Synthesis of Poly [(N – Acryl) Substituted Hydrazone] from Condensation of Poly Acryloyl Chloride with Various Schiff Bases

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Abstract

In the present investigation, new eight polymers of poly [(N–acryl) substituted hydrazone] were synthesized by two steps; first step includes treatment of 2, 4–dinitro phenyl hydrazine with different aldehydes or Ketones to obtain Schiff bases. The second step includes Condensation hydrazone groups (Schiff bases) with poly acryloyl chloride in DMF to obtain poly [(N – acryl) substituted hydrazone].

All the synthesized polymers were characterized by FT– IR spectrum, UV spectrum, melting and softening points and solubility, then study the Biological activity for some of these new polymers.

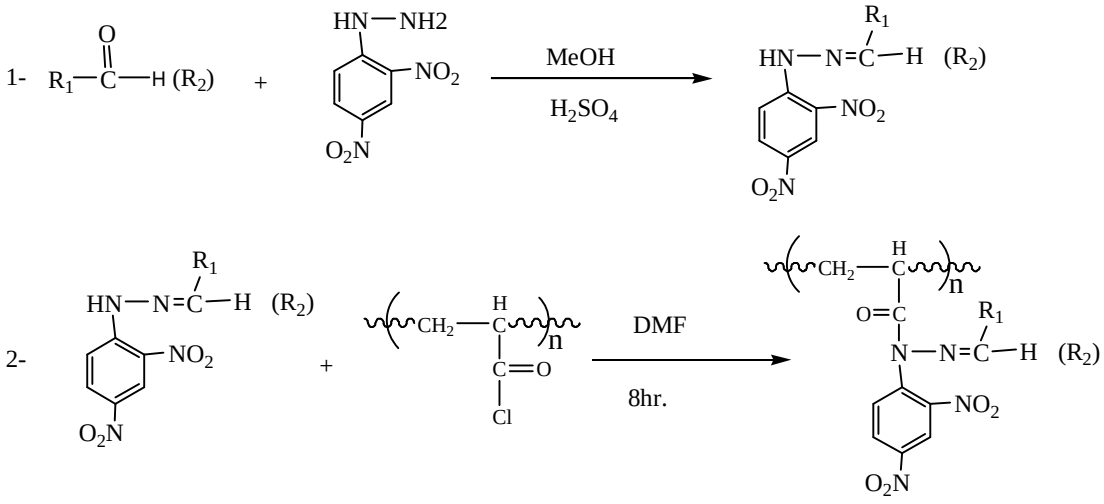
Introduction

Acryloyl chloride can be polymerized easily to linear polymer at room temperature by exposure to ultra-violet light in quartz tubes[1]. This important polymer can be enter many reactions to get a large numbers and types of polymers which added good physical properties and high thermal stability. A series of novel azo poly electrolytes have been synthesized from poly (acryloyl chloride)[2], and new kind of polyesters were modified with palmitoyl chloride and acryloyl chloride[3].

Other route to prepare poly (acryloyl chloride) is by photo initiated polymerization of a cryloyl chloride[4] from which poly amide (PA) known by trade Nylon was prepared and it consists of highly ordered molecules of high tensile strength.

Polyamide, poly hydrazide were synthesized by the same route of amide by the reaction of poly acryloyl chloride with ammonia [5] or hydrazine [6].

One of these routes which was used in this paper was from reaction of poly acryloyl chloride with hydrazone groups of 2, 4 – dinitro phenyl hydrazone to product poly [(N – acryl) substituted hydrazone]I.



compound 1

poly[(N-acryl) substituted hydrazone]

Note : The structure of R1 and R2 are listed in Table (1) .

Experimental

1. Melting points were determined on Gallen kampmelting points apparatus (MFB–600).
2. Softening points were determined using Reichert Thermovar, SP1, 10, 0. 25, 160
3. FT–IR absorption spectra were recorded using KBr disks of FT–IR –8400S, FOURIER TRANSFORM INFRARED SPECTROPHOTO–METER, SHIAMZU.
4. UV absorption spectra were recorded with Schimadsu. Recc–160 spectrophotometer in (DMF).

Preparation of Schiff bases[7] :

(0. 25 gm) of 2, 4–dinitro phenyl hydrazine was dissolved in (15 ml) of methanol, and a few drops of a concentration H2SO4 were added, various aldehydes or Ketones (0.001) mole were dissolved in suitableamount of methanol, and added to acidic hydrazine solution. The mixture was heated at (70-75) C^{O} for few minute. After cooling the yellow or orange precipitate was separated, filtered and recrystallized from ethanol.

Preparation of [(N – acryl) substituted hydrazone] [8] :

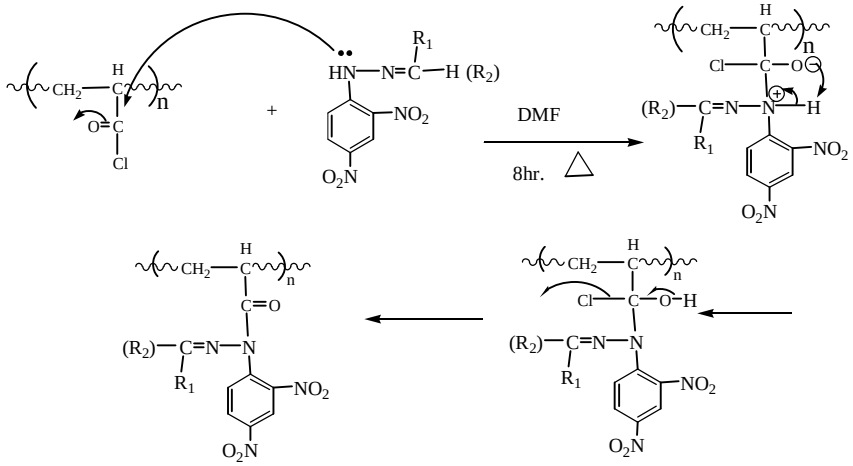
Equimolar of poly acryloyl chloride and the product of Schiff bases were dissolved in (25 ml) DMF, the mixture was refluxed for (8 hr).

