Synthesis of Some Polyimides by Different Methods

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Abstract

In this work the polyimides were prepared as thermally stable polymers by different ways. In order to perform the above mentioned project the following outlines are classified:

1. A- Preparation of a number of new N-substituted maleamic acids.
    B- Dehydration of above maleamic acids to their corresponding N-substituted maleimides.
    C- Polymerization of all the new maleimide monomers.
2. A- Preparation of N-substituted maleimides from reaction of maleimide with alkyl halides.
    B- Polymerization of N-alkyl substituted maleimide monomers.
3. A- Polymerization of maleimide compound free radically by using AIBN as initiator.
    B- Substitution of polyimide by using different alkyl halides.

All the prepared monomers and polymers were characterized by IR, UV spectra, elemental analysis, thermal analysis and chemical reaction. Physical properties and the viscosities for all polyimides were determined by using DMF as a solvent.

We concluded from all the results of different ways that the 3rd method gave the best result than the 2nd and the 1st methods, it gave higher molecular weight and higher softening point.

Introduction

Imides are organic compounds containing two carbonyl groups and one nitrogen atom. These compounds can be written by the general formula and could be as an open chain molecule or cyclic forms (1,2).

In 1901, Kuhara and Fukui (3) obtained n-phenyl phthalimide from reaction of acetyl chloride with n-phenyl phthalamic acid (2).

In 1959, Bender and Neven (3) isomerized the isoimides to maleimides by using acetate ion through nucleophilic attack by acetate ion.

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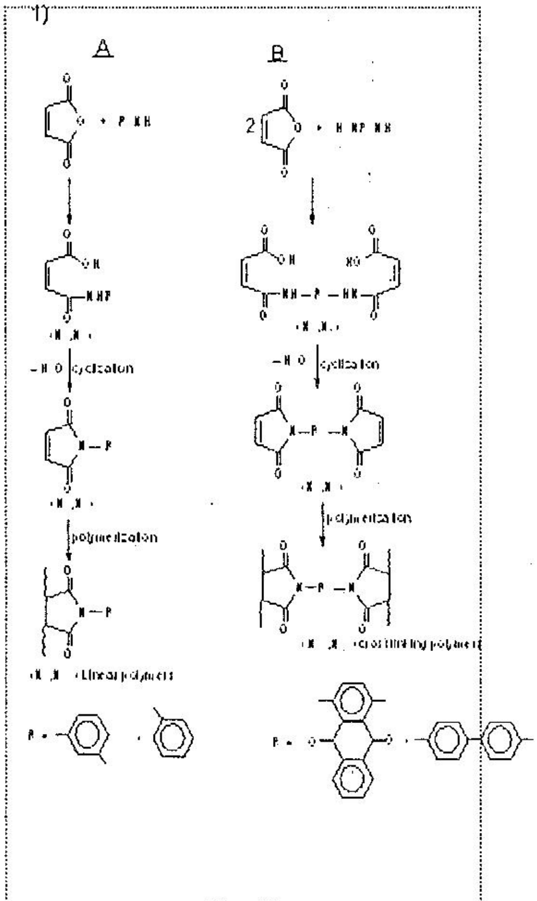
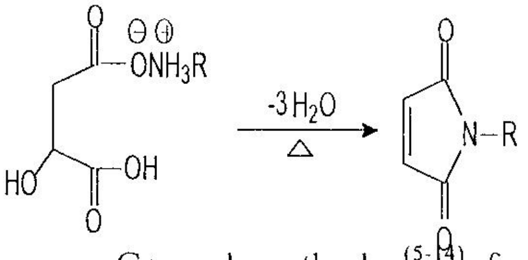


Scheme[1]

N-Substituted maleimides (4) were prepared from ammonium salt of malic acid at high temperature.



General methods (5-14) for preparation of N-substituted cyclic imide include: -

A. Dehydration of Amic Acids Using Proper Dehydrating Agent such as:

1. Phosphorus pentoxide (7).
2. Phosphorus trichloride (7).
3. Acetic anhydride – sodium acetate (8,9).
4. Acetyl chloride (3,10,11).
5. Acetyl chloride with triethylamine (12).
6. Thionyl chloride (13,14).

B. Thermal Dehydration:

Thermal dehydration of N-substituted amic acids (15) produce low yields of corresponding imides.

