁾.

(0.003 mol) of N-(hydroxy phenyl) maleamic acid was dissolved in (10 ml) of N,N-dimethyl formamide in a suitable round bottomed flask.

To the resulted solution (0.042 mol, 4 ml) of acetic anhydride and (0.024 mol, 2ml) of pyridine were added with stirring at room temperature then stirring was continued for 24 hrs.

Excess water was added to the resulted mixture with stirring then the produced precipitate was filtered and dried.

Purification of the prepared imides was performed by recrystallization from benzene.

Melting points, percent yields, U.V and FTIR spectral data of the prepared imides are listed in Table (2).

3. Preparation of N-phenyl maleimidyl Acrylates [9-12]

The titled compounds were prepared according to literature procedure^(10,11) with minor modifications:

In a suitable round bottomed flask fitted with dropping funnel (0.01mol) of N-(hydroxy phenyl) maleimide was dissolved in (40ml) of dry acetone with stirring.

To the resulted solution (0.01mol) of triethyl amine was added through the dropping funnel followed by dropwise addition of (0.01mol) of acryloyl chloride with stirring and cooling then stirring was continued for another 6hrs before filtration.

The filtrate was evaporated under reduced pressure and the residue was extracted with water and chloroform for three times, then the

organic layer was dried and the solvent was evaporated.

The obtained thick oil was purified either by recrystallization from petroleum ether (60-80)C⁰ or passing its chloroform solution through a florisil column.

Table (3) lists percent yields, melting points, U.V and FTIR spectral data of the prepared acrylates.

4. Polymerization of N-phenyl maleimidyl Acrylates [13-16]

The titled monomers were polymerized by following literature procedures^(10,12,13).

In a polymerization bottle (1 g) of the titled monomer was dissolved in (10 ml) of freshly distilled THF then (0.05 g) of AIBN was added and the polymerization bottle was purged with nitrogen gas and stoppered tightly before heating at (70 C⁰) for 3hrs.

The resulted solution was poured into (20 ml) of methanol then the precipitated white polymer was filtered and dried.

The resulted polymer was purified by dissolving in THF then precipitation with methanol.

Table (4) lists softening points, percent conversions, intrinsic viscosities, U.V and FTIR spectral data of the prepared polymers.

Results and Discussion

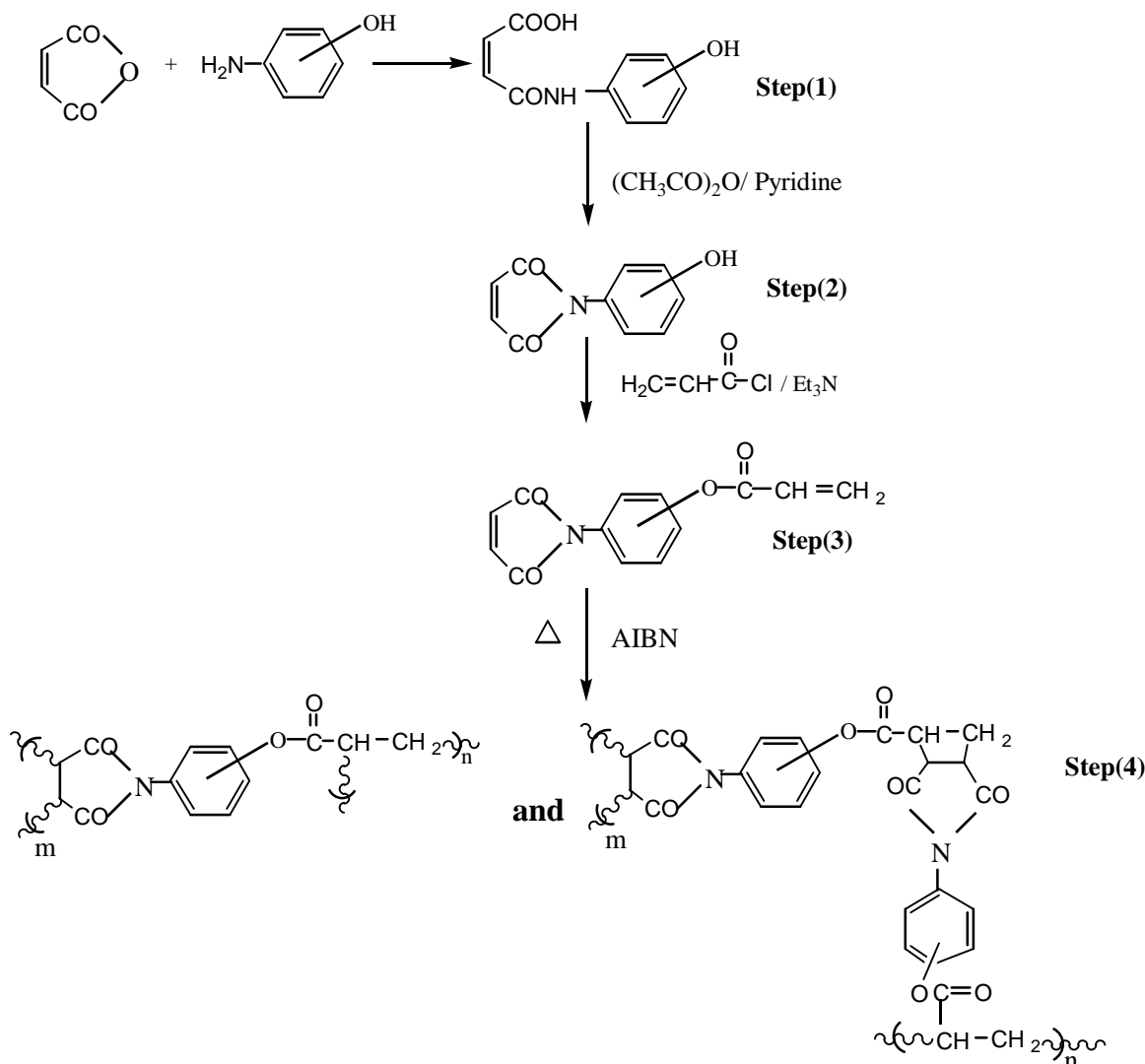
The aim of the present investigation is to synthesize new acrylic polymers having good thermal stability.

