Synthesis and Characterization of New Polyimide by Curing Poly Acryloyl Chloride with Different Amides

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Abstract:

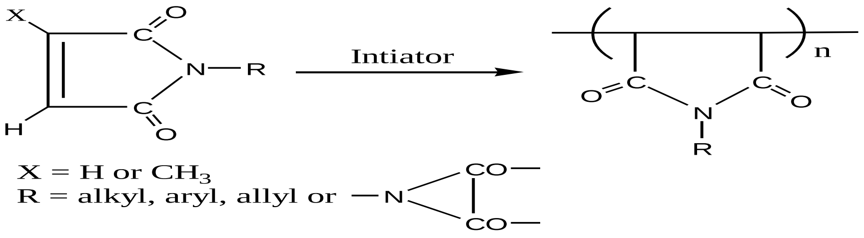
The present work involved preparation of new substituted and unsubstituted and poly imides (1-17) using reaction of acryloyl chloride with different amides (aliphatic ,aromatic) in the presence of a suitable solvent and amount tri ethyl amine (Et_3N) with heating – the structure confirmation of all polymers were proved using FT-IR,^{1}H-NMR,C^{13}NMR and UV spectroscopy ,thermal analysis (TG) for some polymers confirmed their thermal stabilities . Other physical properties including softening and melting points, PH and solubility of the polymers were also measured

Key words: Polyimide, Poly acryloyl chloride, Amides

Introduction:

Poly imides have become one of the most important and versatile classes of high performance polymer due to excellent mechanical and thermal properties[1].

Poly imides can be prepared by the addition of polymerization method, such polymers are prepared from the free radical or anionic chain growth polymerization of the vinylic bond of cyclic N-alkyl, N-aryl substituted maleimides, dimaleimides, itaconimides and cyclopolymerization of N-allyl citraconimide[2-6].



modified polymers containing pendent imide groups,were prepared starting from poly vinyl alcohol and methyl methacryate. In addition to that Abdul Salam synthesized several N,N-substituted bismaleamic acids and poly amic acid from the reaction of maleic anhydride and pyromellitic anhydride with a number of diamines and converted the products to the corresponding poly bismaleimide using acetic anhydride-anhydrous sodium acetate[7].In addition to prepared N-substituted poly diimides by two steps. First step included the preparation of N-substituted diamides by the reaction of adipoyl chloride with different amines. The second step involved the reaction of diamides with poly acryloyl chloride[8].

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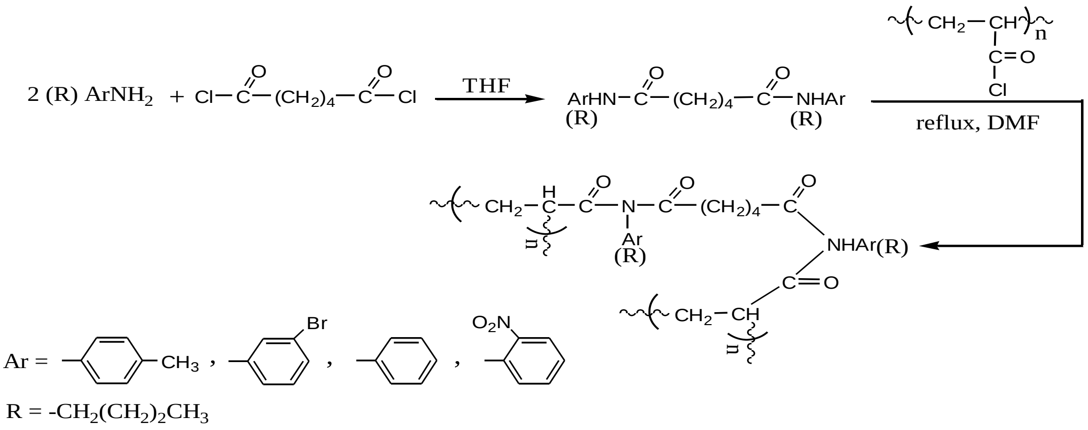
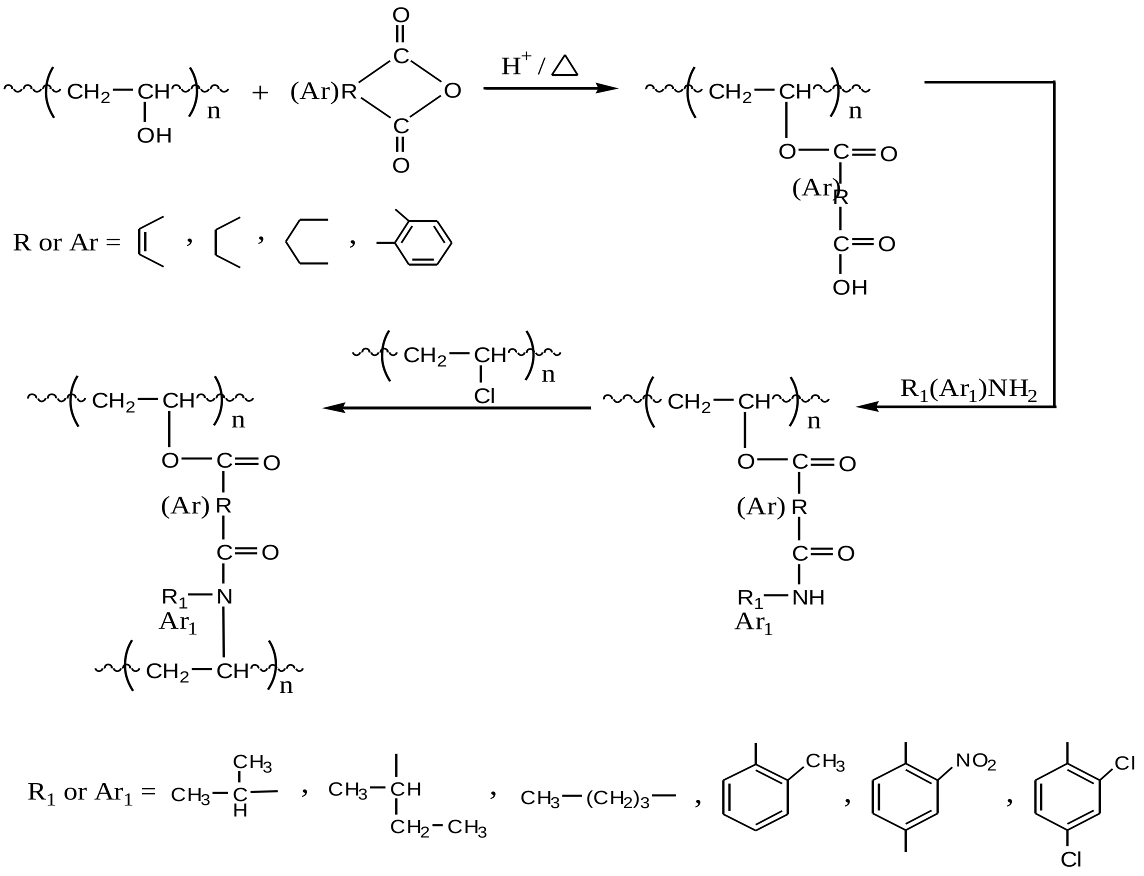


