Synthesis of Poly (N-Substituted imine) Acryl Amides derivatives from poly acryloyl hydrazine

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(Received on 20 /7 /2005) **(Accepted for publication on 4 / 3 /2006)**

Abstract

Reaction of poly (acryloyl chloride) with hydrazine gave Poly (acryloyl hydrazine) which upon treatment with various aldehydes and ketones afforded the corresponded Schiff bases polymers containing pendant amine which added good physical properties and high thermal stability. FT-IR spectrum , C.H.N analysis , softening point , melting point and solubility were used to characterize the synthesized polymers .

الخلاصة

تم في هذا البحث مفاعلة بوليمر الاكريلويل كلورايد Poly acryloyl chloride مع الهيدرازين المائي ليعطي بولي اكريلويل هايدرازين (Poly (acryloyl hydrazine ومن ثم مفاعلته مع الالديهايـدات والكيتونات المختلفة ليعطي ثماني بوليمرات جديدة بشكل قواعد شيف حيث تحوي سلسلتها البوليمريـة علـى مجموعة امينية متدلية التي اضافت الى هذه البوليمرات صفات فيزيائية جيدة من استقرارية وثبات حـراري عالي ، تم تشخيص المركبات المحضرة باستخدام طيف الـ FT – IR وتحاليل الـ C , H , N ودرجـات التلين ودرجات الانصهار والذوبانية وقد دلت النتائج المستحصلة على صحة التراكيب المقترحة .

Introduction

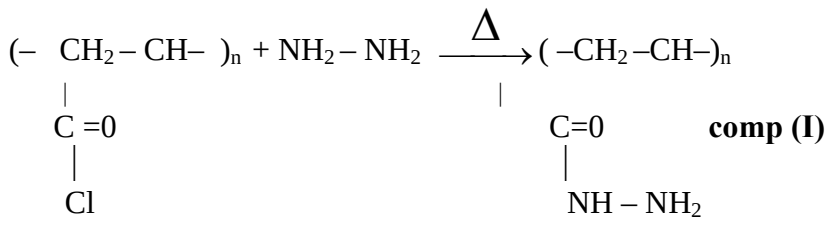
Acryloyl chloride can be polymerized easily to linear polymer at room temperature by exposure to ultra – viotet light in quartz tubes [(1)]. Poly acryloyl chloride can also be prepared by treating poly (acrylic acid) with thionyl chloride [(2).]

Other route to prepare poly (acryloyl chloride) is by photoinitiated polymerization of acryloyl chloride [(3)], from which polyamide (PA) was prepared , which is known by the

trade name nylon , and it consists of highly ordered molecules of high tensile strength.Amides can also be prepared from acids by treatment with thionyl chloride and then with ammonia [4]

The acrylamide solution is stabilized by oxygen and small amounts (25–30) ppm based of acrylamide of cupric ion. Several other types of stabilizers, such as ferric ion [5,6] and ethylenediamine tetracetic acid (EDTA) [7,8,9], Sulfate salt of acryamide can be used as a base on an ion – exchange colum [10] and N – substituted acrylamides [11] . So poly amides were synthesized as the same route of amide, many main routes have been mentioned to prepare these compounds [12 – 17].

One of these routes which was used in this paper was from poly acryloyl chloride with hydrazine to give poly (acryloyl hydrazine)



comp (I)

Modification of polymer I to polymers containing pendant N –substituted amine groups give poly Schiff bases which known to posses biological activity behavior [18 – 24].

Experimental

Melting points were determined on Gallen kamp Melting points apparatus (MFB – 600), Softening points were determined using Reichert thermovar, Sp_1 10/0.25, 160. Elemental analysis of compounds was carried out on C.H.N.S – O, EA7708 Elemental analyzer, CARLO – ERBA instruments, and FT – IR were preformed using FT- IR absorption spectra , KBr discks were used on a RT-IR- 84005 , FOURIER Transform infrared spectrophotometer. SHIMADZU

Preparation of poly (acryloyl hydrazine)[25] [I]

A mixture of poly (acryloyl chloride) (0.1mole) and hydrazine hydrate (99%) (0.1mole) in dimethylformamide (DMF) (25 ml)

was refluxed for 12 hrs. After cooling the excess of solvent was removed under vacum and the solid separated was filtered and purified by dissolving at DMF and reprecipitating from acetone. Conversion of yielded polymer was (65%).All physical properties are listed in Table (1, 2) . The FTIR absorptions for the prepared polymer is shown in Figure (1).