To perform this target many steps have to be done, the first one includes preparation of four N-(hydroxy phenyl) maleamic acids via reaction of maleic anhydride with different amino phenols.

Dehydration of the prepared amic acids to the corresponding imides was performed in the second step by using acetic anhydride and pyridine as dehydrating agent.

In the third step the prepared imides were esterified to the corresponding acrylate esters via treatment with acryloyl chloride in the presence of triethyl amine.

Finally the fourth step of this work involved introducing of the prepared acrylate esters in chain growth polymerization using THF as solvent and AIBN as initiator to produce four new poly (N-substituted maleimidyl acrylates).



Scheme (1) : Illustrates all synthesis steps in this work.

Physical properties and spectral data of all the prepared compounds are listed in Tables (1), (2), (3), (4) and (5) respectively while C.H.N analysis for some of them are listed in Table (6).

Structures of the prepared compounds were confirmed by depending on FTIR, U.V, ^1H NMR spectral data and C.H.N analysis.

FTIR spectra of the prepared maleimides revealed a clear strong absorption band located in the region $(3200-3400)\text{cm}^{-1}$ due to ν (O-H) phenolic Table (2) while FTIR spectra of the prepared acrylates showed disappearance of this band indicating ester formation and at the same time revealed two characteristic clear absorption bands at $(1750-1765)\text{cm}^{-1}$ and $(1180-1199)\text{cm}^{-1}$ due to

ν (C=O) ester and ν (C-O) ester respectively⁽¹⁴⁾ Table (3).

U.V spectra of the prepared amic acids, imides, acrylates and polyacrylates revealed strong absorptions at wave lengths listed in Tables (1), (2), (3) and (4) these absorptions in general were due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions⁽¹⁴⁾ of either enones or π electrons of benzene ring which was in conjugation with neighboring groups .

The presence of acryloyloxy group in compounds (10, 11) shifted U.V absorptions to longer wave lengths since it caused longer conjugation.

Also attachment of chromophoric nitro group to phenyl ring in the prepared imides and polymers shifted absorptions to longer wave lengths.

On the other hand ^1H NMR spectra of the prepared maleimides showed signals at ($\delta=5.11-6.02$ ppm belong to phenolic OH proton while ^1H NMR spectra of the prepared acrylates showed disappearance of this signal and instead appearance of three singlet signals for (3H acryloyloxy protons) which confirmed the success of esterification reaction.

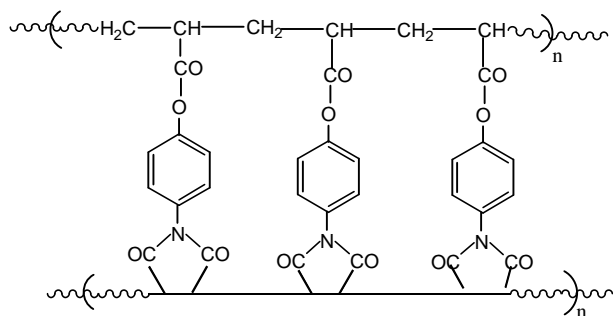
Other details of HNMR spectra for some of the prepared compounds are listed in Table (5).

Also the prepared esters gave positive results in characteristic test for ester (Hydroxamic acid test) by using hydroxyl amine and ferric chloride reagents.

Our strategy used in this work for preparation of new polyacrylates having desirable properties based on preparation of new acrylic monomers having maleimidyl groups in their side chain.

These new monomers have two active sites available for chain growth polymerization represented by vinylic bonds in maleimide ring and acryloyloxy chain respectively, so introducing of these monomers in chain growth polymerization produced new polyacrylates containing maleimidyl groups in their repeating units which in turn exhibit the new polymers good thermal stability since insertion of N-substituted maleimide units in some polymer chains greatly improved their heat resistance and chemical stability^(15,16).

It is necessary to mention here that polymerization of the two mentioned vinylic bonds gave good opportunity for polymer chains to grow from the two positions and this in turn lead to cross-linked polymers as described by the following suggested structure.



Both cross linking and presence of maleimidyl groups in the prepared polymers played a vital role in affecting physical properties of the new polymers.

They exhibit the polymers good resistance for softening and solubility in many organic solvents in addition to good thermal stability.

Thus all the prepared polymers were insoluble in many organic solvent including acetone, ethanol, p-xylene, carbontetrachloride, chloroform and petroleum ether (40-60) $^{\circ}\text{C}$ but they showed good solubility only in DMSO except polymer (15) which was insoluble in it indicating high degree of cross linking.

Intrinsic viscosities of the prepared polymers were in the range (0.27-0.83) dL/g and their measurements were performed at (25 $^{\circ}\text{C}$) using DMSO as solvent.

FTIR spectra of the prepared polymers showed disappearance of

ν (C=C) absorption bands due to saturation during polymerization.

Thermal stability of the prepared polyacrylates was investigated by thermo gravimetric analysis (TGA) and (DTA) analysis.

TGA data showed that the weight of polymer (13) was fell slightly at the temperature range of (127-423) $^{\circ}\text{C}$, while weights of polymers (14) and (15) were fell slightly at temperature ranges (157-513.5) $^{\circ}\text{C}$ and (171-374) $^{\circ}\text{C}$ respectively.

Also thermal analysis data showed that the prepared polymers have good thermal stability thus temperatures of (10 %) weight loss of polymers (13), (14) and (15) were (127) $^{\circ}\text{C}$, (157) $^{\circ}\text{C}$, and (171) $^{\circ}\text{C}$ while the major weight loss of these polymers were occurred at (577) $^{\circ}\text{C}$, (638) $^{\circ}\text{C}$ and (550) $^{\circ}\text{C}$ respectively.

Table (7) lists Thermal gravimetric data of the prepared polymers.

FTIR spectra, U.V spectra and ^1H NMR spectra for some of the prepared compounds are shown in Figs. (1-13) and (TG)(DTA) diagrams of the prepared polymers are shown in Figs. (14-16).

Conclusion

The present work supply us with new vinylic monomers containing two important moieties maleimide ring and acrylate group respectively.