A new polymer ester-imide was prepared from poly (vinyl alcohol). The poly (vinyl alcohol) was modified to poly (carboxylic acid-ester) and then to poly (imide-ester) by the reaction with poly acryloyl chloride [9-10]:



Materials and Methods:

1- Melting points were determined on Gallen Kamp melting points apparatus MFB-600-Olof, and Stuart Scientific Co. LTD melting point SMP1.

2- Softening points were determined using thermal microscope (Kofler-method). Reichert thermovar. SP. 10/0.25, 160.

3- Ultra violet spectra were recorded using Shimadzu (UV-Vis)-160 recording spectrophotometer using DMSO, ethanol and acetone as a solvent, in Baghdad University, College of Science.

4- FT-IR spectra were recorded using solid KBr discs by testing Shimadzu FT-IR 8000 series Fourier transform, infrared spectrophotometer, Baghdad University, College of Science.

5- Thermal analyses were performed using thermal analysis system consisting from TG_{50} Shimadzu, Japan. Such analyses were in made the College of Pharmacy-Faculty of Science and Technology. Aribid-Jordan.

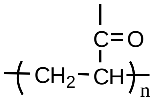
6- ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Fourier transform varian spectrometry, company Bruker, model, Ultra shield 300MHz, origin: Switzerland, with tetramethyl silane as internal standard in DMSO measurements were made at the Chemistry Department, Al-Albyt University, Jordan.

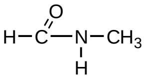
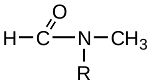
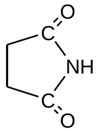
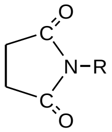
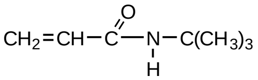
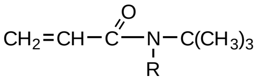
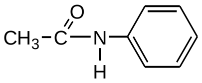
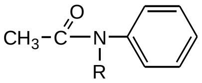
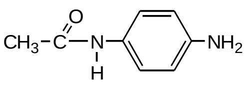
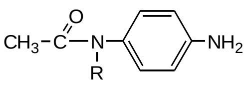
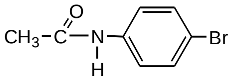
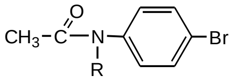
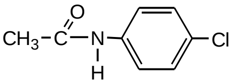
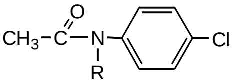
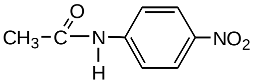
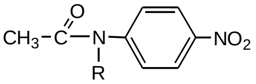
General Procedure Preparation of Poly [Vinyl Alkyl or Aryl N-Substituted Imide][11]

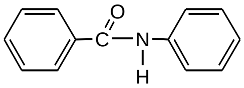
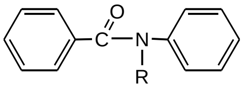
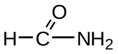
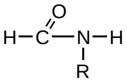
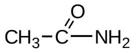
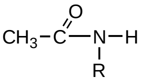
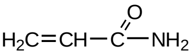
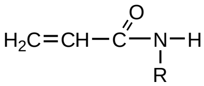
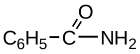
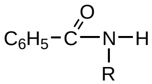
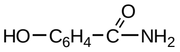
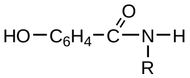
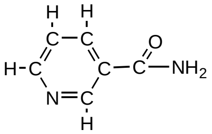
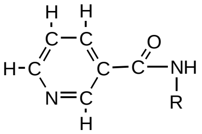
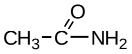
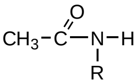
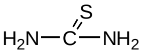
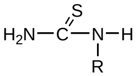
In a round bottom flask equipped with a magnetic bar stirrer and reflux condenser was placed a mixture of poly acryloyl chloride (0.06 mole) and (0. 6 mole) of appropriate primary or secondary amide [(Ar)$RCONH_2$, (Ar)RCONHR] with (2 ml) of Et_3N (triethyl amine) in (25 ml) of suitable solvent (THF, DMF) and refluxed for (6-9) hrs. After cooling the excess of solvent was removed under vacum and the solid separated was filtered and purified by dissolving at DMF or DMSO and reprecipitati from water or acetone or ethanol. This procedure applicated on compounds (1-17) is shown in Table (1).

All physical properties are listed in Table (2).

Table (1): Starting material and conditions of prepared polyimides [1-17]

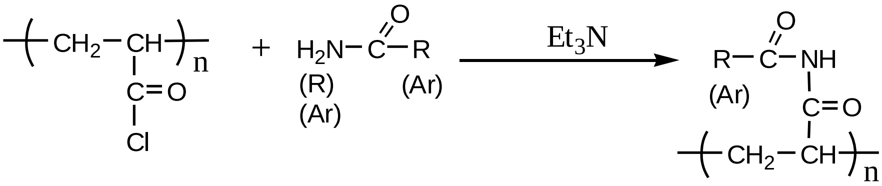
R =

$-\!\!\left(CH_2-\underset{\underset{|}{C=O}}{CH}\right)_n-$

Structure one of starting material	Weight (gm)	Time reaction hr.	Structure of repeated unit of product	No. of product
 $H-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-CH_3$	3.54	7	 $H-\overset{O}{\overset{\|}{C}}-\underset{R}{N}-CH_3$	1
	5.94	9		2
 $CH_2=CH-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-C(CH_3)_3$	7.63	8	 $CH_2=CH-\overset{O}{\overset{\|}{C}}-\underset{R}{N}-C(CH_3)_3$	3
	8.11	9		4
	9	8		5
	12.84	8		6
	10.18	7		7
	10.8	7		8