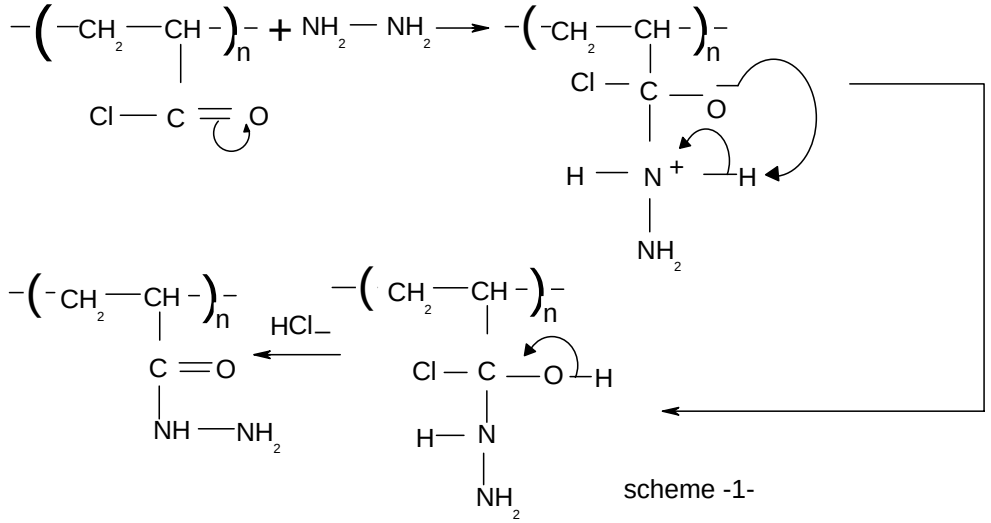
Preparation of N – (substituted imine) acryl amide[poly chiff bases] [2 – 9] [26]:

Compound [1] (0.01 mole) was dissolved in (20 ml) of dry THF, appropriate aliphatic and aromatic aldehydes and ketones (0.01mole) was added to the mixture, that has been refluxed for (8 – 12) hrs and cooled. The product was precipitated and filtered off, then purified from appropriate solvent .All physical properties are listed in Table (1,2) the

FT–IR absorptions spectra for the prepared polymers are shown in Figs (2 – 9).

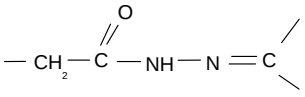
Results and discussion

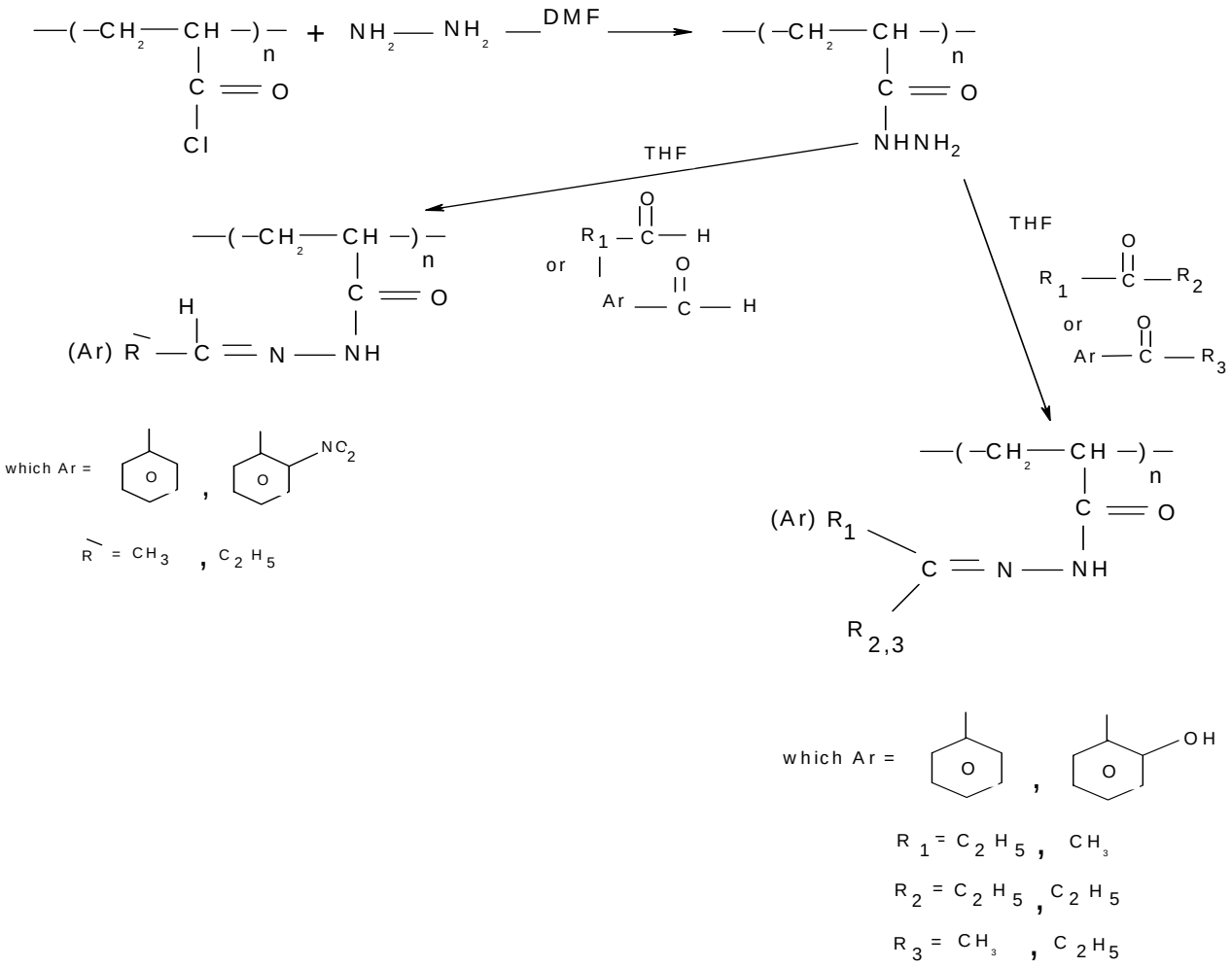
Although there are several procedures for the preparation of N – substituted amides [7, 8, 9], one of them was found suitable for the preparation of poly N – amino acryl amide (or poly acryloyl hydrazine) from reaction of poly acryloyl chloride with hydrazine. The mechanism of the condensation reaction is shown in schem -1- :-



