

Synthesis and Polymerization of Poly Acryl Imide and One of Their Derivatives Then Curing the Product with Alkyl Halide

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Abstract

The present work involved four steps:

First step include reaction of acrylamide ,N- \dot{N} -Methylen-bis(acryl amide) and N-tert Butyl acryl amide with poly acryloyl chloride in the presence of triethyl amine (Et₃N) as catalyst, the second step include homopolymerization of all products of the first step by using benzoyl peroxide(BPO) as initiator in (80-90)C° in the presence of Nitrogen gas(N₂). In the third step the poly acrylimide which prepare in second step was convert into potassium salt by using alcoholic potassium hydroxide solution.

Fourth step include Alkylation of the prepared polymeric salts in third step by react it with different alkyl halides(benzyl chloride, allylbromide , methyl iodide) by using DMF as solvent for(10-12) hours.

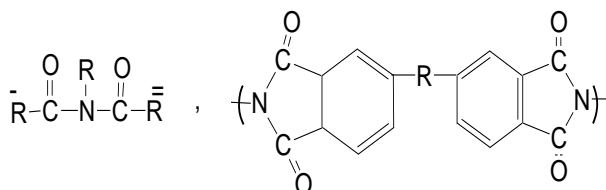
Structure Confirmation of all prepared polymers were proved using FT-IR, ¹H-NMR and C¹³-NMR spectroscopy for some polymers. Other physical properties including softening and melting points of the polymers were also measured.

Keywords: Synthesis, Polymerization, Poly Acryl Imide, Alkyl Halide

Introduction

Poly imides have became one of the most important and versatile classes of high performance polymer due to excellent mechanical and thermal properties [1]. Poly imides are step polymers or condensation

polymers derived from both aliphatic or aromatic dianhydrides and diamines, or their derivatives (acid chlorides and amides). The poly imides contain either a hetero cyclicimide linkage or open imide linkage in the repeating unit.

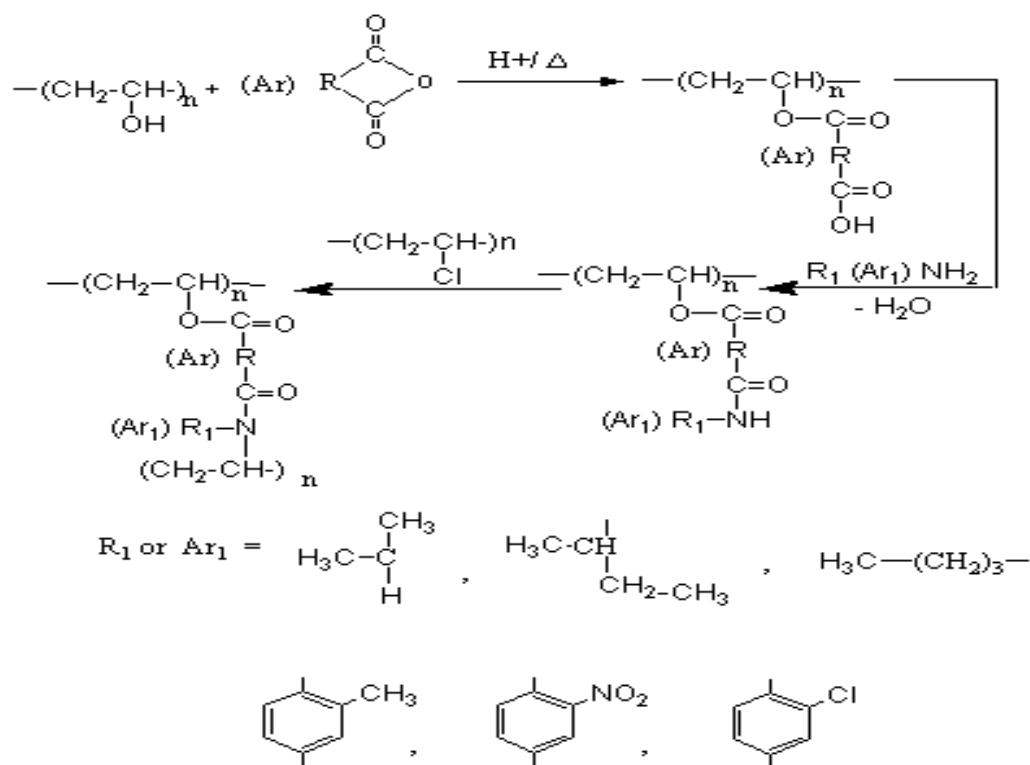


Mola [2] prepared a new polymer ester-imide starting from polymer (vinyl alcohol). The poly (vinyl alcohol) was modified to poly (carboxylic acid-ester) and then to poly