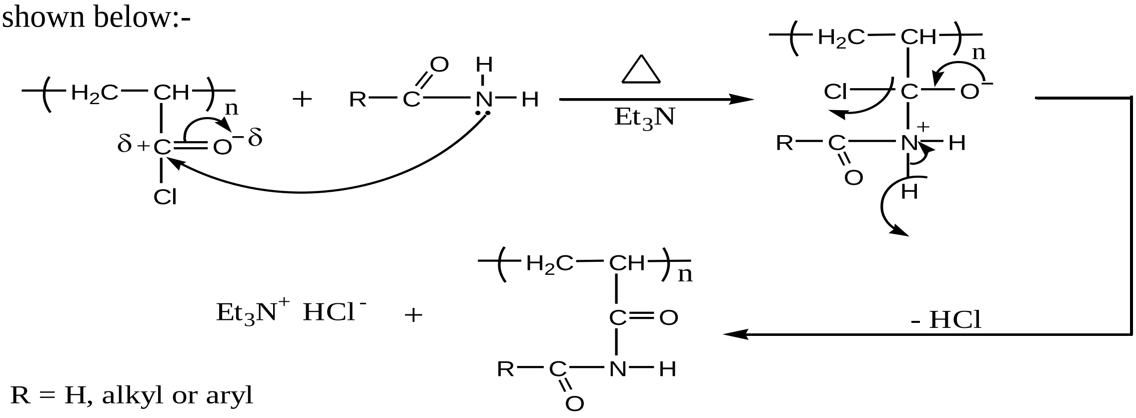
	11.82	9		9
 $H-\overset{O}{\overset{\|}{C}}-NH_2$	2.70gm 2.39ml	8	 $H-\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{\vert}{N}}-H$	10
 $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$	3.54	7	 $CH_3-\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{\vert}{N}}-H$	11
 $H_2C{=}CH-\overset{O}{\overset{\|}{C}}-NH_2$	4.26	6	 $H_2C{=}CH-\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{\vert}{N}}-H$	12
 $C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2$	7.27	9	 $C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{\vert}{N}}-H$	13
 $HO-C_6H_4-\overset{O}{\overset{\|}{C}}-NH_2$	8.22	8	 $HO-C_6H_4-\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{\vert}{N}}-H$	14
	7.33	8		15
 $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$	4.5	9	 $CH_3-\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{\vert}{N}}-H$	16
 $H_2N-\overset{S}{\overset{\|}{C}}-NH_2$	4.57	9	 $H_2N-\overset{S}{\overset{\|}{C}}-\underset{R}{\underset{\vert}{N}}-H$	17

Results and Discussion:

Preparation of poly (N-acryl substituted imide) [1-17], seventeen new polymers were prepared by the reaction of poly (acryloyl chloride) with different primary or secondary amides in the presence of triethylamine (Et_3N) as a catalyst. as shown below[12]:



The mechanism of the reaction involves a nucleophilic attack on the carbonyl as shown below:-



R = H, alkyl or aryl

Scheme (1): Mechanism of preparation of poly [vinyl alkyl or aryl N-substituted imides

The products in part one were corroborated by measuring the pH, which was found ranging between (4-4.5).

Structures confirmation of all prepared polymers in this part were proved using FT-IR, UV, ^{1}H-NMR and ^{13}C-NMR spectroscopy$^{(13,14]}$. Thermal analysis (TG) of some of the prepared polymers confirmed their thermal stabilities. Physical properties including melting point, softening point, solubility and percent conversion of the polymers were also measured. These and other physical properties are summarized in Table (2).

Poly [N-(acryl) substituted imide]

Compound [1] was prepared by refluxing poly acryloyl chloride with methyl formamide in the presence of triethylamine (Et_3N) as a catalyst in THF for 7 hours. Polymer [1] solidified in DMF as mentioned in chapter two was a pale yellow solid with softening point range of (200-220)°C, and its percent conversion was (76%).

Compounds [2-17] were synthesized by the same way and purified as mentioned inTable (2) by dissolving in a suitable solvent such as (DMF, DMSO) with gentle heating and filtered; the clear filtrate was added to suitable solvent such as (water, acetone, ethanol) and the precipitate was filtered and dried.

FT-IR spectrum of compound [1,2] as shown Stretching band at 1670 cm^{-1} ν(C=O), (2800-2920) cm^{-1} aliphatic ν(C-H), 1410 cm^{-1} ν(C-N) imide and at 1242 cm^{-1} ν(C-O) as shown in table (3).

FT-IR spectrum of compound [3] showed the same bands in compound [1,2] except ν(C=C) which due to vinylic groups shown at 1650 cm^{-1}. These bands and others are shown in table (3).

^{1}H-NMR spectrum of polymer [3] showed a doublet at δ4.283 ppm (integrated for 2H) which was attributed to the ($H_2C=$) protons, while the signal at δ3.739 ppm (1H, triplet) was attributed to (=HC) proton, and the signal at δ1.223 ppm (2H, triplet) was attributed to (H_2C-) for polymer group $\left(H_2C-CH\right)_n$ while the signal at δ2.482 ppm (1H, multeplet) was attributed to (-CH) for polymer group $\left(H_2C-CH\right)_n$ and a singlet at δ3.349 ppm (integrated for 9H) was attributed to the three methyl protons ($C(CH_3)_3$), as shown in Table (3).

The ^{13}C-NMR spectrum of [3], showed the signals at 176.22 ppm for carbonyl group (C=O) and a signal at 27.87 and 28.92 for three methyl carbon of $-C(CH_3)_3$ group, while ($H_2C=CH$) appeared at 39.95 and 40.78 ppm, and $\left(H_2C-CH\right)_n$ appeared at 35.37 and 50.48 ppm. as shown in Fig.(4).