scheme -1-

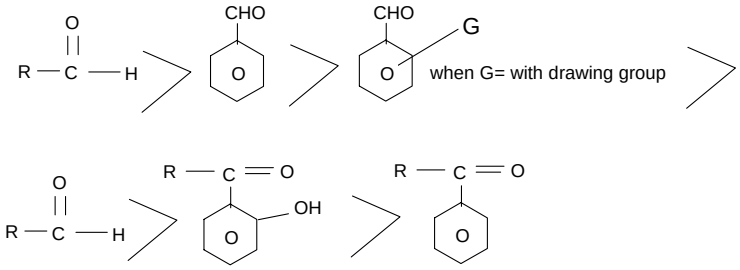
All physical properties and elemental analysis for poly acryloyl hydrazine (I) are listed in Tables (1 – 3) .The FT–IR spectrum show absorption band at 3400 – 3450 cm^{-1} for NH_2 group and at 3317 cm^{-1} for N – H group , and the absorption band around 2343 cm^{-1} due to stretching for

primary and secondary amines , the FT – IR spectrum showed strong absorption band in the region 1690 cm^{-1} which is typical for the C=0 stretching vibration of carbonyl amide .The chemical reactivity of the NH_2 group in compound (I) plays a significant role in using this compound as a good synthon in the synthesis of new schiff bases as poly N – (substituted imine) acryl amide or poly N- hydrazines acrylate by reaction of compound (I) with various aldehydes and ketones in dry THF. The FT – IR spectra of polymers (2 – 9) show strong absorption band in the region 1662 – 1687 cm^{-1} which are typical for the C=N stretching vibration of poly N- substituted imine (poly hydrazones) [27]. In the spectra of the N – acryl hydrazones the absorption band of these groups are shifted to higher frequency and appear at 1700 – 1701 cm^{-1}. [28].It is know that N – acryl hydrozones  can exist in four stereoisomeric forms due to geometrical isomers about the C=N band (E and Z – isomers) and rotational (conformational) isomerism due to hindered amide rotation around the C – N band of the acryl fragment[29 – 30] . In The FT – IR spectra [31] of the poly N- substituted imine which contain N – acryl hydrazones the stretching vibrations of the C=0 group appear as doublet absorption band in the region 1700 – 1660 cm^{-1} (table 4). Associates with an intermolecular hydrogen band of the type C=0 ····· H – N are absent in solution since the appearance of the spectrum is not changed with dilution. These poly hydrazones acrylate were characterize by useing physical properties and elemental analyses and structures and FT–IR spectray all these characterized listed in tables(1–4) and in Figs (2–8) . Scheme (2) summarized all the performed reactions in this work



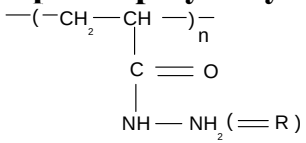
Scheme-2-

All aliphatic aldehydes and ketones have a good conversion in comparison with aromatic aldehydes and ketons as can be seen in the following arrangement



This arrangement is due to steric hindrance and electronic effect. The solubility and melting points of all prepared poly N – (substituted imine) acryl amides indicate the formation of high thermal stable polymers .