(imide-ester) by the reaction with poly acryloyl chloride :

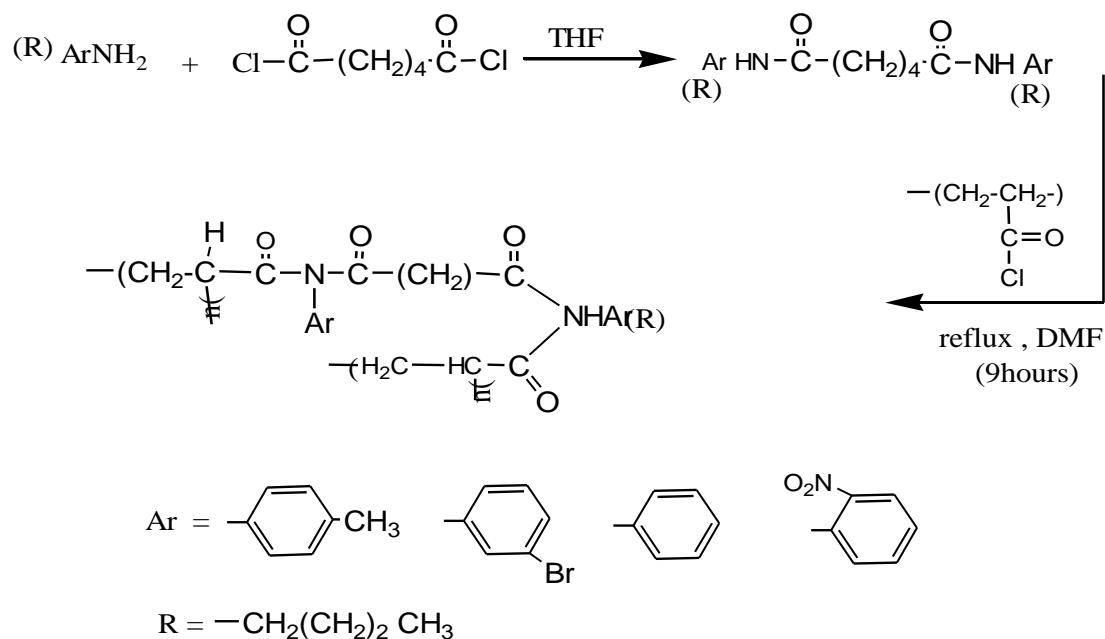
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Pyradi and Altamimi [3-6] synthesized several new poly [N-(allyl)- substituted imides] curing the unsaturated resins by free radical. Nabil [7] prepared modified polymers containing pendent imide group starting from poly vinyl alcohol and methyl methacrylat. Also,

Al-Tamimi. Et.al [8] prepared N-substituted poly dimides by two steps. First step, include the preparation of N-substituted diamides by the reaction of a dipoyl chloride different amines. The second step involved the reaction of diamides with poly acryloyl chloride.



Poly imides is often used in the electronics industry for flexible cables, as an insulating film on magnet wire and for medical tubing for example, in laptop computer [9-10]. Also, electrode membrane Assemblies EMA using sulfonated polyimide membranes as polymer electrolyte and sulfonated polyimide solutions as protonic conductors was realized [11].

Poly acrylamide PAM is a generic term applying to an extensive class of organic chemical compounds [12]. Poly acryl amides (PAMS) have many different applications because of their high viscosity. PAMS are also used as an additive in drilling muds for oil extraction as well as for photographic film and battery housings. In addition, PAMS are the major components used in gel electrophoresis for proteins and nucleic acids [13]. PAM applications often allow higher water applications without run off. Center pivot and linear move system travel speeds can be reduced to permit greater applied depths per rotation which, in turn, may reduce the amount of time poling is wetted (less disease), have less evaporation losses and increased efficiencies. Then from PAM applications, for examples synthetic polyelectrolytes based on Acryl amide and their application as a Flocculent in the treatment of palm oil mill effluent [14-15].