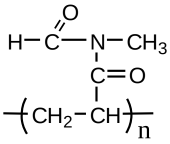
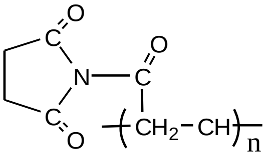
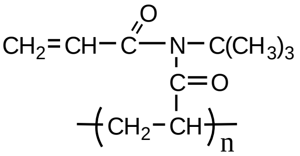
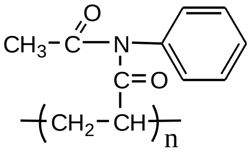
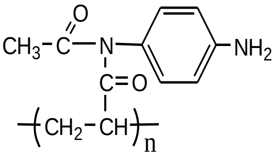
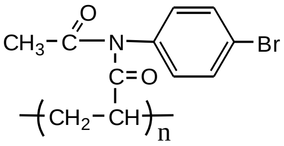
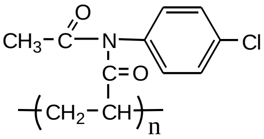
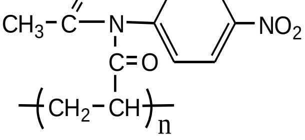
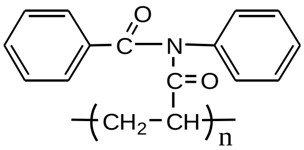
FT-IR Spectrum of compound [15] showed characteristic absorption bands at 3217 cm^{-1}, 1456 cm^{-1} and 1635 cm^{-1} due to ν(C-H) aromatic, ν(C=N) aromatic and ν(C=C) aromatic respectively as shown in Table (3).

In the ^{1}H-NMR spectrum of polymer [15] showed a signal at between δ(7.473-8.701) ppm for hetro aromatic hydrogen (^{1}H, H^2+H^4), the signal at δ7.948 ppm (1H, singlet) was attributed to (-NH) proton, and the signal at δ2.502 ppm (2H, triplet) was attributed to (H_2C-) for polymer group $\left(H_2C-CH\right)_n$ while the signal at δ1.476 ppm (1H, multeplet) was attributed to (-CH) for polymer group $\left(H_2C-CH\right)_n$ as shown in Fig (5).

The ^{13}C-NMR spectrum of [15], showed the signals at 162.78 and 176.26 ppm for two carbonyl groups (C=O), the signals at 123.87 and 135.61 ppm attributed to aromatic carbon, while (C=N) appeared at 152.35 ppm, and $\left(H_2C-CH\right)_n$ appeared at 35.66 and 40.76 ppm as shown in Fig(6)

Thermal analysis for compound [6] and [14] showed amoderate stability at 400C^0 as shown in Fig (7)and (8).

Table (2): Physical properties of the prepared poly imides

Comp. No.	Structure	%Conversion	Softing point °C	Colour	Solvent used in reaction	peak	
						λ_{max} nm	ABS
1	 poly [N-acryl methyl formimide]	76	200-220	Pale yellow	THF	300 380	2.412 0.868
2	 poly [N-acryl succmimide]	69	190-215	Yellow	THF	326	1.669
3	 poly [N-acryl-N-tertbutyl acrylimide]	86.6	180-200	Yellow	THF	234 416	1.402 0.611
4	 poly [N-acryl-N-phenyl acetimide]	74	240-265	Milky	THF	274 421	1.111 0.985
5	 poly [N-acryl-N-(p-aminophenyl acetimide]	44	170-200	Black	THF	218 343	0.787 1.902
6	 poly [N-acryl-N-(p-bromophenyl acetimide]	71.6	210-230	Yellowish white	THF	279 344	1.104 1.262
7	 poly [N-acryl-N-(p-chlorophenyl) acetimide]	86	190-220	Milky	THF	249	2.160
8	 poly [N-acryl-N-(p-nitrophenyl) acetimide]	73	180-195	Pale yellow	THF	299	2.138
9	 poly [N-acryl-N-phenyl benzimide]	50.7	230-255	Gray	THF DMF	300	2.031

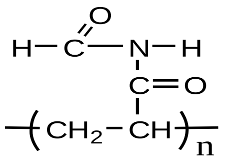
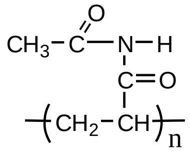
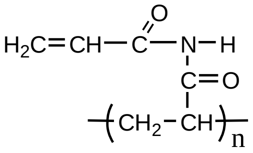
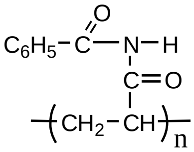
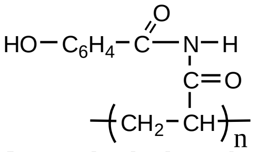
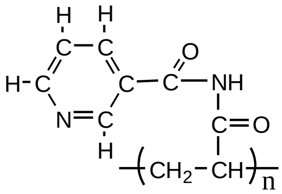
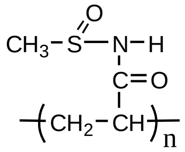
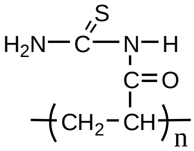
10	 poly [N-acryl formimide]	77.8	210-230	Reddish yellow	THF	300	2.288
11	 poly [N-acryl acetimide]	84.7	200-230	Yellowish brown	THF	246	2.006
12	 poly [N,N-diacryl imide]	93.6	195-230	Milky	THF	300	2.199
13	 poly [N-acryl benzimide]	88	220-245	Very pale brown	THF	247	1.994
14	 poly [N-acryl-p-hydroxy benzimide]	60.8	200-230	Very pale brown	THF	300	2.193
15	 poly [N-acryl nicotinimide]	90.8	230-255	Dark yellowish brown	THF	247	2.147
16	 poly [N-acryl thioacetimide]	80	240-265	brown	THF DMF	300	2.289
17	 poly [N-acryl thiocarbimide]	89.7	190-220	Milky	THF DMF	229 337	1.185 2.387

Table (3): FT-IR spectra of prepared poly imides and heterocyclic poly imide

Comp. No.	ν(N-H)	ν(C=O) imide	ν(C-N)	ν(C=C) aromatic	ν(C-H) aliphatic	ν(C-H) aromatic	ν(C=N)	ν(C-S)	ν(C-O)	Other band
1	-	1670	1410	-	2800 2920	-	-	-	1242	-
2	-	1640	1400	-	2902	-	-	-	1240	-
3	-	1720	1350	-	2970	-	-	-	1226	(C=C) vinylic 1650
4	-	1700	1410	1554	2965	3140	-	-	1240	-
5	3055 3271	1658	1404	1512	2931	3031	-	-	1249	-
6	-	1670	1420	1535	2970	3120	-	-	1250	(C-Br) 675
7	-	1674	1492	1604	2869 2908	3124	-	-	1257	1087 (C-Cl)
8	-	1681	1404	1596	2830 2950	3093	-	-	1265	1350 1566 ($C-NO_2$)
9	-	1650	1410	1612	2970	3220	-	-	1257	-
10	3417	1620	1342	-	2947	-	-	-	1226	-
11	3440	1643	1388	-	2854 2923	3052	-	-	1257	-
12	3448	1700	1410	-	2850 2910	3050	-	-	1250	(C=C) vinylic 1650
13	3309	1728	1400	1643	2869 2931	3062	-	-	1288	-
14	3193	1674	1357	1589	2977	3062	-	-	1249	(O-H) 3394
15	3440	1720	1410	1635	2754-2985	3217	1456	-	1242	-
16	3425	1635	1388	-	2880 2923	-	-	-	1257	(S=O) 1110
17	3217 3340	1710	1405	-	2880 1960	-	-	601	1234	(C=S) 1157 16202