Table 1: Physical properties of prepared poly acryl hydrazine and its derivatives



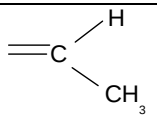
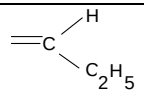
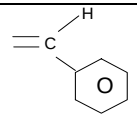
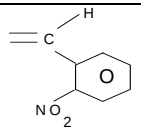
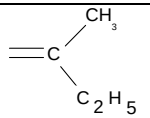
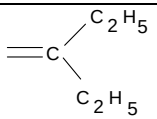
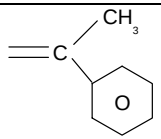
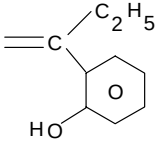
Comp No.	Poly	= R Substituted	Conversion %	Co lour	Softening point S.P. C°	Melting point Tm C°
1.	acryl hydrazine		65	Yellowish		Dec.
2.	N- (methyl imine) acryl amide		89	Red	260-280	>360
3.	N-(ethyl imine) acryl amide		63	Yellow	154-170	>360
4.	N-(pheny imine) acryl amide		48	Yellow	260-285	>360
5.	N-(o-nitro pheny imine) acryl amide		29	Yellow	200-215	>360
6.	N,N-(methyl ethyl imine) acryl amide		53	Yellow - reddish	180-205	>360
7.	N,N-(Diethyl imine)acryl amide		50	Yellow - reddish	240-256	>360
8.	N,N-(methyl phenyl imine) acryl amide		30	Yellow	200-215	>360
9.	N,N-(ethyl –o-hydroxy phenyl imine) acryl amide		44	Yellow	260-280	>360

Table 2: Solubility of prepared poly – N – (substituted imine) acryl amide.

Comp No.	MeOH	EtOH	THF	DMF	$CHCl_3$	CCl_4	$(CH_3)_2CO$	$(C_2H_5)_2O$	$C_4H_4O_2$	$PhCH_3$	C_6H_6	C_6H_{12}
1.	–	–	+	++	–	–	–	–	–	–	–	–
2.	–	–	+	+	–	–	–	–	–	–	–	–
3.	–	+	+	+	–	–	+	+	–	–	–	–
4.	–	+	+	+	–	–	+	+	–	–	–	–
5.	–	+	+	+	+	–	+	–	–	+	+	–
6.	+	+	+	+	–	–	+	–	–	–	+	–
7.	–	–	–	+	–	+	+	–	–	–	–	–
8.	+	+	+	+	–	–	+	–	+	+	–	–
9.	+	+	+	–	+	+	+	+	–	+	–	–

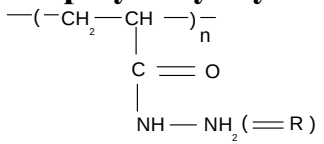
C_6H_{12}:Cyclohexane
$C_4H_8O_2$:Dioxane

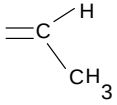
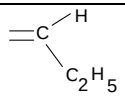
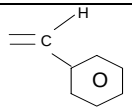
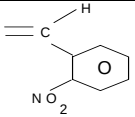
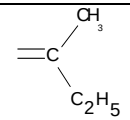
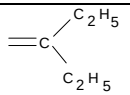
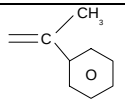
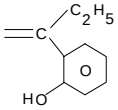
Table 3: Elemental analyses of poly acryl hydrazine and some of poly – N – substituted imine acryl amides.

Comp No.	Elemental analyses	C %	H %	N%
1.	Calc. Fou.	41.86 42.09	6.98 5.87	32.56 31.98
2.	Calc. Fou.	53.57 53.09	7.14 7.55	25.01 25.00
4.	Calc. Fou.	68.97 68.16	5.75 5.24	16.09 15.87
6.	Calc. Fou.	60.00 59.76	8.57 8.43	20.00 20.41
8.	Calc. Fou.	70.21 70.01	6.38 5.98	14.89 14.28

Calc. = Calculated
Fou. = Found

Table 4: FT-IR spectra of poly acryl hydrazine and its derivative



Comp. No.	=R	ν (N-H) cm^{-1}	ν (C-H) ar.cm^{-1}	ν (C-H) Vinyl.cm^{-1}	ν (C-H) allph. cm^{-1}	ν (C=O) cm^{-1}	b(N – H) cm^{-1}	ν (C=C) ar.cm^{-1}	ν (C-N-N) ν (O-C-N) cm^{-1}	ν (C=N) cm^{-1}	Others cm^{-1}
1		3317			2750 2890	1690	2343		1430 1350	1668	V – NH_2 3400 - 3450
2		3413		3022	2927 2850	1701	2345		1420 1373	1670	
3		3340		3100	2920 2835 2736	1676	2364		1394 1326	1622	
4		3411	3236	3056	2927	1637	2376	1612 1508 1490	1448 1363	1627	
5		3473	3178	3020	2937	1701	2345	1610 1590 1508	1357 1332	1629	
6		3433			2933 2897	1701	2345		1442 1346	1637	
7		3315			2990 2877 2812	1700	2345		1382 1355	1629	
8		3310			2970 2810	1701	2345		1410 1323	1687	
9		3303	3238		2999 2935 2877	1710	2345	1610 1508 1490	1448 1373	1629	V- OH Phenolic 3530