Materials and Methods:

Preparation of poly [vinyl Alkyl or Aryl N-substituted Imide] [16]

In a round bottom flask equipped with a magnetic bar stirrer and reflux condenser was placed a mixture of poly (acryloyl chloride) (0.06 mole) and (0.06 mole) of acryl amide N, N' - methylen-bis (acryl amide) and N-tert butyl acryl amide with (2ml) of Et₃N (triethyl amine) in 25 ml of suitable solvent (DMF, DMSO) and

refluxed for (6-9) hrs. After cooling the excess of solvent was removed under vacuum and the solid separated was filtered and purified by dissolving in DMF or DMSO and reprecipitating from water or acetone or ethanol. This procedure applied on compounds (1-2). All physical properties are listed in Table (1)

Homo polymerization of poly [vinyl Alkyl or Aryl N-substituted Imide] [17]

Literature procedures were used in the free radical homopolymerization of poly [N,N-di acryl imide], poly N, N' - Methylen- bis (acryl amide) and poly [N-acryl-N-tert butyl acryl imide] with some modification pure monomer, poly {N, N' -diacryl imide}, poly N, N' - methylen-bis (acryl amide) and poly [N-acryl-N-tert butyl acrylimide (1-2) g were dissolved in (25-30) ml of freshly distilled dry DMF or DMSO in a screw-capped polymerization bottle, an amount equal to 0.02% of the monomers weight of benzoyl peroxide was added. The bottle was flushed with nitrogen for few minutes inside a glove bag and firmly stoppered. The clear solution was maintained at (70-80) °C in a constant temperature water bath for (3-4) hours. The solution was then poured into about 100 ml of methanol and a precipitate was settled. The precipitate was collected by filtration, washed with methanol several times and dried.

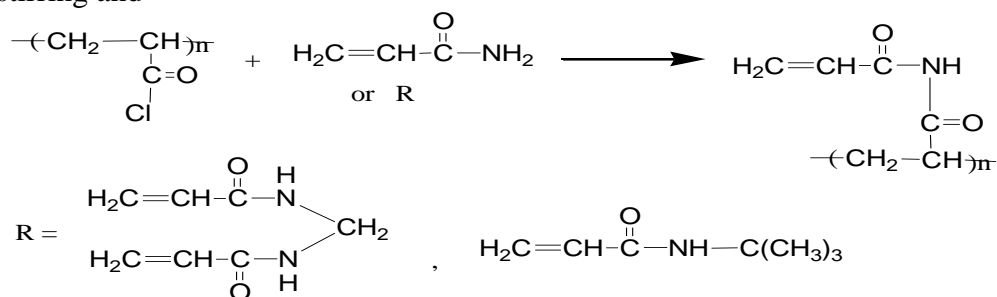
Preparation of poly imides salts [9]

Literature procedure was used with some modification, in a round bottom flask equipped with a magnetic bar stirrer and reflux condenser was placed a product of homo polymerization of poly [N, N' -diacryl imide] in paragraph (2-4) (0.02 mole) and dissolved in absolute ethanol (150

ml) with 20 ml of DMSO and heated for (6-10) hrs until the solution almost became clear. The hot solution was poured into a solution of potassium hydroxide (0.02g) in 20 ml of absolute ethanol. The mixture was cooled, the formed precipitate was filtered and washed with a solvent such as ethanol, acetone.....etc. All physical properties of the products are listed in table (1).

Preparation of poly Imides Alkylates [19]

The product in (2-5) was transformed to 250 ml round bottom flask fitted with a dropping funnel, then (250ml) of absolute ethanol was added, after (10.6 g, 0.1 mol) of sodium carbonate was added (14.6 ml; 0.1 mol) of alkyl halide (allyl bromide, benzyl chloride, methyl iodide) was allowed to run through the dropping funnel dropwise with stirring for 1 hr, the stirring and



Physical properties for polymers (1-2) including softening point range of (195-295)°C and percent conversion were range of (74-93.6) then spectroscopic identification of the prepared polymer such as fourier transform infrared spectra (FT-IR) [20].

FT-IR spectrum of compound (1). Shown characteristic absorption bands at 3448 cm⁻¹, 1700 cm⁻¹, 1410 cm⁻¹, (2850-2910) cm⁻¹ and 1650cm⁻¹ due to ν (N-H), ν (C=O) imide, ν (C-N), ν (C-H) aliphatic and ν (C=C) vinylic

refluxing continued for (11-16) hrs. Then the reaction mixture was filtered and purified by dissolving at DMF or DMSO and reprecipitating from water or ethanol, methanol, dioxane....etc.