C. Via Diels Alder Adducts (16):

Frill prepared maleimides from heating maleic anhydride with cyclopentadiene to form the Diels Alder adduct which converted to the imide and heated with excess maleic anhydride at 400 °C. Hedaya and coworkers (17) used a similar method in preparing bis maleimide.

D. By Gabriel Type Synthesis:

N-Cinnamyl phthalimide (18) was prepared in high yield.

Polyimides prepared two types of polymers:

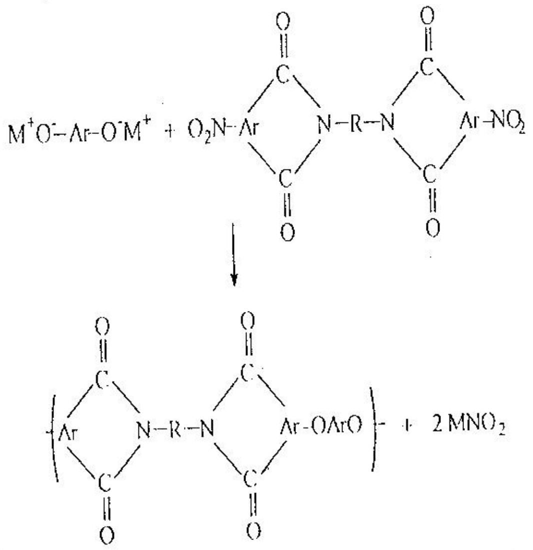
1. Chain growth-addition polymerization (19,20).
2. Chain growth-condensation polymerization (21).

Pyriadi and Fraih (22) prepared N-phenyl, N-p-tolyl, N-p-methoxy phenyl, N-o-ethyl phenyl and N-p-chloro phenyl itaconimides and polymerized free radically to yield low molecular weight polymers (23).

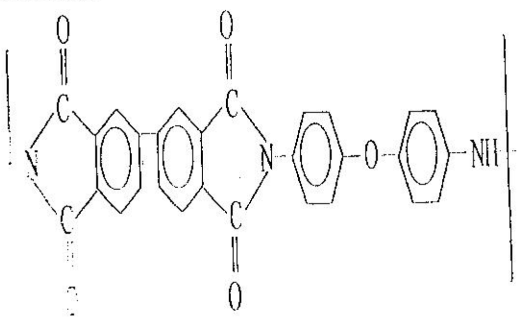
In 1989, Pyriadi and Alasli (24) synthesized n-ethylene phthalimidyl acrylate and polymerized resulting esters free radically and anionically.

Several isoimide and imide were prepared and allowed to react with acryloyl chloride to form the corresponding acrylate esters (25).

In 1981, aromatic polyetherimides have been prepared from bis-phenoxide salts and aromatic dinitrobisimides by nucleophilic aromatic substitution reactions (26).



4,4-Oxydianiline with 3,3,4,4-bis phenyl tetracarboxylic dianhydride was prepared (27) as follow:



Experimental

❖ **Instruments:**

1. Gallen-Kamp MFB-600 melting point apparatus.
2. Electronic spectra measurements using Cintra-5 *UV-Visible* spectrophotometer.
3. Infrared spectrophotometer measurements using SP3-100 Pye-Unicam (600-400 cm^{-1}).
4. Viscosity *measurements* using capillary viscometer type Ostward viscometer, at 30 °C.
5. Thermogravimetric analysis using NETSCH Geratebau Gmbtt Model STA-409.
6. Elemental analysis using C.H.N. analyzer, type 1106 Carlo-Erba.
7. Acid number determination by the titration of polymer solution with alcoholic KOH.
8. Polymer swelling determination using water, DMFand acetone as a solvent.

All chemical materials were purchased from Fluka and BDH.

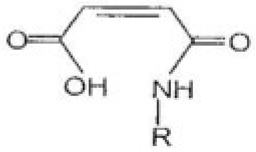
❖ **Synthetic Methods of Polyimides:**

1. **Preparation of N-Substituted Amic Acids (N_1-N_4):**

N-Substituted maleamic acids were prepared according to the procedure of Liwschitiz et al (28). DMF instead of ethter was used to dissolve maleic anhydride. Most of the amic acids produced were precipitated spontaneously after the addition of primary amine. In 1:1 and 1:2 molar ratio with diamine compound.