Polymerization of these monomers produced new cross-linked polymers

Presence of maleimide groups and cross linking in polymeric chains exhibit the prepared polymers good resistance for softening and solubility in addition to good thermal stability which inturn make these polymers suitable for certain applications.

Table (1)
Melting points, percent yields and spectral data of Maleamic Acids.

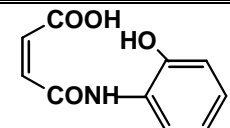
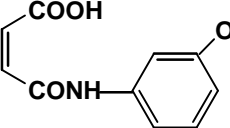
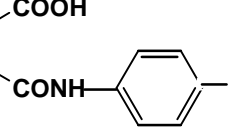
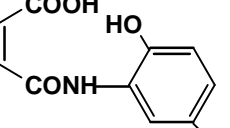
Comp. No.	Compound structure	Melting Point C ⁰	Yield %	U.V λ_{max} nm	Major IR absorptions cm ⁻¹			
					ν O-H	ν N-H Amide	ν C=O carboxylic	ν C=O Amide
1		174-176	92	206, 306	3161	3392	1699	1620
2		178-180	94	229, 303	3218	3336	1701	1616
3		193-195	95	232, 334	3178	3301	1697	1620
4		185-187	90	234, 307	3150	3450	1700	1600

Table (2)
Melting points, percent yields and spectral data of Maleimides.

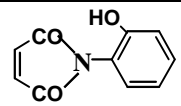
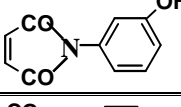
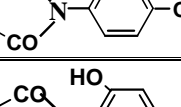
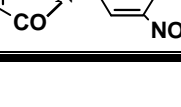
Comp. No.	Compound structure	Melting Point C ⁰	Yield %	U.V λ_{max} nm	Major IR absorptions cm ⁻¹			
					ν O-H phenolic	ν C=O Imide	ν C=C	ν C-N
5		222-225	80	306, 330	3300	1702	1602	1350
6		168-170	75	210	3350	1708	1604	1390
7		209-210	70	223	3400	1702	1602	1380
8		158-160	78	211, 324	3350	1714	1602	1350

Table (3)
Melting points, percent yields and spectral data of Maleimidyl Acrylates.

Comp. No.	Compound structure	Melting Point C ⁰	Yield %	U.V λ_{max} nm	Major IR absorptions cm ⁻¹			
					ν C=O Esters	ν C=O Imide	ν C-O Esters	ν C=C
9		oil	60	213, 281	1765	1722	1194	1602
10		oil	65	212, 300 307	1750	1740	1180	1620
11		175-177	63	314	1750	1712	1164	1643
12		oil	60	211, 259 299	1765	1722	1182	1600

Table (4)
Physical properties and spectral data of poly(maleimidyl acrylates).

Comp. No.	Compound structure	Softening Point C ⁰	Conv. %	[η] dL/g	Major IR absorptions cm ⁻¹			
					U.V λ_{max} nm	ν C=O Ester	ν C=O Imide	ν C-O Ester
13		210-230	60	0.52	260, 281	1740	1700	1182
14		190-200	75	0.72	276	1765	1720	1197
15		185-200	77	*	*	1755	1714	1199
16		210-220	55	0.83	266, 310 416	1780	1725	1185

*Insoluble in all solvents.

Table (5)
HNMR chemical shifts for some of the prepared compounds.

Comp. No.	Compound structure	Chemical shift ppm
6		δ 5.46(1H,OH phenolic), δ 8.14(2H,), δ 6.63,6.71,6.98,7.15(4H,Aromatic)
7		δ 5.11(1H,OH phenolic), δ 8.14(2H,), δ 6.8,7.56(4H,Aromatic)
8		δ 6.02(1H,OH phenolic), δ 8.14(2H,), δ 6.95,7.95,8.08(3H,Aromatic)
9		δ 8.14,(2H,), 5.6(1H,), δ 6.05,6.37(2H,), δ 7.05,7.13,7.34,7.56(4H,Aromatic)
11		δ 8.14(2H,), δ 5.6(1H,), δ 6.15,6.4(2H,), δ 7.2,7.5 (4H Aromatic)

Table(6)
C.H.N Analysis of the prepared compounds.

Comp. No.	Calculated			Found		
	C%	H%	N%	C%	H%	N%
3	57.97	4.35	6.76	57.60	4.40	6.30
5	63.40	3.70	7.41	63.00	4.10	7.10
6	63.40	3.70	7.41	63.20	3.70	7.70
8	51.28	2.56	11.97	50.80	3.30	11.20
9	64.2	3.70	5.70	63.60	3.60	5.20
10	64.2	3.70	5.70	63.60	3.60	5.61

Table(7)
Thermal Gravimetric Data of the prepared polymers.

Comp. No.	First Stage		Temperature C ⁰	Second Stage		Temperature C ⁰	Third Stage		Temperature Of 10 % Weight loss	
	Weight%			Weight%			Weight%			
	Residue	loss	Residue	loss	Residue	loss	Residue	loss		
13	80.00	20.00	180.0	37.14	62.86	423.0	28.57	71.47	577.0	127.0
14	66.00	34.00	263.5	30.67	69.33	513.5	25.33	74.67	638.0	157.0
15	67.37	32.63	250.0	47.37	52.63	374.0	52.11	47.89	550.0	171.0

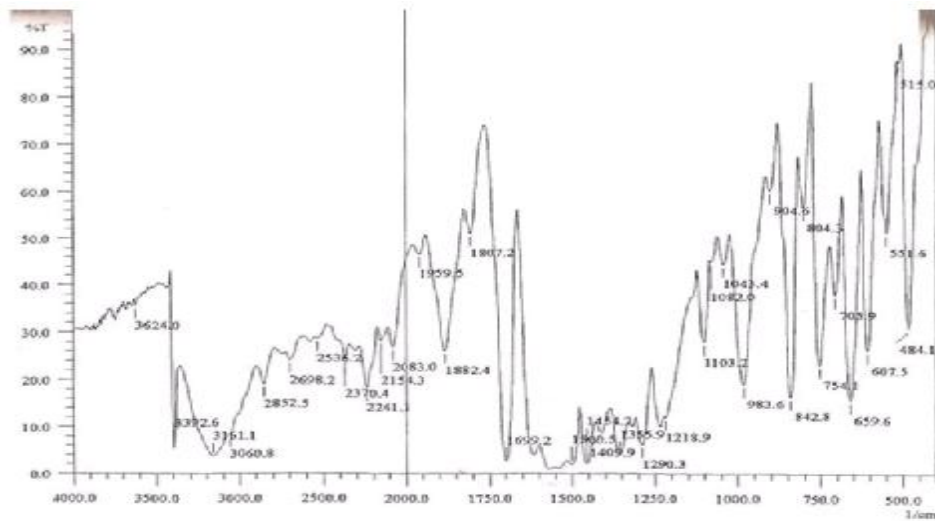


Fig.(1) : FTIR spectrum of compound(1).