All physical properties of the products are listed in table (1).

Results and Discussion

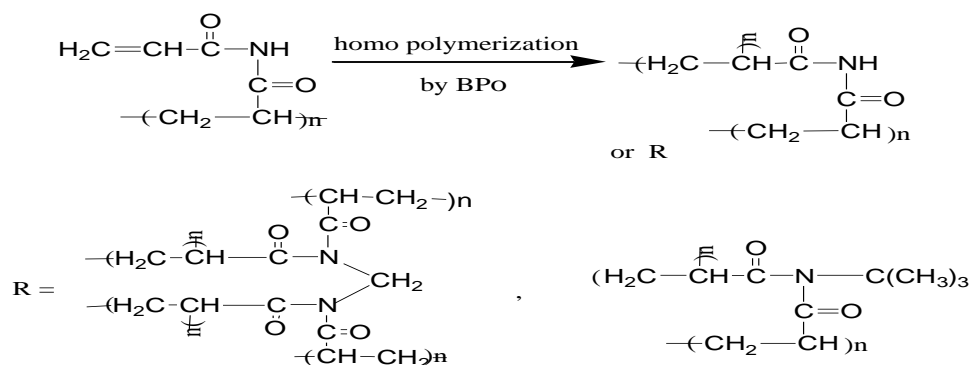
The present work involved four steps:

3.A- First step: preparation of poly (N-acryl substituted imide[1-2] two new polymers were prepared by the reaction of poly (acryloyl chloride) with acrylamide, N, N - methylen-bis-(acryl amide) and N-tert Butyl acryl amide in the presence of trimethylamine (Et₃N) as acatalyst. As is shown below: [19]

respectively as shown in table (2) Fig (1). FT-IR spectrum of compound (2), showed characteristic absorption bands at 1658 cm⁻¹, 1380 cm⁻¹, 2947 cm⁻¹ and 1527 cm⁻¹ due to ν (C=O) imide, ν (C-N), ν (C-H) aliphatic and ν (C=C) vinylic respectively as shown in table (2).

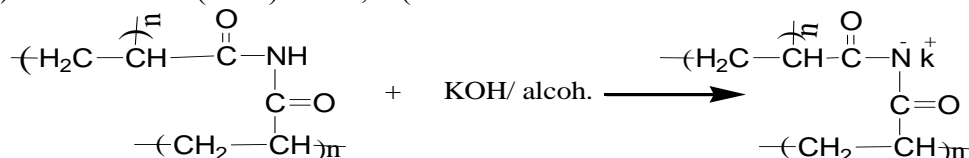
3.B- Second step: the second step include homopolymerization of all products of the first step by using benzoyl peroxide (BPO) as imitator in (80-90)°C in the presence of nitrogen gas (N₂).

As is shown below [20]:



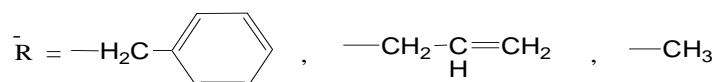
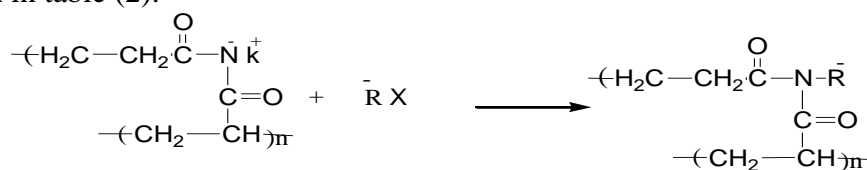
Physical properties for polymers (3-5) including softening point range of (220-330)°C and percent conversion were range of (50.7-87.5). Then spectroscopic identification of the prepared polymer such as Fourier transform Infrared spectra (FT-IR). FT-IR spectrum of compound (3), showed characteristic absorption bands at 1650 cm⁻¹, 3325 cm⁻¹, 1388 cm⁻¹ and (2877-2931) cm⁻¹ due to ν (C=O) imide, ν (N-H), ν (C-N) and ν (C-H) aliphatic respectively as shown in table (2).

FT-IR spectrum of compound (4), showed characteristic absorption bands at 1665 cm⁻¹, 1395 cm⁻¹ and (2860-2910) cm⁻¹ due to ν (C=O) imide, ν (C-



Then spectroscopic identification of the prepared polymer such as Fourier transform Infrared spectra (FT-IR).