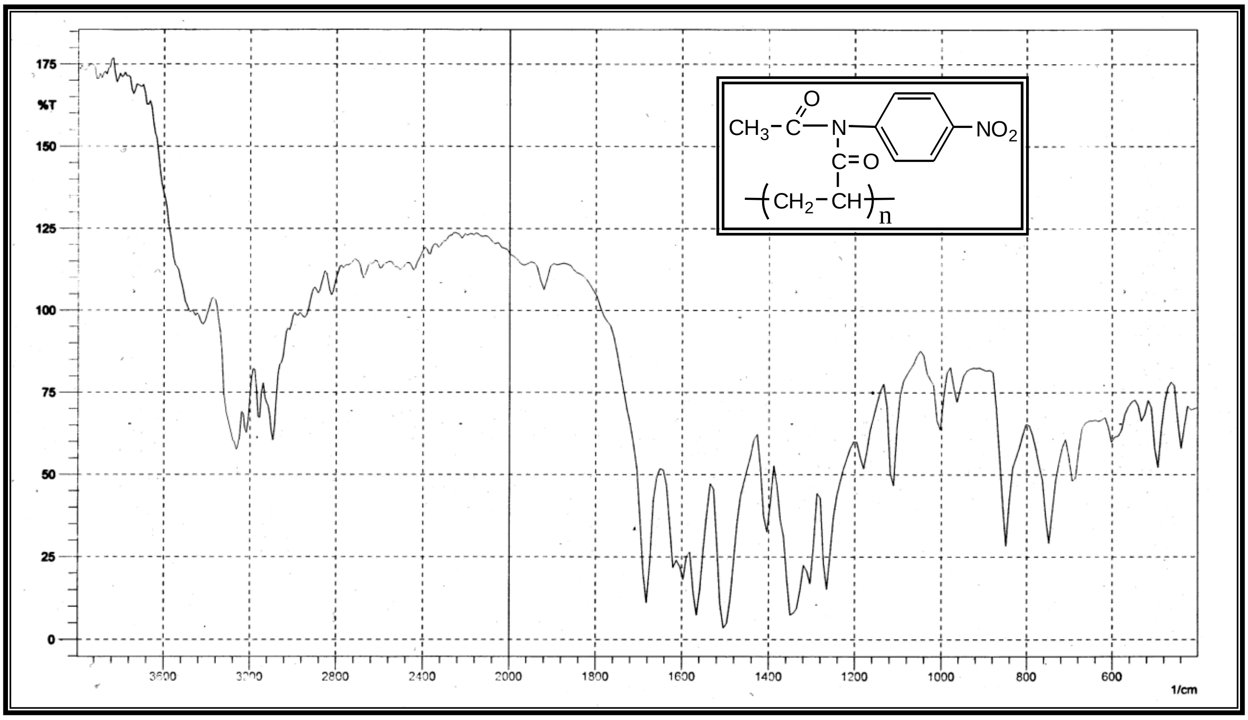


Fig. (1) : FT-IR spectrum of polymer [8]