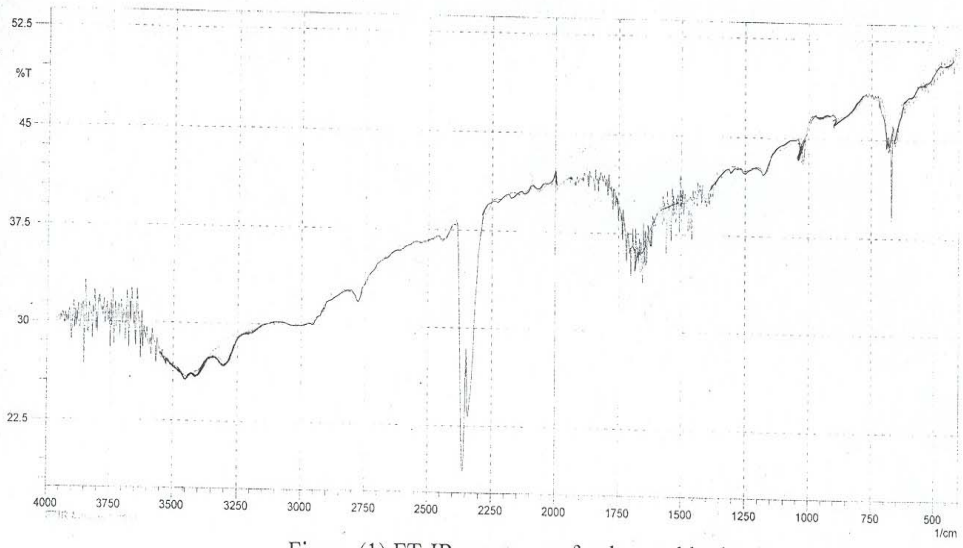


Figure (1) FT-IR spectrum of poly acryl hydrazine

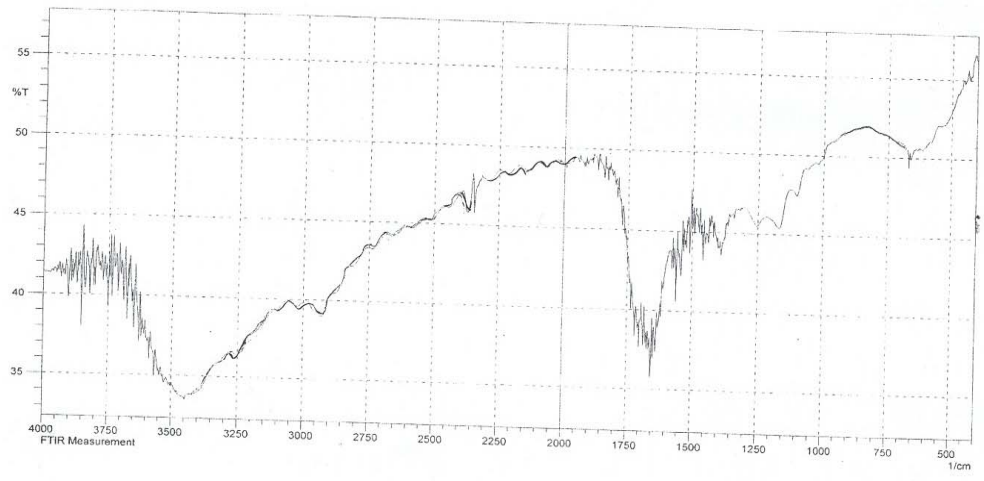


Figure (2) FT-IR spectrum of N- (methyl imine) acryl amide

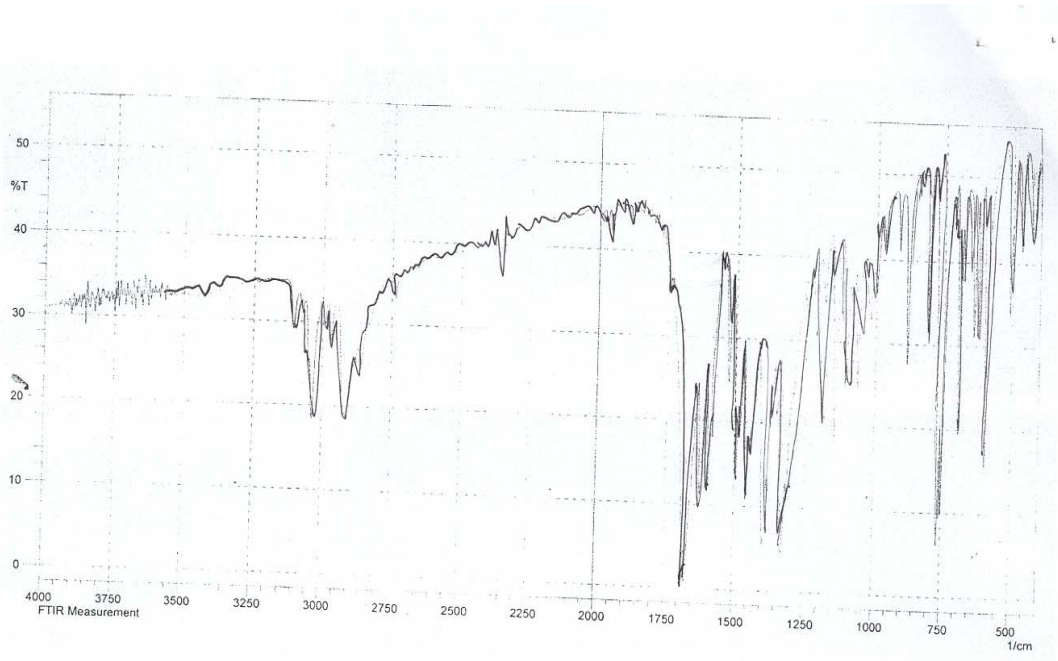