FT-IR spectrum of compound [6] showed characteristic absorption bands at 1650 cm⁻¹, 1400 cm⁻¹ and (2815-2947) cm⁻¹ due to ν (C=O) imide, ν (C-N) and ν (C-H) aliphatic respectively as shown in table (2).



N) and ν (C-H) aliphatic respectively as shown in table (2).

FT-IR spectrum of compound (5), showed characteristic absorption bands at 1712 cm⁻¹, 1442 cm⁻¹ and (2746-2931) cm⁻¹ due to ν (C=O) imide, ν (C-N) and ν (C-H) aliphatic respectively as shown in table (2).

3.C- third step: In the third step the poly acrylimide which prepared in second step was convert into potassium salt by using alcoholic potassium hydroxide solution with time reflux ranging between (6-8) hrs with softening point range of (285-326) °C and its percent conversion was (77.8). as shown below :

3.D- Fourth step: This step include Alkylation of the prepared polymeric salts in third step by react it with different alkyl halides (benzyl chloride, allyl bromide, methyl iodide) by using DMF or DMSO as solvent for (10-12) hours.

As shown below:

New three polymers were prepared in the present work from compound (7-9). Physical properties including softening point, solubility and percent conversion of all the polymers were also measured. Physical properties for alkylated the salt of poly imides by benzyl chloride the softening point range of (255-290)°C and its percent conversion was (60.8). while physical properties for alkylated the salt of polyimides by allyl bromide the softening point range of (255-296) and its percent conversion was (63.5) while physical properties for alkylated the salt of polyimide by methyl iodide the softening point range of (265-300) and its percent conversion was (62.4). Then spectroscopic identification of the prepared polymers by Fourier Transform Infrared Spectrum (FT-IR), $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$. FT-IR spectrum of compound [7] showed the following characteristic features: significant band at 1620 cm^{-1} , 3047 cm^{-1} , 1411 cm^{-1} , 1558 cm^{-1} and $(2877-2900)\text{ cm}^{-1}$ due to $\nu(\text{C=O imide})$, $\nu(\text{C-H aromatic})$, $\nu(\text{C-N})$, $\nu(\text{C=C aromatic})$ and $\nu(\text{C-H aliphatic})$ respectively as reported in Table (2).

FT-IR spectrum of compound [8] showed the following characteristic features: significant band at 1620 cm^{-1} ,

1404 cm^{-1} , 2940 cm^{-1} and 1567 cm^{-1} are attributed to stretching vibration of $\nu(\text{C=O imide})$, $\nu(\text{C-N})$, $\nu(\text{C-H aliphatic})$ and $\nu(\text{C=C vinylic})$ respectively as reported in table (2).

FT-IR spectrum of compound [9] showed the following characteristic features: 1650 cm^{-1} , 1419 cm^{-1} , $(2893-2954)\text{ cm}^{-1}$ due to $\nu(\text{C=O imide})$, $\nu(\text{C-N})$ and $\nu(\text{C-H aliphatic})$ respectively as shown in table (2).

$^1\text{H-NMR}$ spectra of some of the prepared polymers were obtained DMSO- d_6 as solvents with TMS as internal standard.

All $^1\text{H-NMR}$ spectra of the prepared polymers revealed the monomer group of $-(\text{CH}_2-\text{CH}_2)_n-$

$\delta(1.038-2.890)$ (t, 2H, $-(\text{CH}_2-\text{CH}_2)_n-$), $\delta(1.125-3.102)$ (m, 1H, $-(\text{CH}_2-\text{CH}_2)_n-$).

Then the $^{13}\text{C-NMR}$ spectrum obtained from a $^{13}\text{C-NMR}$ spectrometer operating in the normal mode consists of series of sharp signals. Each signal represents a different $^{13}\text{C-NMR}^{(22)}$. In addition, the calibration signals TMS as an internal standard. All $^{13}\text{C-NMR}$ spectra of some of the prepared polymers showed two types signals at $(24.47-35.22)$, $(162.77-176.22)$ which were due to $(\text{CH}, \text{CH}_2, \text{CH}_3)$, C=O respectively).