However, some additional amic acid was left in the solvent, and it was obtained by the addition of some cyclohexane. The crude amic acids were purified either by recrystallization from cyclohexane or by dissolving them in dilute sodium bicarbonate solution followed by reprecipetation of the amic acid with dilute hydrochloric acid. Physical properties of the prepared amic acids are listed in tables (1&2).

Table (1): Physical Properties of Amic Acids (N_1&N_2)



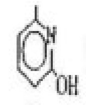
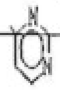
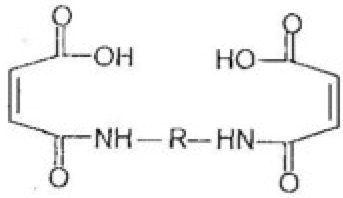
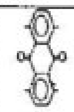
Comp. No.	R	Color	Yield (%)	M.P ℃
N_1		Brown	75	157-159
N_2		White	77	131-133

Table (2): Physical Properties of Amic Acids (N_3&N_4)

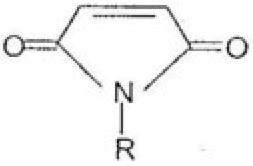


Comp. No.	R	Color	Yield (%)	M.P ℃
N_3		Yellow	71	192-194
N_4		Brown	65	185-187

2. Preparation of N-Substituted Maleimides from Amic Acids (N_5-N_8):

In a (100 ml) round bottom flask provided with a magnetic bar were placed for example (5 gm) of N-(6-hydroxy-2-pyridine) maleamic acid (N_1), (50 ml) of dry acetone, (30 ml) of acetic anhydride and (3 gm) of anhydrous sodium acetate. The mixture was refluxed f0r (2 hrs) until a clear solution was obtained. The solution was cooled to room temperature before pouring it into a beaker containing ice and water with vigorous stirring. The precipitate was filtered, then washed with cold distilled water several times before drying. The products were recrystallized from cyclohexane until a constant melting point was obtained. Physical properties of N-substituted maleimides (N_5-N_8) are listed in table (3&4).

Table (3): Physical Properties of N-Substituted Maleimides (N_5&N_6)



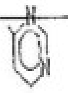
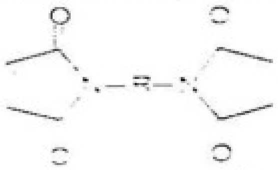
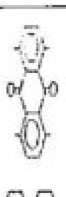
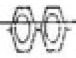
Comp. No.	R	Color	Yield (%)	M.P °C
N_5		Dark brown	65	146-148
N_6		White	74	162-164

Table (4): Physical Properties of N,N -Substituted Bis Maleimides (N_7&N_8)

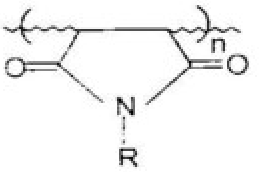


Comp. No.	R	Color	Yield (%)	M.P °C
N_7		Brown	81	203-205
N_8		Black	67	215-217

3. Polymerization of Prepared Maleimides (N_9-N_{12}):

(2 gm) of the pure N-substituted maleimides (N_5-N_8) was dissolved in (10 ml) of freshly distilled dry acetone in a screw-capped polymerization bottle. An amount equal to 0.02% of the monomer's weight of azobisisobuteronitrile was added as initiator. The mixture was flushed with nitrogen for few minutes inside a glove bag and firmly stopped. The clear solution was maintained at (55 °C) in a constant temperature water bath for (2 hrs). The solution was then poured into about (20 ml) of ethanol to obtaine coagulate polymers, then washed with ethanol several times, dried in a vacuum oven overnight. The results of these experiments are listed in table (5&6).

Table (5): Physical Properties of Poly N-Substituted Maleimides (N_9&N_{10})



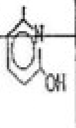
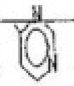
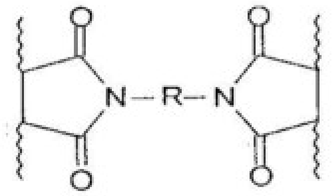
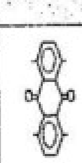
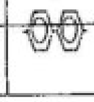
Comp. No.	R	Color	$[\eta]$ dL/g	Conversion (%)	Softening point °C
N_9		Brown	0.65	74	227-234
N_{10}		Yellow	0.64	77	190 Dec.