Figure (3) FT-IR spectrum of N-(ethyl imine) acryl amide

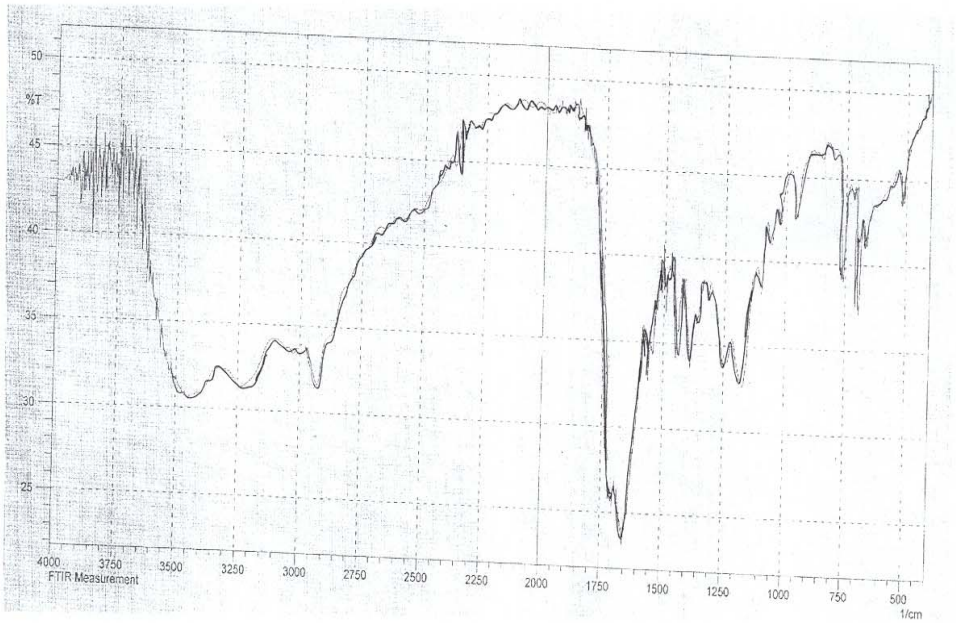


Figure (4) FT-IRspectrum of N-(pheny imine) acryl amide

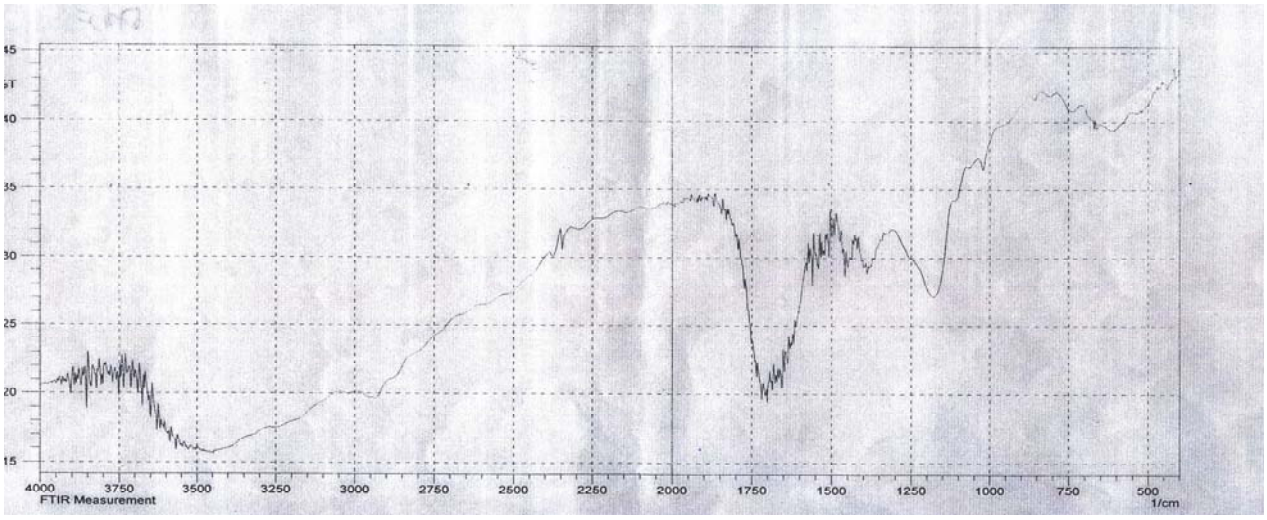