Table (1): Physical properties of the prepared polymers

Comp. No.	Structure	% Conversion	Softing point (°C)	Colour	Solvent used in reaction
1	$\begin{array}{c} \text{H}_2\text{C}=\text{CH}-\text{C}(=\text{O})-\text{N}-\text{H} \\ \\ \text{C}=\text{O} \\ \\ -(\text{CH}_2-\text{CH})_n- \end{array}$	93.6	195-230	Milky	THF
2	$\begin{array}{c} -(\text{CH}-\text{CH}_2-)_n \\ \\ \text{C}=\text{O} \\ \\ \text{H}_2\text{C}=\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2 \\ \\ \text{H}_2\text{C}=\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2 \\ \\ \text{C}=\text{O} \\ \\ -(\text{CH}-\text{CH}_2-)_n \end{array}$	74	260-295	white	DMF DMSO
3	$\begin{array}{c} \text{H} \\ \\ -(\text{H}_2\text{C}-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{H} \\ \\ \text{C}=\text{O} \\ \\ -(\text{CH}-\text{CH}_2-)_n \end{array}$	65.5	225-286	Yellowish brown	DMF
4	$\begin{array}{c} -(\text{CH}-\text{CH}_2-)_n \\ \\ \text{C}=\text{O} \\ \\ -(\text{H}_2\text{C}-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2 \\ \\ -(\text{H}_2\text{C}-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2 \\ \\ \text{C}=\text{O} \\ \\ -(\text{CH}-\text{CH}_2-)_n \end{array}$	87.5	270-330	white	DMF DMSO
5	$\begin{array}{c} \text{H} \\ \\ -(\text{CH}_2-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{C}(\text{CH}_3)_3 \\ \\ \text{C}=\text{O} \\ \\ -(\text{CH}_2-\text{CH})_n- \end{array}$	50.7	220-290	Yellowish brown	DMF
6	$\begin{array}{c} \text{H} \\ \\ -(\text{CH}_2-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{K} \\ \\ \text{C}=\text{O} \\ \\ -(\text{CH}_2-\text{CH})_n- \end{array}$	77.8	285-326	Very pale brown	DMF DMSO
7	$\begin{array}{c} \text{H} \\ \\ -(\text{CH}_2-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2-\text{C}_6\text{H}_5 \\ \\ \text{C}=\text{O} \\ \\ -(\text{CH}_2-\text{CH})_n- \end{array}$	60.8	255-290	yellow	DMF DMSO
8	$\begin{array}{c} \text{H} \\ \\ -(\text{CH}_2-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2 \\ \\ \text{C}=\text{O} \\ \\ -(\text{CH}_2-\text{CH})_n- \end{array}$	63.5	255-296	Yellowish brown	DMF DMSO
9	$\begin{array}{c} \text{H} \\ \\ -(\text{CH}_2-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ -(\text{CH}_2-\text{CH})_n- \end{array}$	62.4	265-300	Pale yellow	DMSO

Table (2): FT-IR spectra of prepared polymer

Comp No.	Structure	$\nu(\text{N-H})$	$\nu(\text{C=O})$ imide	$\nu(\text{C-N})$	$\nu(\text{C=C})$ aromatic	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C-H})$ aromatic	Other band
1	$\text{H}_2\text{C}=\text{CH}-\text{C}(=\text{O})-\text{N}-\text{H}$ $\text{C}=\text{O}$ $-(\text{CH}_2-\text{CH})_n$	3448	1700	1410	-----	2850 2910	-----	(C=C) Vinylic 1650
2	$-(\text{CH}-\text{CH}_2)_n$ $\text{C}=\text{O}$ $\text{H}_2\text{C}=\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2$ $\text{H}_2\text{C}=\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2$ $\text{C}=\text{O}$ $-(\text{CH}-\text{CH}_2)_n$	-----	1658	1380	-----	2947	-----	(C=C) Vinylic 1527
3	$-(\text{H}_2\text{C}-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{H})_n$ $\text{C}=\text{O}$ $-(\text{CH}-\text{CH}_2)_n$	3325	1650	1388	-----	2877 2931	-----	-----
4	$-(\text{H}_2\text{C}-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2)_n$ $\text{C}=\text{O}$ $-(\text{H}_2\text{C}-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2)_n$ $\text{C}=\text{O}$ $-(\text{CH}-\text{CH}_2)_n$	-----	1665	1395	-----	2860 2910	-----	-----
5	$-(\text{CH}_2-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{C}(\text{CH}_3)_3)_n$ $\text{C}=\text{O}$ $-(\text{CH}_2-\text{CH})_n$	-----	1712 1650	1442	-----	2746 2931	-----	-----
6	$-(\text{CH}_2-\text{CH}-\text{C}(=\text{O})-\text{NR})_n$ $\text{C}=\text{O}$ $-(\text{CH}_2-\text{CH})_n$	-----	1650	1400	-----	2815 2947	-----	-----
7	$-(\text{CH}_2-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2-\text{C}_6\text{H}_5)_n$ $\text{C}=\text{O}$ $-(\text{CH}_2-\text{CH})_n$	-----	1620	1411	1558	2877 2900	3047	-----
8	$-(\text{CH}_2-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_2\text{CH}=\text{CH}_2)_n$ $\text{C}=\text{O}$ $-(\text{CH}_2-\text{CH})_n$	-----	1620	1404	-----	2940	-----	(C=C) Vinylic 1557
9	$-(\text{CH}_2-\text{CH}-\text{C}(=\text{O})-\text{N}-\text{CH}_3)_n$ $\text{C}=\text{O}$ $-(\text{CH}_2-\text{CH})_n$	-----	650	1419	-----	2893 2954	-----	-----