Table (6): Physical Properties of Prepared Cross-Link Poly Malimides (N_{11}&N_{12})



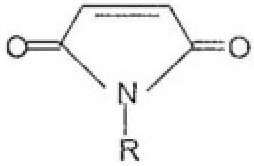
Comp. No.	R	Color	Conversion (%)	Softening point °C
N_{11}		Brown	64	>350
N_{12}		Dark brown	60	>350

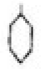
4. Preparation of N-Substituted Maleimides from Alkyl Halides(N_{13}-N_{15}):

Three N - substituted maleimides were prepared from reaction between maleimide with different aliphatic halides such as cyclohexyl iodide as in follow procedure:-

In (100 ml) round bottom flask was added (2 gm, 0.1 mole) of maleimide, dissolved in (10 ml) of dry DMF. The stochiometric amount of alkyl halide such as cyclohexyl or butyl or isobutyl halide was added, (3 ml) of pyridine was added as catalyst, the mixture was refluxed for (1 hr), the clear solution was cooled to room temperature, a white precipitate of N-substituted maleimide was separated by filteration, washed and recrystallized with dioxane for several times, until a constant melting point was obtained.

Table (7): Physical Properties of N-Substituted Maleimides Monomers (N_{13}-N_{15})

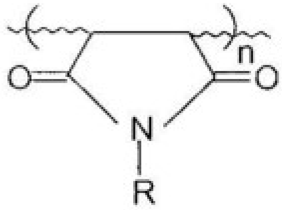


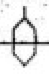
Comp. No.	R	Color	Yield (%)	M.P °C
N_{13}		Brown	68	166-168
N_{14}	$CH_2CH_2CH_2CH_3$	Yellow	63	115-117
N_{15}	$\dot{C}H$ H_3C CH_2CH_3	Orange	75	143-145

5. Polymerization of N-Alkyl Maleimides (N_{16}-N_{18}):

To a screw capped polymerization bottle containing (2 gm) of N-alkyl maleimides (N_{13}-N_{15}) were added (0.05 gm) (0.025% by weight of the monomer concentration) of AIBN and (20 ml) of freshly distilled DMF. The clear solution was flashed with pure nitrogen, followed by stream nitrogen gas. The bottle was then closed and incubated in water bath at (65 °C) for (1 hr). The mixture was cooled and the contents poured into a beaker. A polymeric precipitate was formed which coagulated when warmed. The precipitate was filtered, washed with ethanol and dried in vacuum oven overnight. The yield of polymer was (46-59%).

Table (8): Physical Properties of Prepared Poly Maleimides (N_{16}-N_{18})

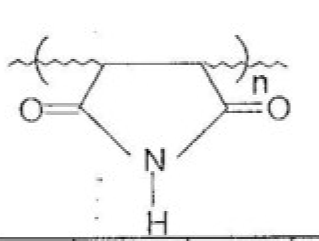


Comp. No.	R	Color	[η] dL/g	Conversion (%)	Softening point °C
N_{16}		Dark brown	0.51	59	192-198
N_{17}	$\dot{C}H_2CH_2CH_2CH_3$	Brown	0.66	52	161-166
N_{18}	$\dot{C}H$ H_3C CH_2CH_3	Red	0.57	46	205 Dec.

6. Free Radical Polymerization of Maleimide Monomers:

(5 gm) of maleimide was dissolved in (15 ml) of DMF in polymerization bottle then added (0.05 gm) of dibenzoyl peroxide. The bottle was flushed with argon for few minutes inside a glove bag. Heated at (90 °C) in a constant temperature water bath for (2 hrs). The solution was poured into (50 ml) of ethanol to obtain polyimide coagulate which was washed with ethanol several times. then dried in a vacuum oven for overnight. Table (9) shows physical properties of polymalimides.