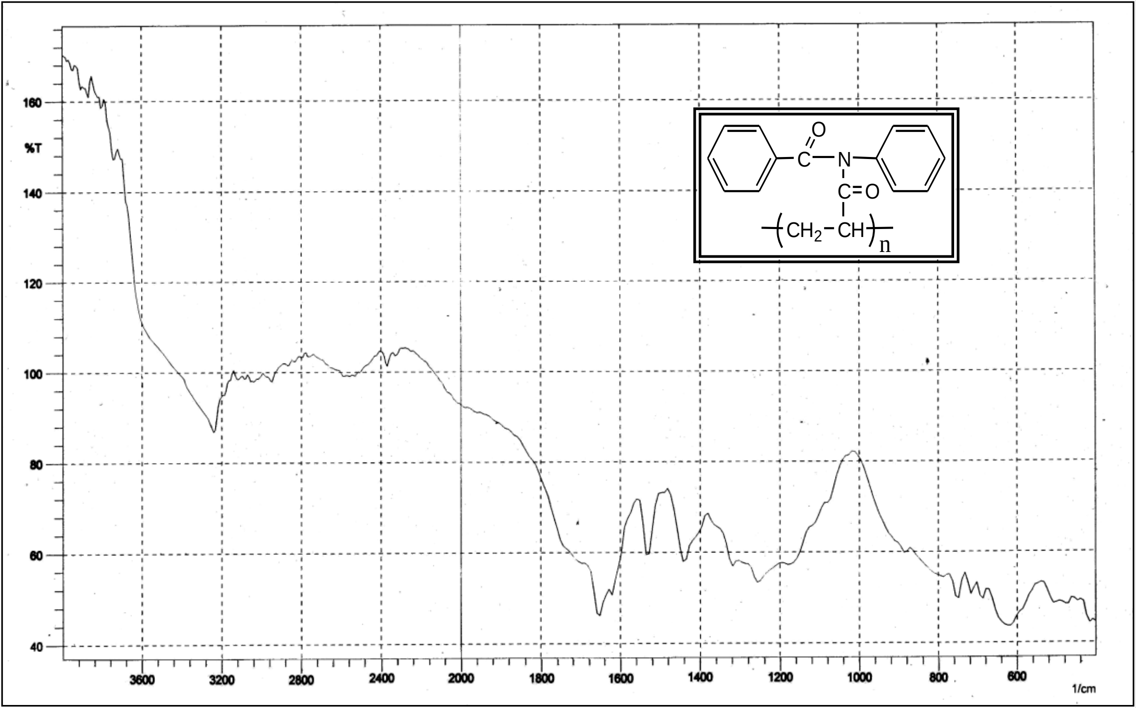
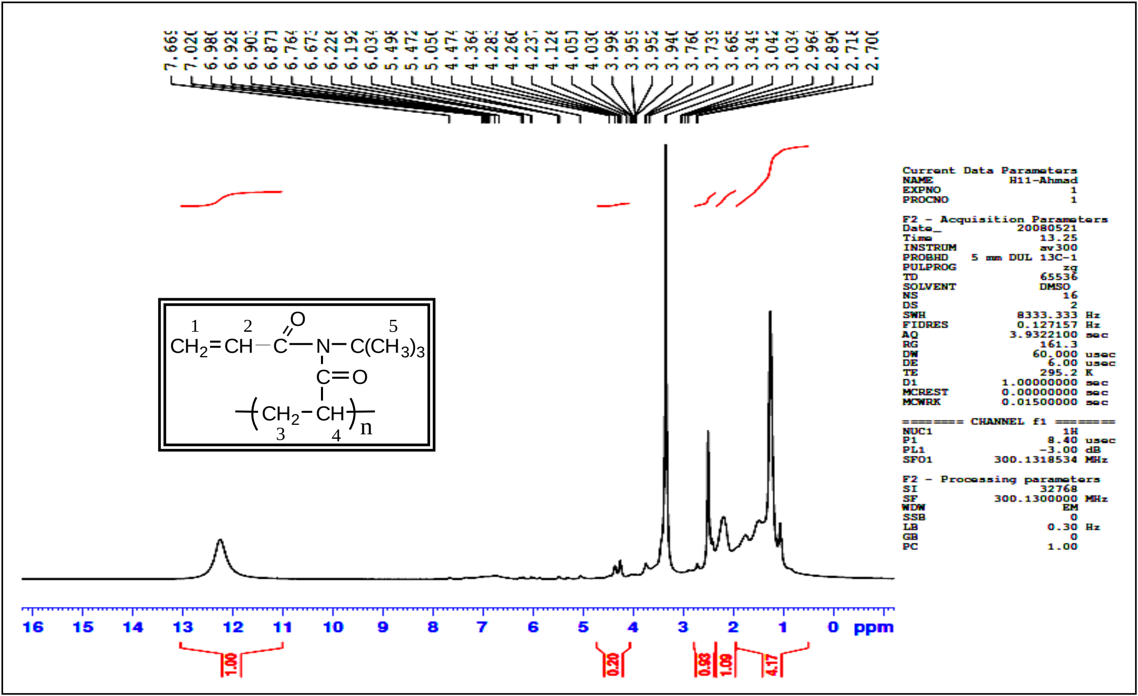


Fig. (2) : FT-IR spectrum of polymer [9]



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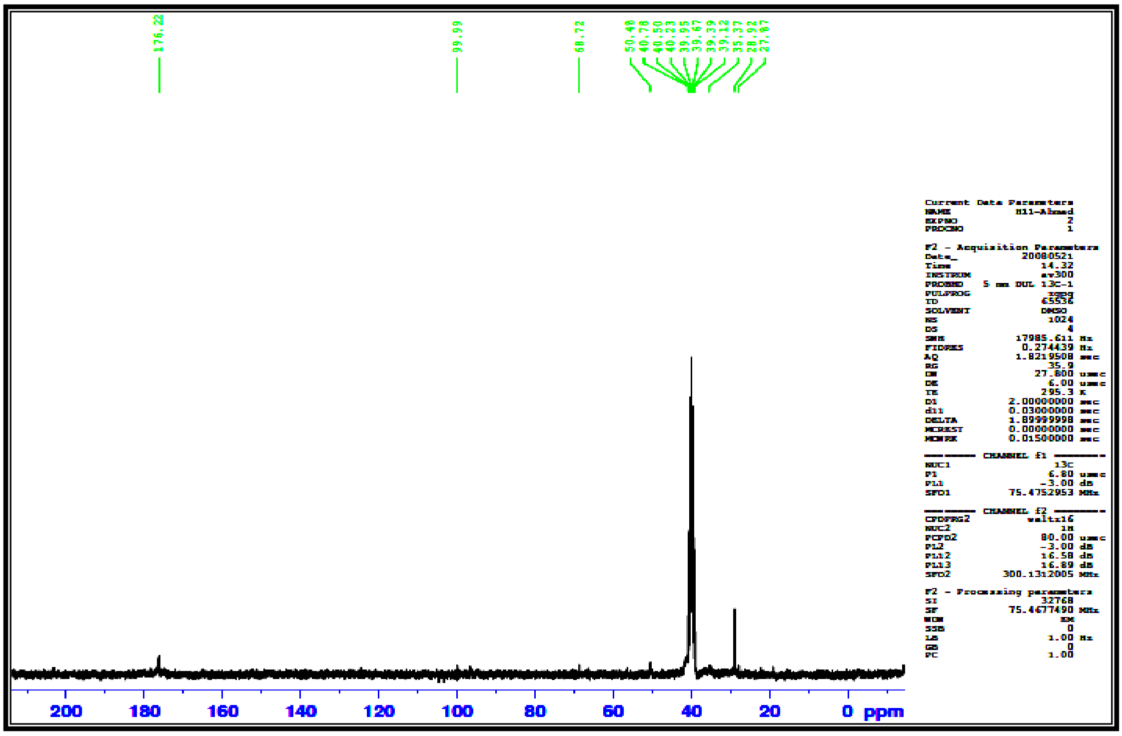
Current Data Parameters
NAME              H11-Ahmad
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080521
Time                  13.25
INSTRUM               av300
PROBHD   5 mm DUL 13C-1
PULPROG                  zg
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                8333.333 Hz
FIDRES             0.127157 Hz
AQ                3.9322100 sec
RG                    161.3
DW                   60.000 usec
DE                     6.00 usec
TE                    295.2 K
D1               1.00000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                     8.40 usec
PL1                   -3.00 dB
SFO1            300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF              300.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

Fig. (3) : ^{1}H-NMR spectrum of polymer [3]