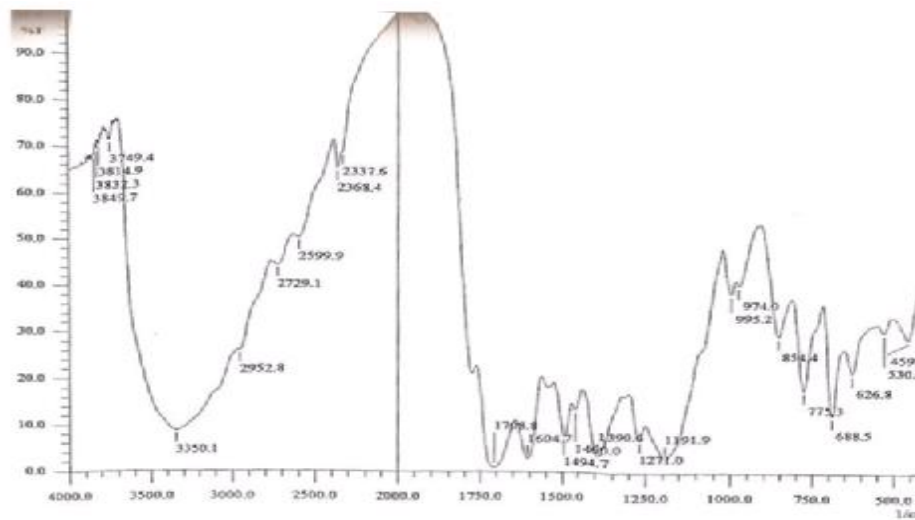


Fig.(2) : FTIR spectrum of compound(6).

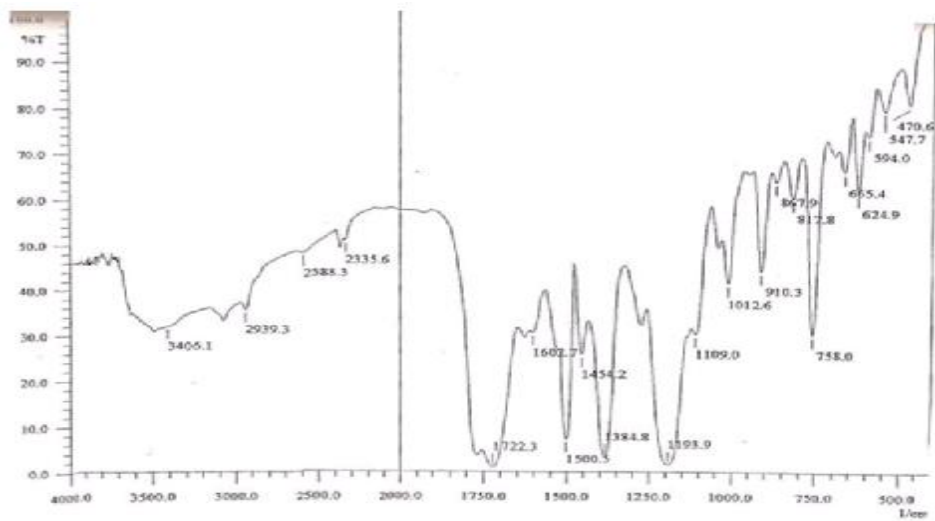


Fig.(3) : FTIR spectrum of compound(9).

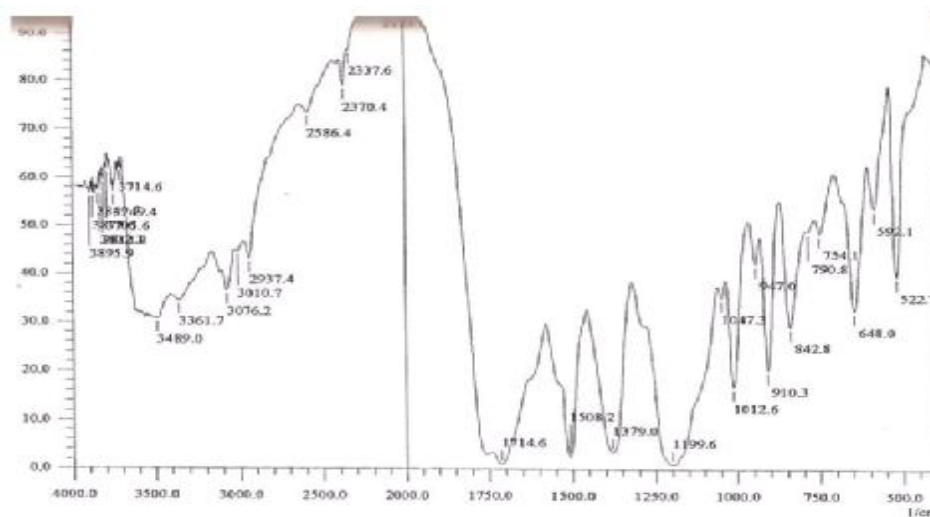


Fig.(4) : FTIR spectrum of compound(15).