Figure (5) FT-IR spectro of N-(o-nitro pheny imine) acryl amide polymer

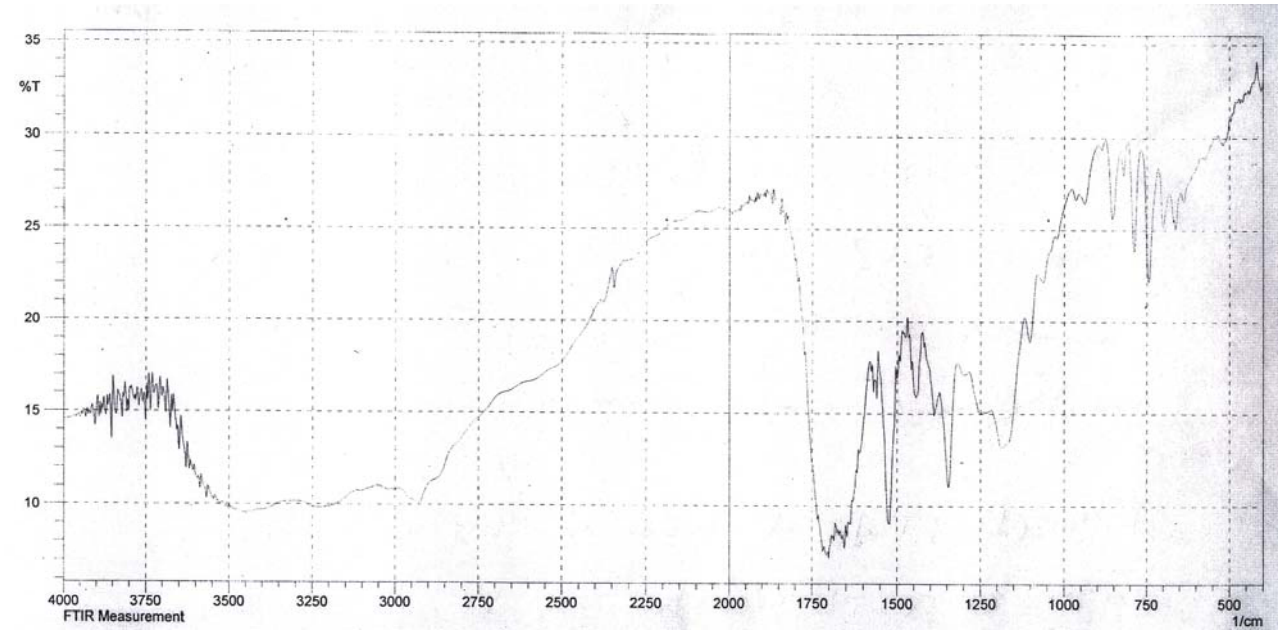


Figure (6) FT-IR spectro of N,N-(methyl ethyl imine) acryl amide polymer

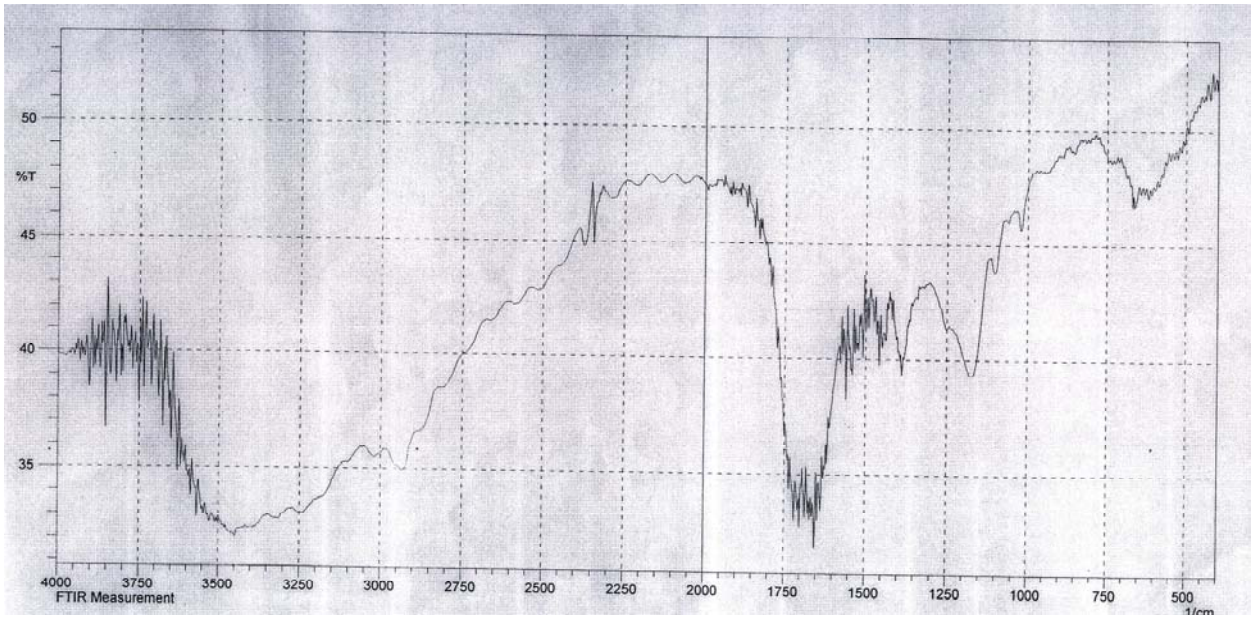