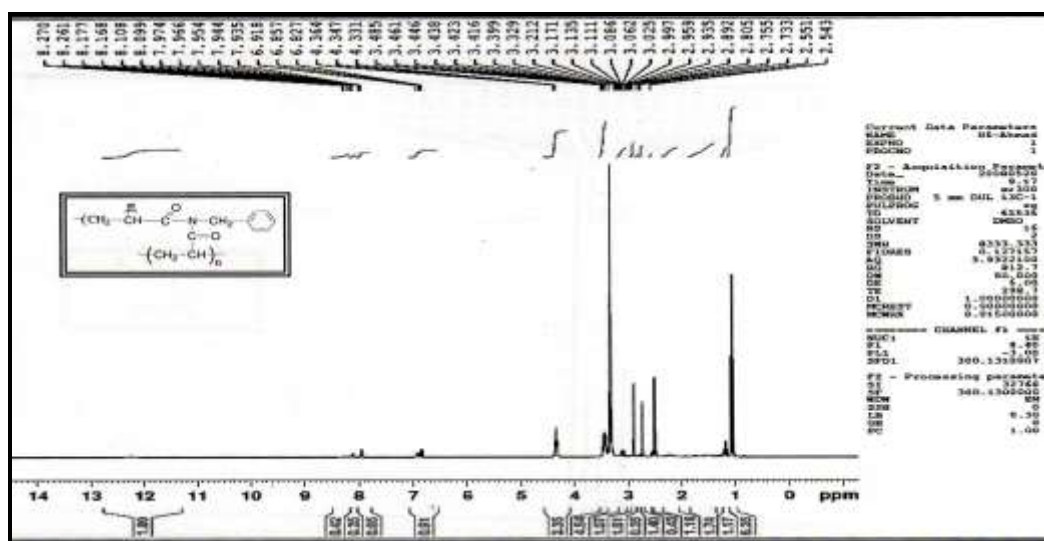
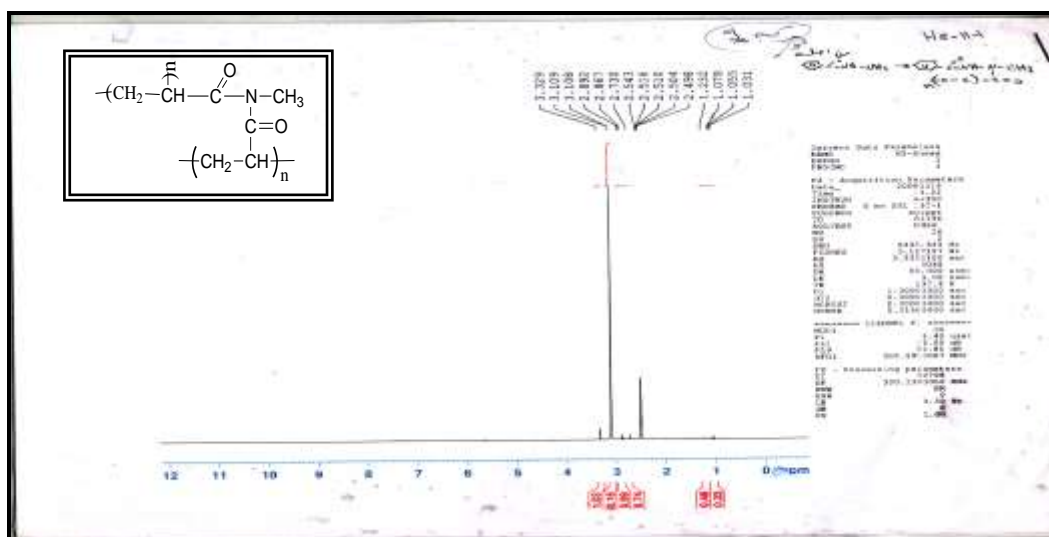
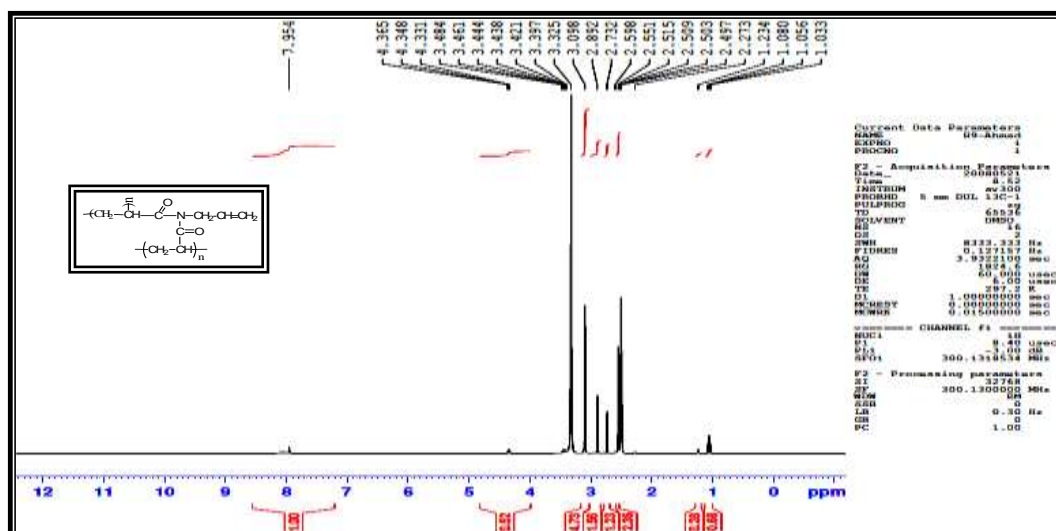