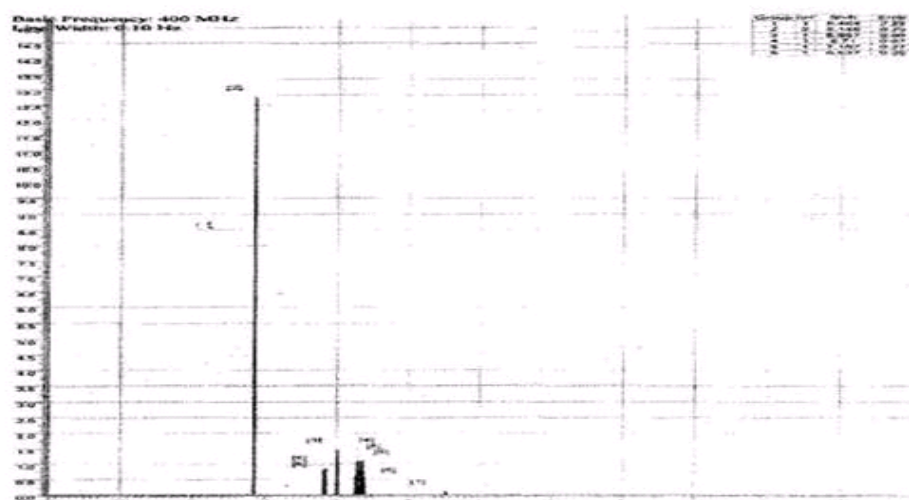


Fig. (5) : ¹HNMR spectrum of the prepared compound (6).

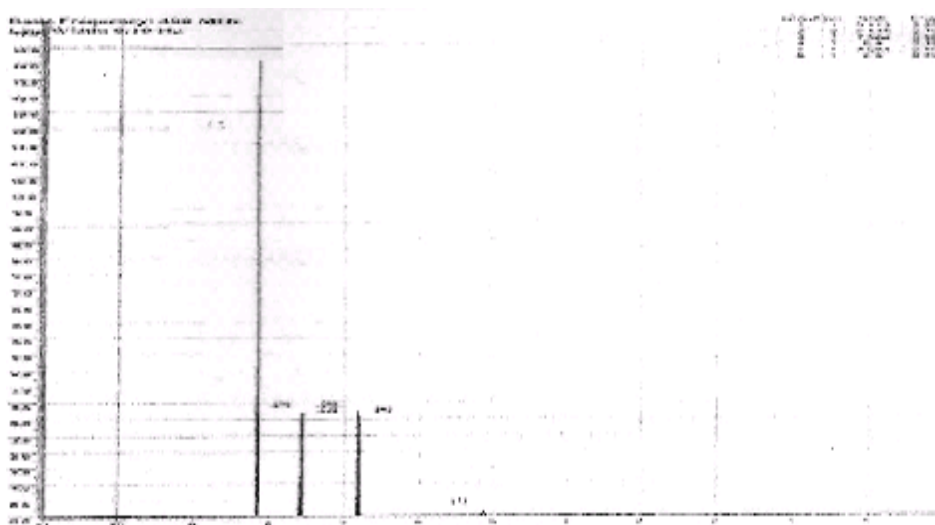


Fig. (6) : ¹HNMR spectrum of the prepared compound (7).

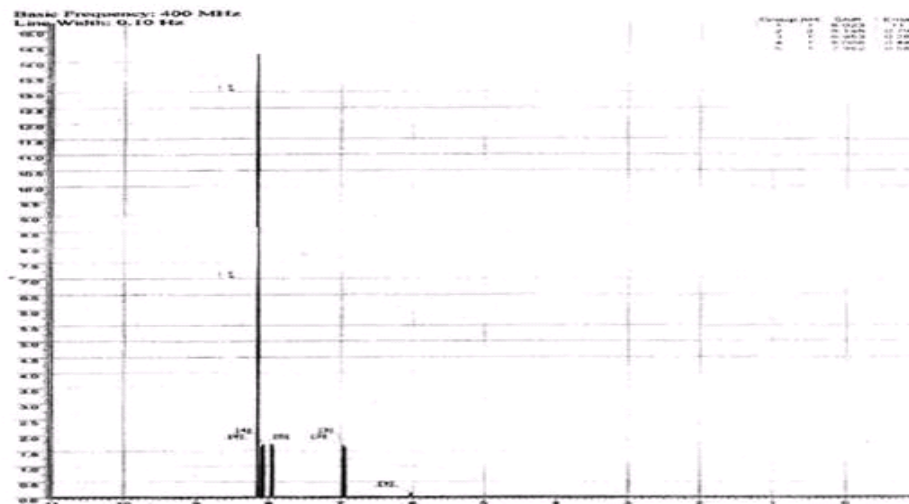


Fig. (7): ^1H NMR spectrum of the prepared compound (8).

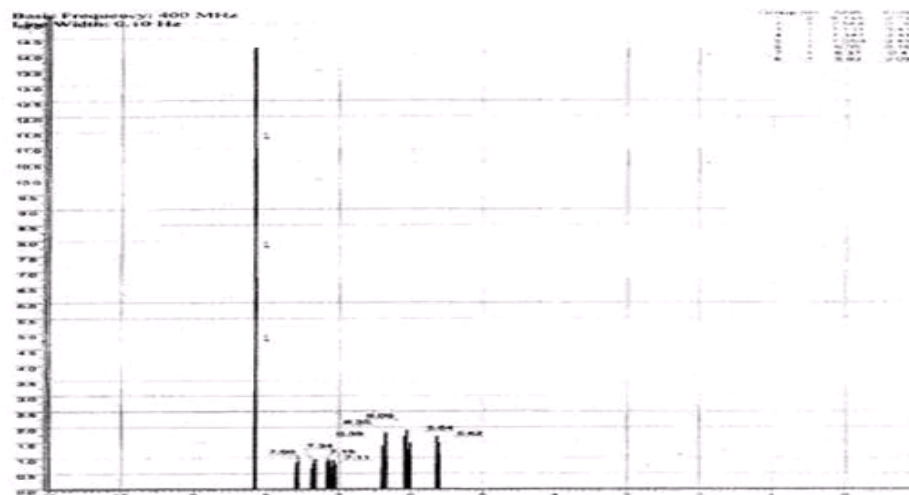


Fig. (8): ^1H NMR spectrum of the prepared compound (9).