Table (9): Physical Properties of Polymaleimides

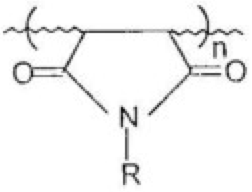


Color	[η] dL/g	Conversion (%)	Softening point °C	Solubility		
				DMF	Water	Acetone
Red	0.71	84	Oily	+	-	-

7. Preparation of N-Alkyl Substituted Maleimides Polymers (N_{16}-N_{18}):

Polymaleimide was modified to N-substituted maleimide polymers from reaction polymaleimide with different alkyl halide by using pyridine as catalyst, the DMF was used as a solvent, the reaction refluxed about (4 hrs), the product was reprecipitated in CCl_4. the polymers were dried in a vacuum oven at (50 °C), the conversion % was about (70-84%). The physical properties were listed in table (10).

Table (10): Physical properties of prepared N-alkyl maleimide polymers (N_{16}-N_{18})



Comp. No.	R	Color	[η] dL/g	Conversion (%)	Softening point °C
N_{16}		Red	0.64	66	350
N_{17}	$CH_2CH_2CH_2CH_3$	Red	0.78	84	317-325
N_{18}	CH H_3C CH_2CH_3	Brown	0.68	81	Oily

Results and Discussion

There are several procedures for preparations of N-substituted cyclic imides, the first method was found suitable for the preparation of N-substituted maleimides as a valuable procedure involve heating of the intermediate amic acid produced from the reaction of the desired primary amine with maleic anhydride. Heating of the amic acid may be performed alone or in presence of a dehydrating agent as acetic anhydride with anhydrous sodium acetate. Produced N-substituted maleimide, which polymerized free radically to linear polyimide. Also, the reaction of maleic anhydride with primary diamines produces bis amic acid, which is converted to the corresponding bis maleimide upon heating.

The various combinations of the monomers available for polyimide synthesis provide access a vast array of structures. New monomers are constantly being evaluated and the commercialization of processes for their manufacture depends on the properties that they impart to the polyimides, which depended on chemical and physical variables. The former include monomers, purity, reactivity and solvent purity, catalyst and crosslinkage reactions for bis maleimide monomers to produce crosslinkage polymers through two double bonds free radically by using dibenzoyl peroxide as initiator. Scheme (1) illustrates the two types of monomers and their polymers, A- Linear polymer (N_9, N_{10}), B- Crosslinking polymers (N_{11}, N_{12}).

These polyimides derived from aromatic diamines exhibit outstanding thermal stability. The thermal stability of crosslinking polyimides are evaluated by different thermal analysis (DTA) and thermal gravimetric analysis (TGA), which recorded a function of temperature with loss of weight of polymer samples N_{11}, poly (N,N-1,4-anthraquinonyl dimaleimide), and polymer N_{12}, (N,N-diphenyl dimaleimide) are listed in table (11).

Table (11): Thermal Decomposition Temperatures for Typical Aromatic Polymaleimides

Polym. No.	Temp. °C	Loss Weight %	Temp. °C	Loss Weight %	Temp. °C	Loss Weigh %
N_{16}	250	10	380	30	516	80
N_{12}	280	15	400	50	620	85

N-Aromatic substituted maleimide such as N_5 (N-2-pyridinyl maleimide) and N_6 (N-2-pyrimidinyl maleimidinyl maleimide) were polymerized as linear polyimides having good stability due to containing heterocyclic groups. Also, crossed linked aromatic maleimides polymers are insoluble in most organic solvents, such as N_{11} and N_{12}. The conversion% of polymerization was (60-64%). The results of polymerization are summarized in table (5 and 6).

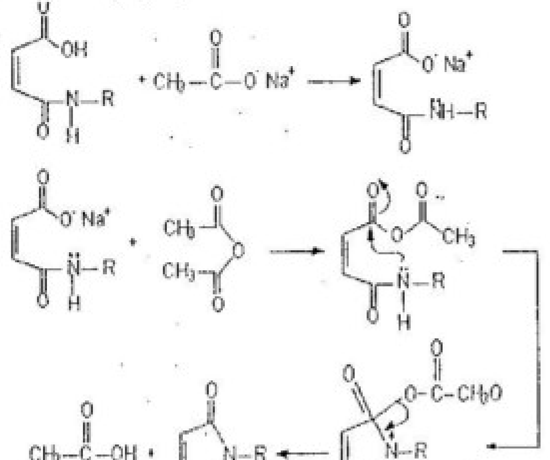
The high molecular weight of prepared polyimides with high inherent viscosities (0.64-0.9 dL/g) were obtained.