Figure (1): H-NMR spectrum of polymer [7]



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تحضير وبلمرة بولي اكريل امايد ومعاملة احد نواتج مشتقاته مع هاليد الاكليل

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الخلاصة

يتضمن البحث أربع خطوات:

تتضمن الخطوة الاولى تفاعل كل من أكريل أمايد و N- \dot{N} -مثيلين -بس أكريل أمايد N، -ثلاثي بيوتيل اكريل امايد مع بوليمر كلوريد الاكريلويل بوجود ثلاثي أثيل أمين (Et_3N) كعامل مساعد، أما الخطوة الثانية ففيها تتم إجراء عملية البلمرة الذاتية لكل من النواتج من المرحلة الاولى باستخدام بيروكسيد البنزويل (BPO) كعامل بادئ للبلمرة وبدرجة حرارة $(80-90)^\circ C$ بمعزل عن الهواء وبوجود غاز النتروجين (N_2). الخطوة الثالثة تضمنت تحويل بولي اكريل ايماید المحضر في الخطوة الثانية الى ملح بعد إذابته في هيدروكسيد البوتاسيوم الكحولي وإجراء عملية التصعيد لمدة (10 ساعة)، أما الخطوة الرابعة فتم فيها إجراء عملية الالكلية للملح البوليمري المحضر في الخطوة الثالثة مع هاليدات الكيل مختلفة (كلوريد البنزيل ، بروميد الأليل ، يوديد المثيل)، وأجري التفاعل باستخدام مذيب الـ DMF بعملية التصعيد التي إستغرقت (10-12 ساعة). تم تشخيص البوليمرات المحضرة بمطيافية الـ FT-IR والبعض منها باستخدام مطيافية الرنين النووي المغناطيسية 1H -NMR و ^{13}C -NMR بالإضافة الى القياسات الفيزيائية المختلفة من درجات التلين ودرجات الإنصهار وكذلك قياس PH المحلول للبولي ايماید المحضر.