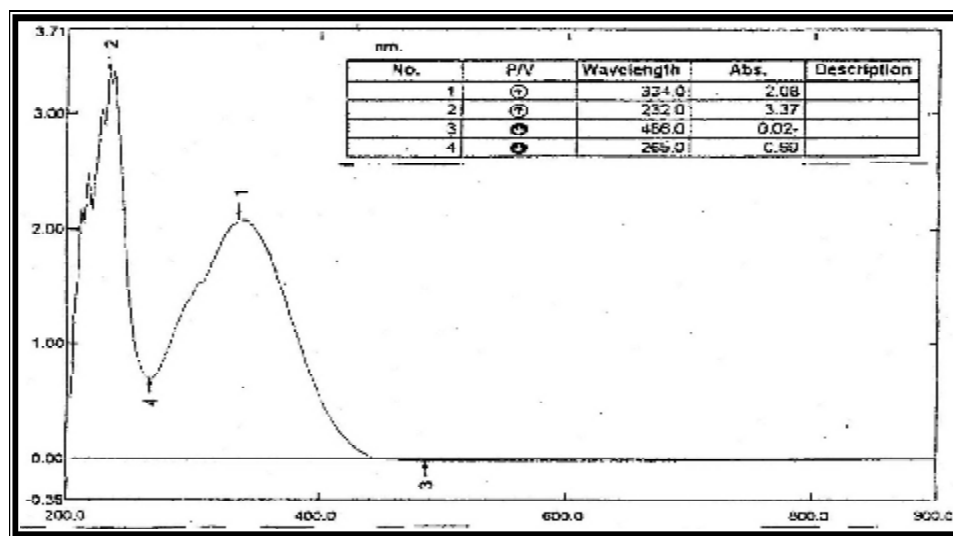


Fig.(9):U.V spectrum of the prepared compound(3).

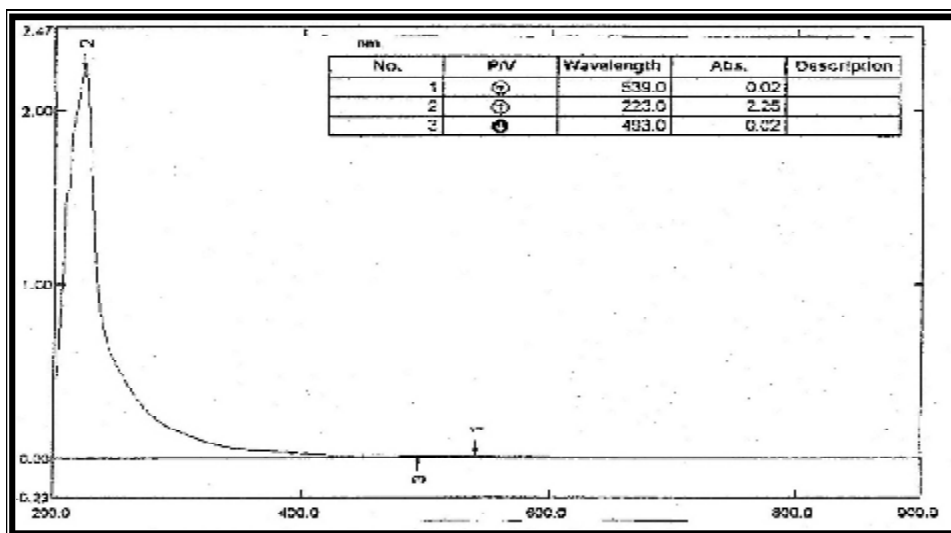


Fig.(10) : U.V spectrum of the prepared compound(7).

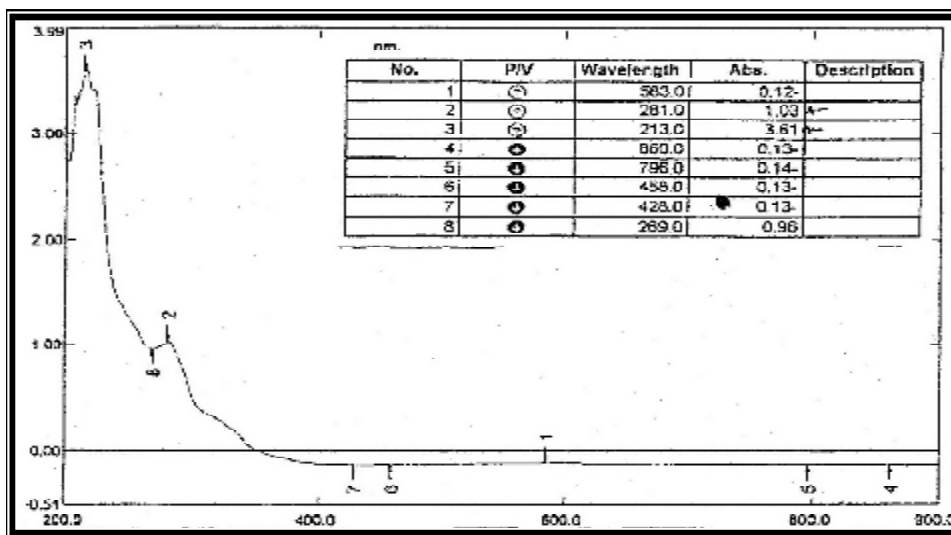


Fig. (11) : U.V spectrum of the prepared compound (9).

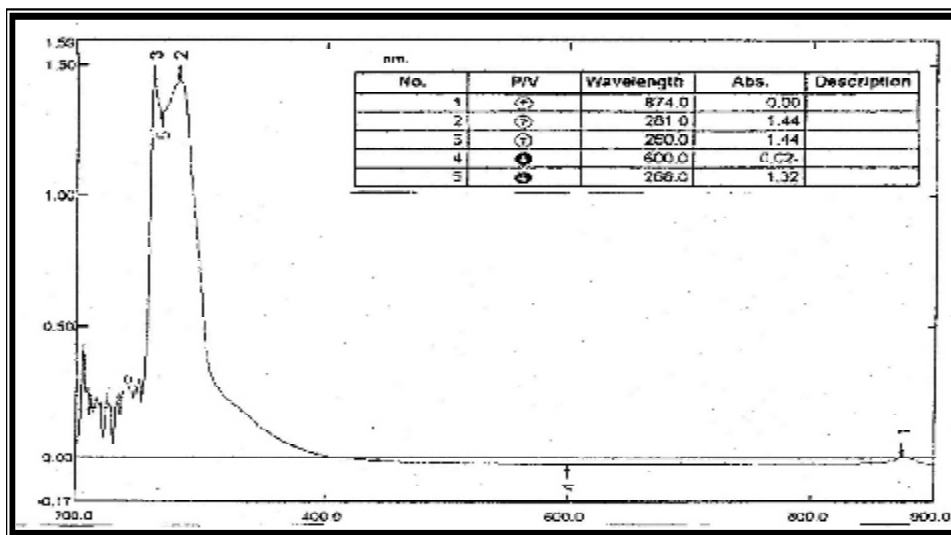


Fig. (12) :U.V spectrum of the prepared compound (13).