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Current Data Parameters
NAME            H11-Ahmad
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080521
Time                14.32
INSTRUM             av300
PROBHD   5 mm DUL 13C-1
PULPROG              zgpg
TD                  65536
SOLVENT              DMSO
NS                   1024
DS                      4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                   35.9
DW                 27.800 usec
DE                   6.00 usec
TE                  295.3 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   6.80 usec
PL1                 -3.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -3.00 dB
PL12                16.58 dB
PL13                16.89 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
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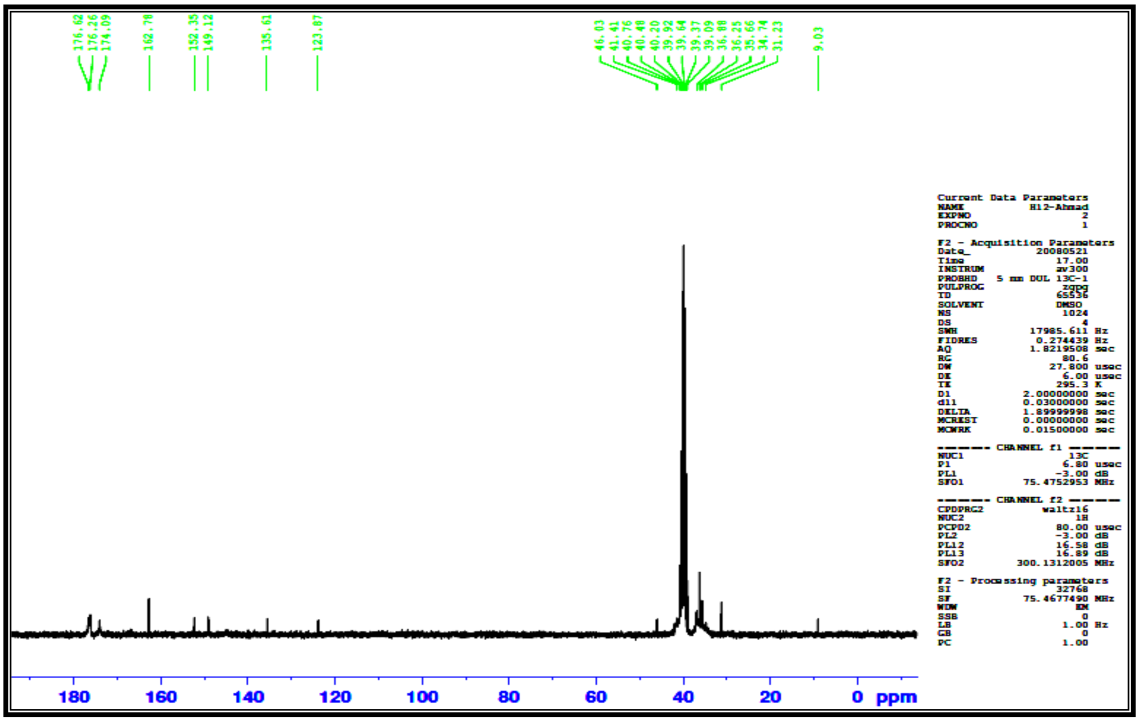
Fig.(4) : ^{13}C-NMR spectrum of polymer [3]



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Current Data Parameters
NAME            H12-Ahmad
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080521
Time                17.00
INSTRUM             av300
PROBHD   5 mm DUL 13C-1
PULPROG              zgpg
TD                  65536
SOLVENT              DMSO
NS                   1024
DS                      4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                   80.6
DW                 27.800 usec
DE                   6.00 usec
TE                  295.3 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   6.80 usec
PL1                 -3.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -3.00 dB
PL12                16.58 dB
PL13                16.89 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

Fig. (6) : ^{13}C-NMR spectrum of polymer [15]

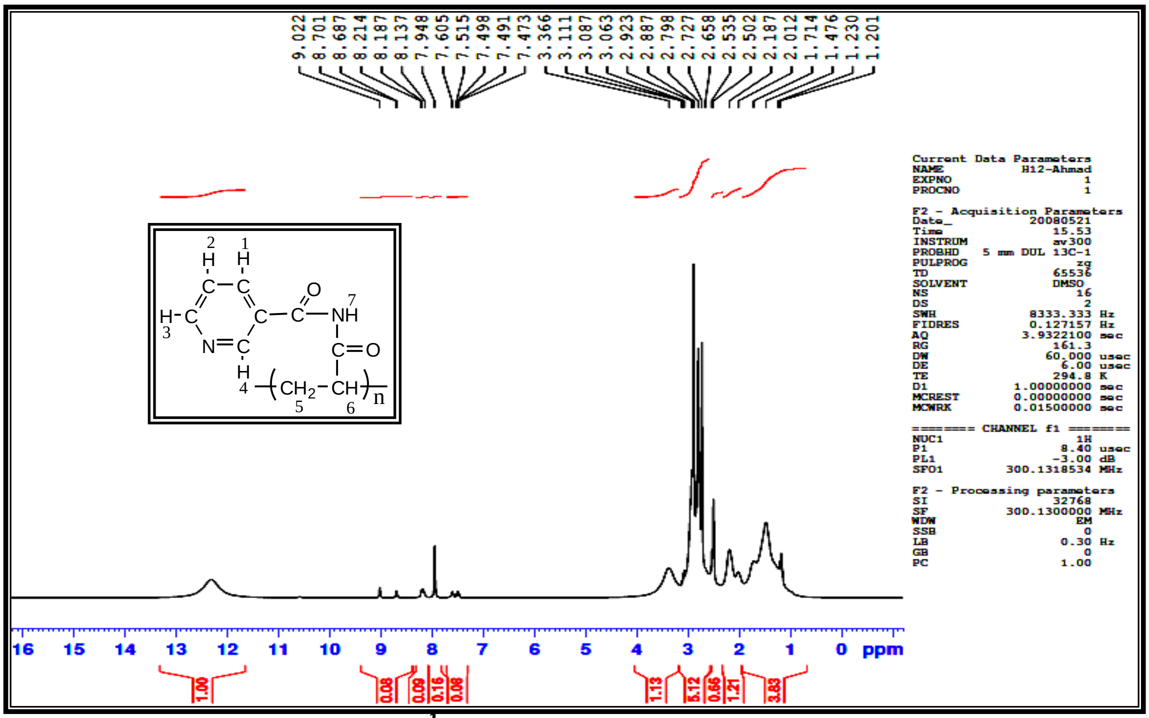

Fig. (5) : ^{1}H-NMR spectrum of polymer [15]