The elemental analysis values agreed quite well with the calculated values for the proposed structure of prepared polyimides. The IR spectra Fig. (1 and 2) show the characteristic absorption bands of the prepared amic acid (N_1, N_2), appeared absorption at 3500-3000 cm^{-1} due to OH carboxylic acid and at 3200 cm^{-1} for –NH group.

IR Fig. (3) shows the characteristic absorption bands of the imide prepared N_6 appeared near 1780 cm^{-1} asym. for (C=O), 1720 cm^{-1} sym. for (C=O), 1390 cm^{-1} for (C-N) and 745 cm^{-1} for imide ring deformation.

Tables (11&12) show the IR absorptions of prepared new monomers.

The mechanism of imide formation is illustrated as in scheme (3).



Scheme [3]

The UV absorptions as in Fig. 4 for N_7 and Fig. 5 for N_{11} polymers show the electronic shift due to (π-π^*) transitions.

Poly [N-alkyl maleimides] were prepared according to two ways as in scheme (2).

A. Preparation of N-alkyl maleimide monomers (N_{13}-N_{15}), then polymerized free radically gave polymers (N_{16}-N_{18}) with conversion (46-59%) with low molecular weight have [η_{in} = 0.51-0.54 dL/g], their m.p. was lower than (205 °C).

B. Polymerization of maleimide monomer, then condensed with different alkyl halides gave the similar structure of polymers (N_{16}-N_{18}), which prepared previously with different physical properties and with higher conversion % and higher [η_{in} = 0.68-0.78 dL/g], so with higher softening point above (350 °C).

Tables (8&10) list all physical preperties of N-alkyl maleimide polymers were prepared by different methods A and B.

We conclude from all results of these different ways, which appeared that the modification of polymaleimide gave better results than classical methods, which polymerized as a bulky unsaturated maleimide.

IR spectra of polymer N_{17}, Fig. (7) was compared with IR spectra of polymaleimide Fig. (6), which indicated disappearance of a band at 3250 cm^{-1} for NH group when substituted with alkyl halide.