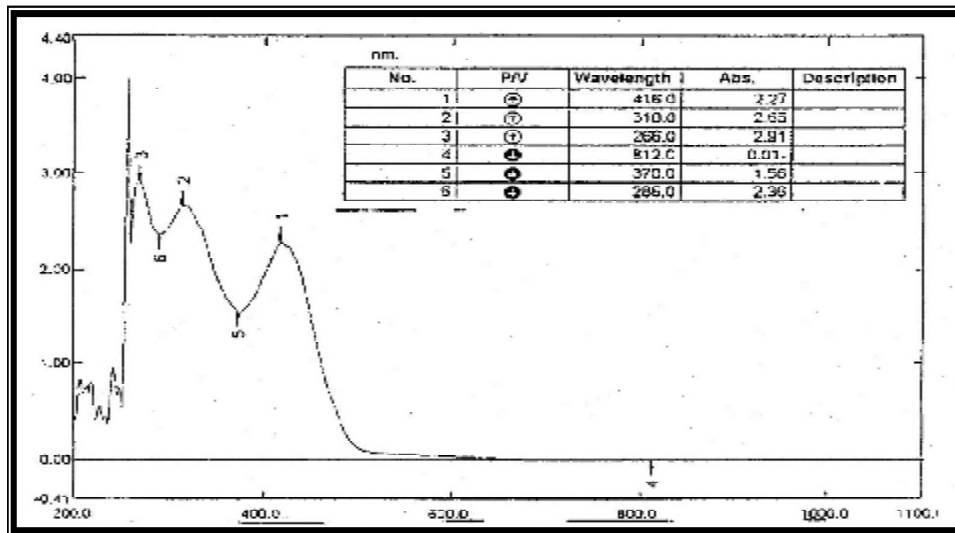


Fig. (13): U.V spectrum of the prepared compound (16).

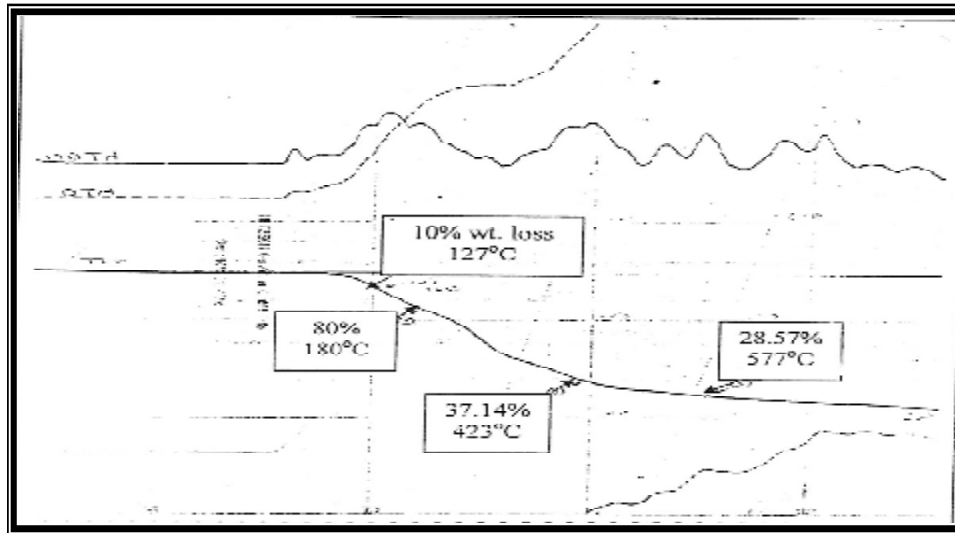


Fig.(14):TG and DTA diagram of the prepared compound (13).

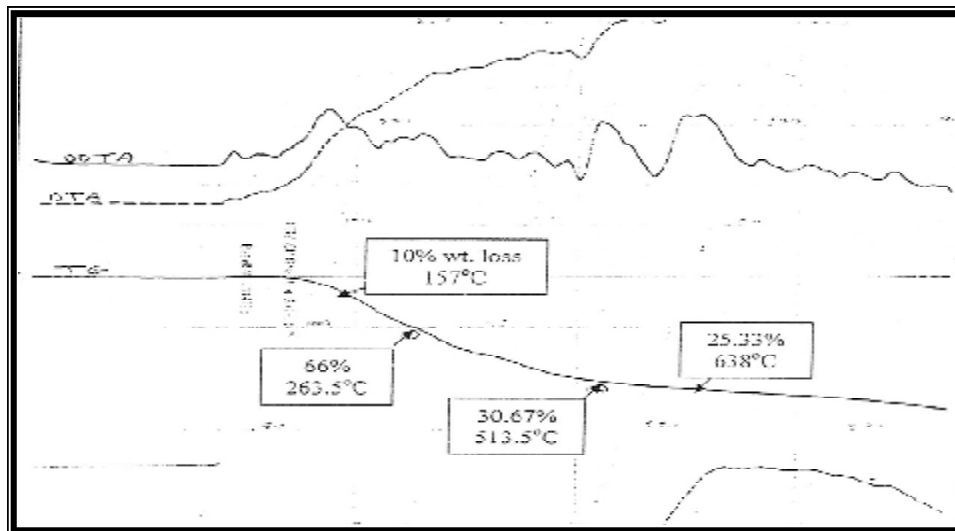


Fig. (15):TG and DTA diagram of the prepared compound (14).