Figure (7) FT-IR spectro of N,N-(Diethyl imine)acryl amide polymer

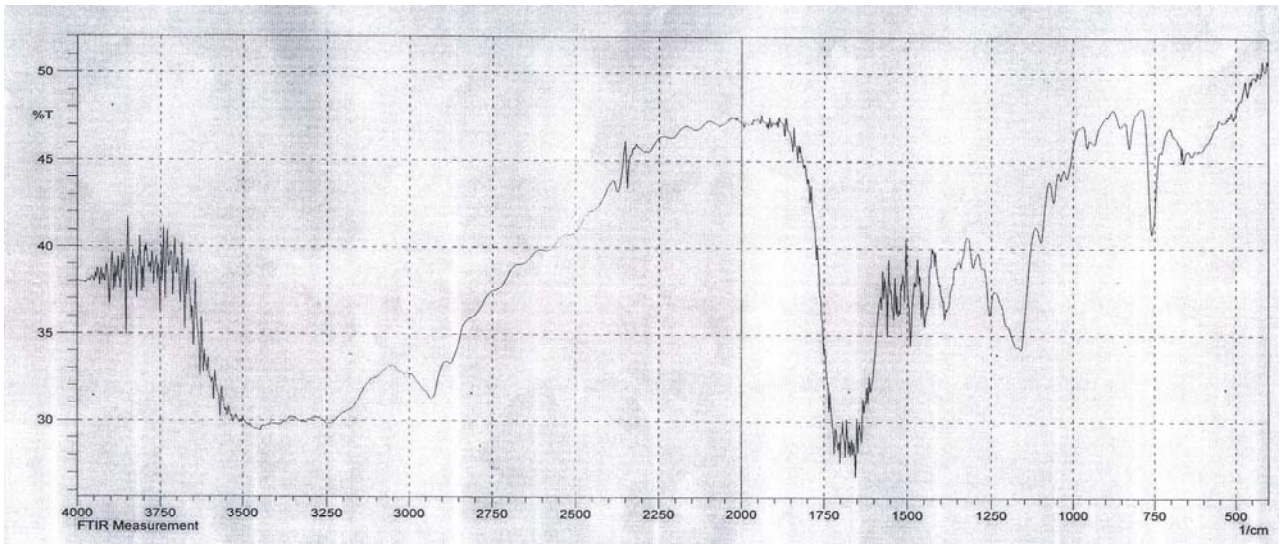


Figure (8) FT-IR spectro of N,N-(ethyl –O-hydroxy phenyl imine) acryl amide polymer

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