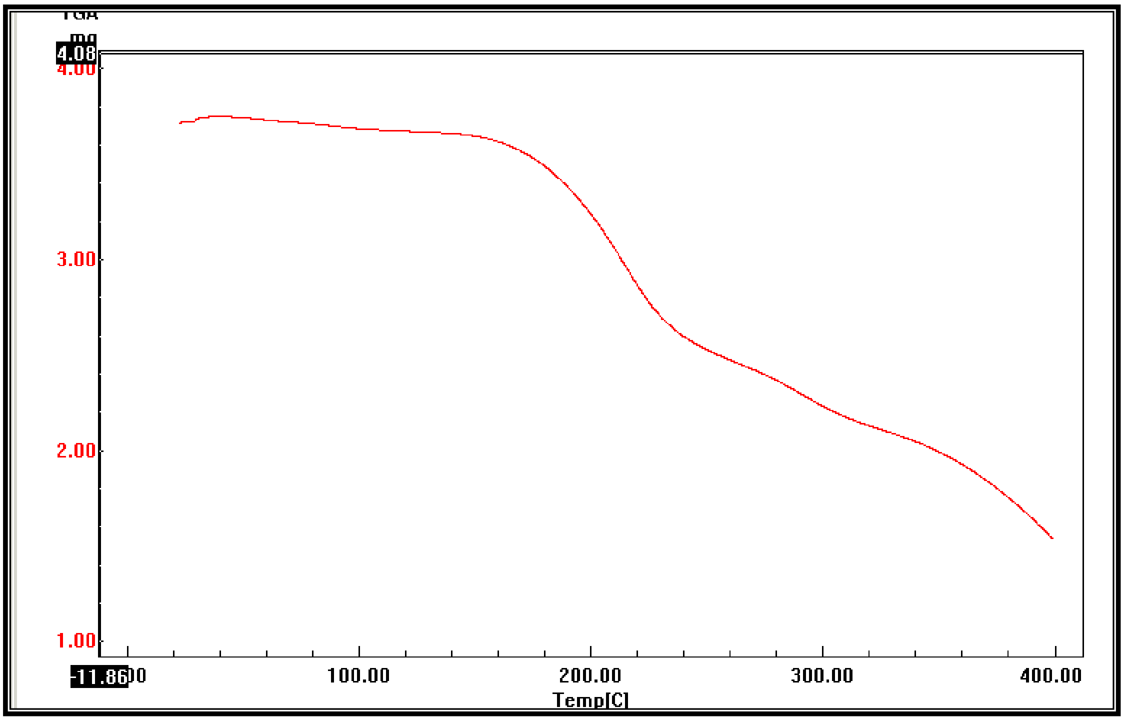

Fig.(7): TG for compound [6]

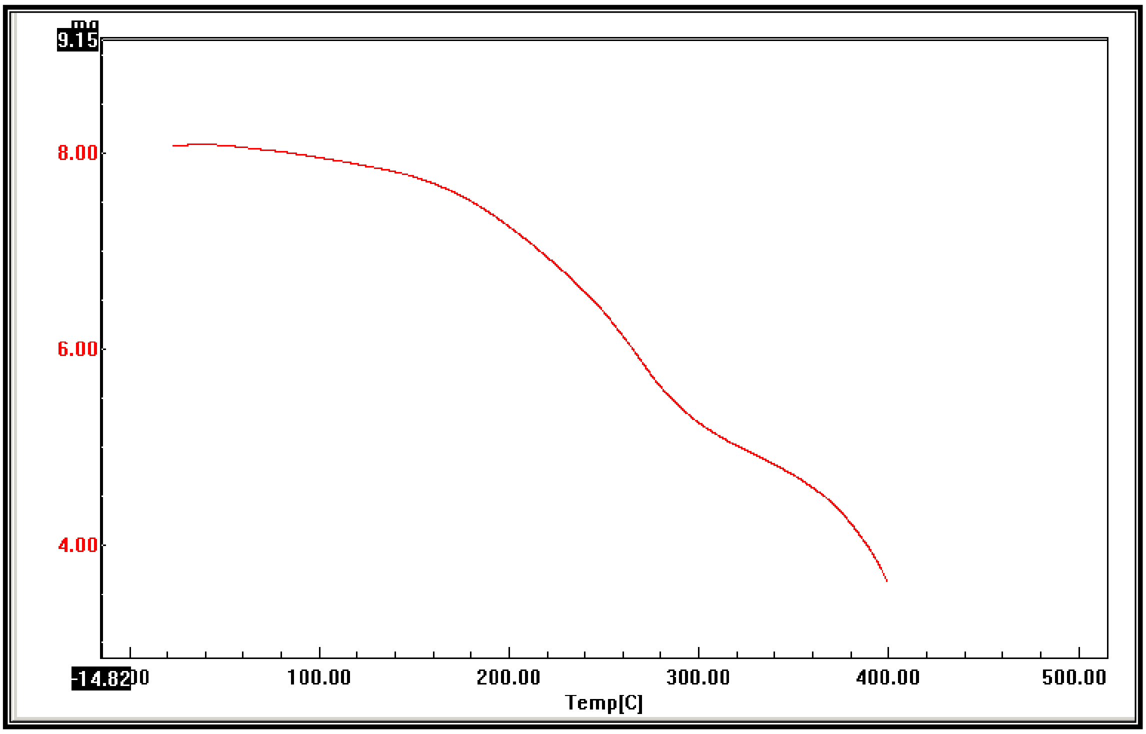

Fig.(8): TG for compound [14]

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تحضير وتشخيص بولي إيمايدات جديدة بواسطة بولي أكريل كلورايد مع أمايدات مختلفة

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الخلاصة :

حضر في هذا البحث بولي ايمايدات جديدة معوضة وغير معوضة (1-17) من تفاعل بولي كلوريد الاكريلويل مع امايدات مختلفة (اليفاتية , اروماتية) بوجود مذيب مناسب وكمية مناسبة من ثلاثي اثيل امين Et_3N مع التسخين وتم اثبات وبرهنة التراكيب الكيميائية للبوليمرات المحضرة باستخدام الطرق الطيفية ,اطياف الاشعة تحت الحمراء FT-IR , اطياف الرنين النووي المغناطيسي ^{1}H-NMR واطياف ^{13}C-NMR واطياف الاشعة فوق البنفسجية UV كماتم التعرف على استقرارية بعض البوليمرات المحضرة حرارياً عن طريق التحاليل الحرارية بالاضافة إلى القياسات الفيزيائية المختلفة من درجات التلين ودرجات الانصهار والذوبانية وقياس PH .