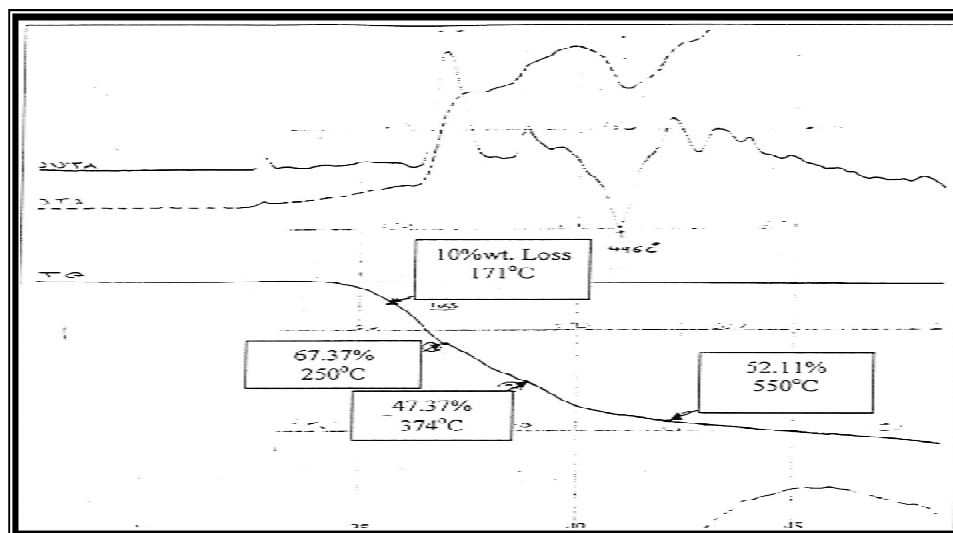


Fig. (16) : TG and DTA diagram of the prepared compound (15).

References

- [1] N. A. Ghanem, "Polymerization of methylacrylate in the presence of Graphite", *J.Poly.Sci.*, vol.14,1976,p.2327.
- [2] J.M.Shi and Y.Z.Bao, "Preparation of poly methyl methacrylate by in-situ emulsion polymerization ", *J.Zhejiang Univ.Sci.*, vol.5,2004, p.709.
- [3] F.M.Peng, *Encyclopedia of polymer science and Engineering*, Wiley: New York, 1995.
- [4] C.Liu, X.Xu and J.Huang," spontaneous copolymerization of N -Butyl maleimide and Ethyl α -phenyl acrylate",*J. Apply. Poly. Sci.*,vol. 94, 2004, p.355.
- [5] M.K.Ghosh and K.L.Mittal, "Polyimides fundamentals and applications", Eds.Marcel Dekker, New York, 1996.
- [6] S.H Hsiao,C.P.Yang and S.H.Chen,"Synthesis and properties of ortho- linked aromatic polyimides", *J.Poly.Sci.*, vol.38, 2000, p.1551.
- [7] M.P.Cava, A.A.Deana, K.Muth and M.J.Mitchell, *Org.Synth.*, vol.41,1961, p.93.
- [8] I.Abdulameer, "Synthesis of phenolic resins with pendant phthalisoimides", *J.Poly.Sci.*, vol.38,2000,p.3244.
- [9] K.H.Chae,J.S.Park, C.H.Cho and J.Y.Chang,"Synthesis and properties of polyimides containing fluoro groups "*Korea poly. J.*,vol.6(2), 1998,P.174.
- [10] T.Mohamed "Synthesis,Polymerization and curing of N-substituted citraconimidyl acrylates", *J.Poly.Sci.*,vol.37, 1999, p.427.
- [11] A.M.Hussein,"Synthesis of novel N-phenyl phthalimidyl esters and their applications as plasticizers for PVC", *J. Um-Salama* ,vol.3(4),2006, p.677.
- [12] K.Matyjaszewski, *Controlled Radical polymerization*, American chemical society : Washington,D.C.,1998.
- [13] K.Matygaszewski,Ed.*Controlled /living radical polymerization*, Progress in ATRP,American chemical society, Washington,D.C.,2000.
- [14] R.M.Silverstein and G.C.Bassler," spectrometric Identification of organic compounds", Fourth Edition, Joun Wiley and sons, Inc., New York, (1980).
- [15] W.T.Leu and S.H.Hsiao, "Synthesis and properties of novel aromatic poly (ester-imide) bearing benzoyloxy Naphthalene units", *Eur.. Poly.J.*, vol.42,2006,p.328.
- [16] S.H. Hsiao, C.P.Yang and C.W.Chen, "Synthesis and properties of novel poly (amide-imide) containing pendant diphenyl amino groups", *Eur. Poly. J.*, vol.41,2005,p.511.

الخلاصة

تضمن البحث تحضير عدد من حوامض N-(هيدروكسي فنيل) مالي اميك بمنتوج عالي قدره (90-95) % من تفاعل مركبات اورثو ، ميتا وبارا امينو فينول مع انهيدريد الماليك .

تم سحب الماء والغلق الحلقي لحوامض المالي اميك المحضرة من خلال معاملتها مع انهيدريد الخليك بوجود البردين وبذلك تم تحويلها الى مركبات N-(هيدروكسي فنيل) مالي ايميدات المقابلة و بمنتوج جيد قدره (70-80) % .

بعدها تم تحويل الايميدات المحضرة الى استرات N-فنيل مالي ايميديل اكريلات وذلك بمعاملتها مع كلوريد الاكريلويل بوجود ثلاثي اثيل امين .

اما في الخطوة الاخيرة من البحث فقد تمت بلمرة الاسترات المحضرة وفق الجذور الحرة مما أسفر عن إنتاج أربعة بوليمرات (بولي اكريلات) جديدة .

شخصت المركبات المحضرة في هذا البحث باستخدام مطيافية الأشعة تحت الحمراء و الاشعة فوق البنفسجية واطياف الرنين النووي المغناطيسي كما ايدت نتائج التحليل الحرارية (TG) و (DTA)

للبوليمرات المحضرة بانها ذات ثبات حراري جيد .