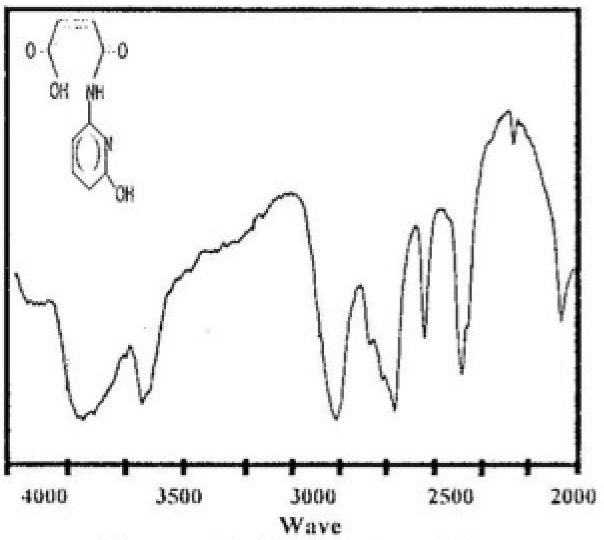


Figure (1): IR Spectra of N_1

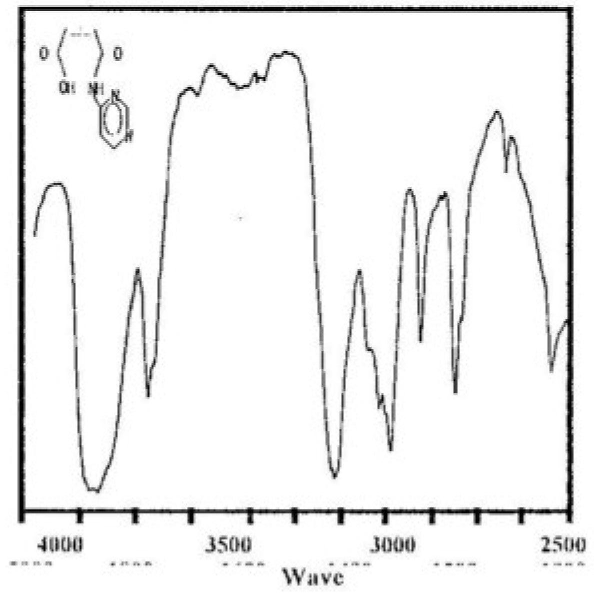


Figure (2): IR Spectra of N_2

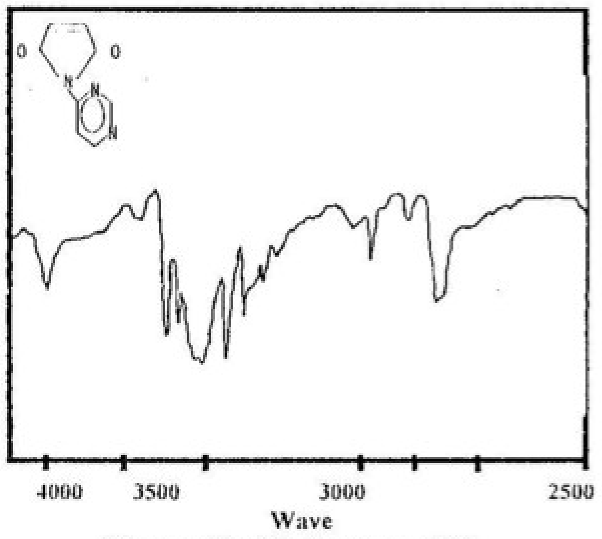


Figure (3): IR Spectra of N_6

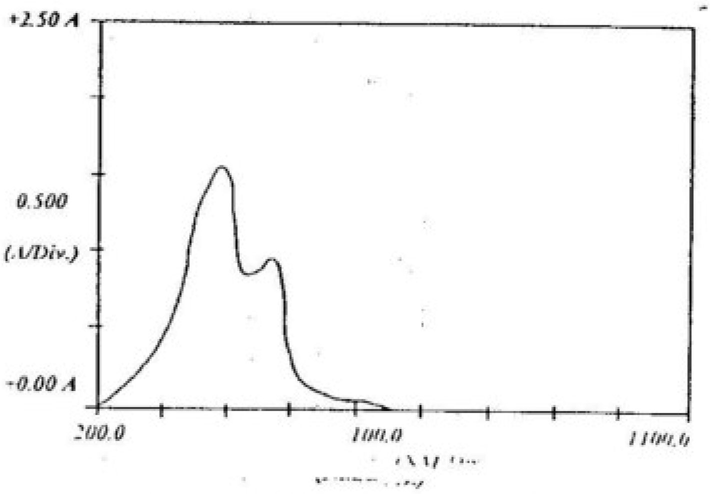


Figure (4): UV Spectra of N_7

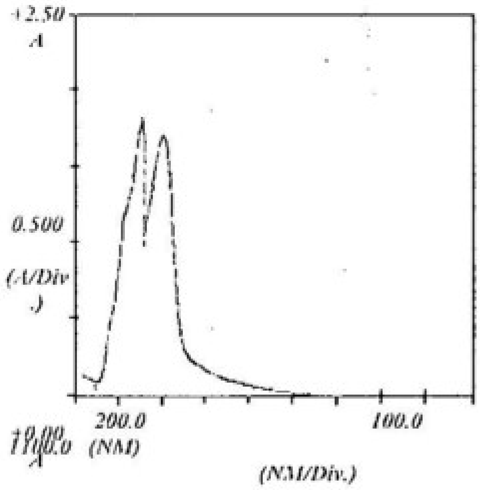


Figure (5): UV Spectra of N_{11}

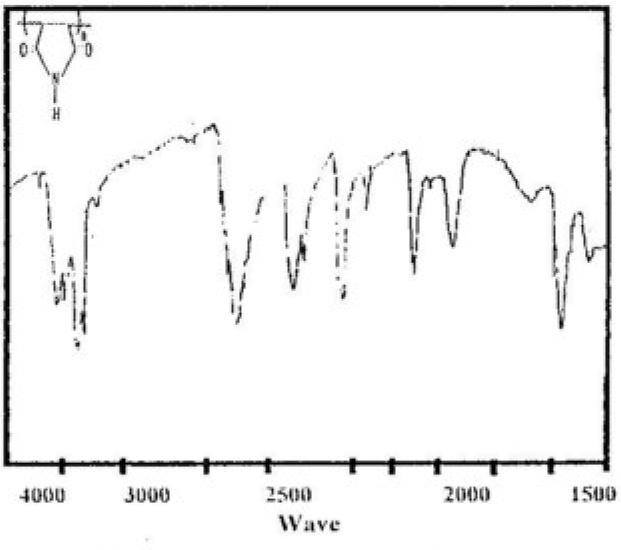


Figure (6): IR Spectra of Polymaleimide

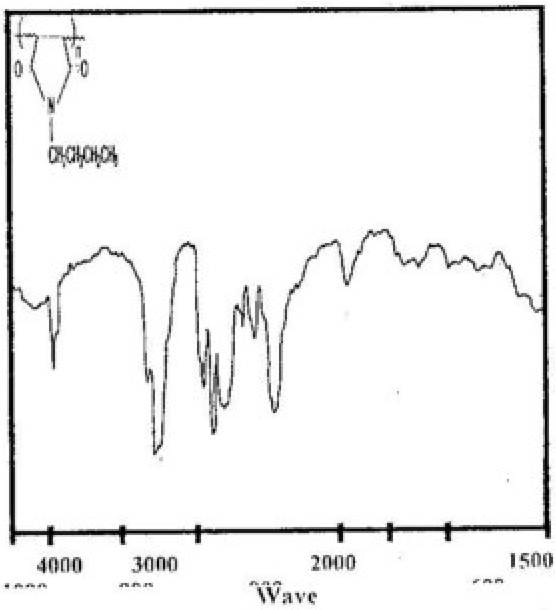


Figure (7): IR Spectra of N_{17}

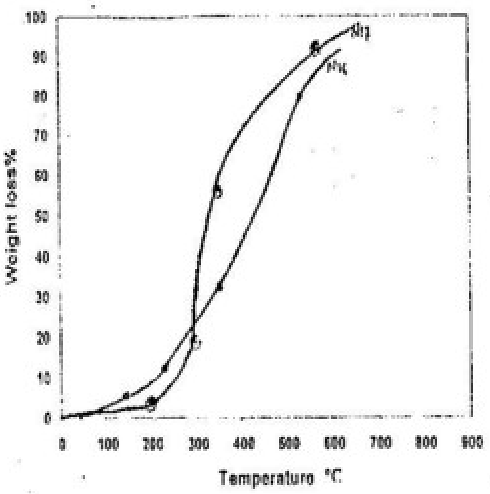


Figure (8): Weight loss-temperature curves for N_{16} and N_{17}

تحضير بعض بوليمرات الإيمايد بطرائق مختلفة

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الخلاصة

تضمن هذا البحث تحضير بوليمرات الإيمايد المستقرة حراريا بطرائق مختلفة صنفت كما يلي:

1. أ- تحضير عدد من حوامض الماليأميك المعوضة الجديدة.
   ب- سحب جزيئة ماء من حوامض الماليأميك أعلاه وتحويلها إلى الماليئمايدات المعوضة المقابلة.
   ج- بلمرة جميع مونومرات الايمايد الجهيدة.
2. أ- تحضير مونومرات الماليئمايد من تفاعل الماليئمايد مع هاليدات الالكيل.
   ب- بلمرة مونومرات الماليئمايد المعوضة.
3. أ- بلمرة مركب الماليئمايد من تفاعل الماليئمايد مع هاليدات الالكيل
   ب- تعويض البولي ماليئمايد باستخدام هاليدات الالكيل.

شخصت جميع المونومرات والبوليمرات المحضرة بواسطة طيف الأشعة فوق البنفسجية، الأشعة تحت الحمراء، تحليل العناصر، التحاليل الحرارية الوزنية والفحوصات الكيميائية. قيست الصفات الفيزياوية واللزوجة لجميع البوليمرات الناتجة الجوهرية باستعمال الداي مثيل فورماميد مذيبا.

نستنتج من نتائج الطرق المختلفة أن الطريقة الثالثة أعطت نتائج أفضل مقارنة بالطريقة الأولى والثانية لأنها أعطت أوزان جزيئية عالية ودرجات انصهار أعلى.