After cooling, the viscous liquid was poured into (100 ml) cooled distilled water, the precipitated was separated, filtered and purified by dissolving in THF and repreciptated from water.

Physical properties were listed in Table (2).

Results and Discussion

Although there are several procedures for the preparation of N – substituted amides,[9-11] one of them was found suitable for the preparation of poly acryloyl hydrazone from reaction of poly acryloyl chloride with serious products of hydrazone derivatives, the mechanism of the condensation reaction is shown in Scheme (1) :



Scheme (1).

In the present work eight new polymers were synthesized by two steps of reactions:

The first step include reaction of 2, 4_dinitro phenyl hydrazine with various (aliphatic and aromatic aldehydes and Ketones), prepared schiff bases were reacted in the second step with poly acryloyl chloride to get eight new colored polymers as shown in Scheme (2).

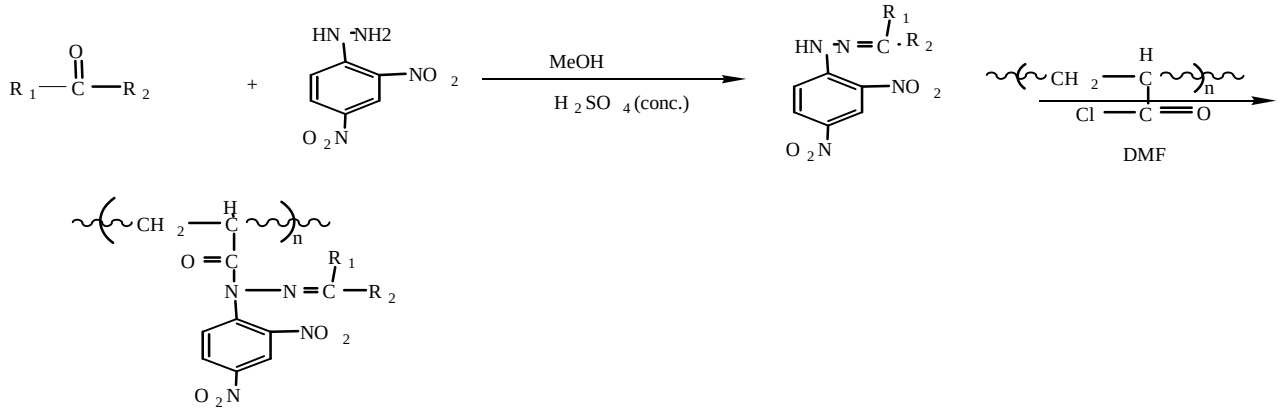
All physical properties of these polymers are listed in Table (2).

The FT – IR spectra of polymers (1 – 8) show a strong absorption band in region (1580 – 1620) cm^{-1} which are typical for the C=N stretching vibration and in region (1630 – 1720) cm^{-1} for the C=O stretching vibration of poly(N – acryl) substituted hydrazone [12] and show absorption band of (C–H) aromatic and aliphatic stretching vibration in 3100 cm^{-1}, 2920 cm^{-1} respectively for various aldehydes and Ketones.

In the region (1520 – 1330) cm^{-1} we characterized the stretching vibration for – NO_2 groups.

UV spectra show different values of λ max between (300 – 550) nm in visible region, other spectral data shown in Table (3).

The Biological behavior [13 – 19] for four synthesized polymers had been studied towards two types of bacteria ; (E. coli & S. aureus) it was found they had no inhibition effects towards these types of bacteria. All of these polymers were soluble in DMF, THF and acetone and all of these were precipitated by water as shown in Table (4).



Scheme (2).

Table (1)
Structure of R1, R2.

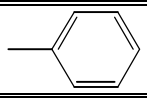
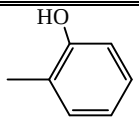
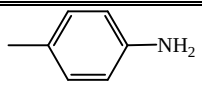
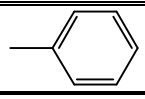
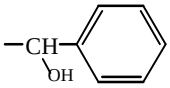
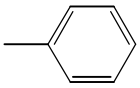
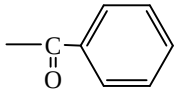
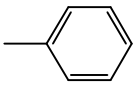
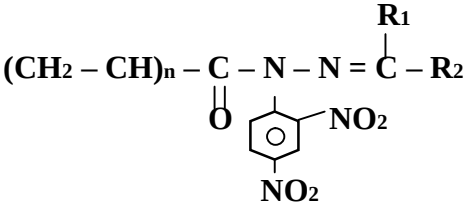
Comp. No.	R_1	R_2
1		—H
2		—H
3		—H
4	—CH_3	—CH_3
5	—CH_2CH_3	—CH_3
6		—CH_3
7		
8		

Table (2)
Physical properties of poly [(N – acryl) substituted hydrazone].



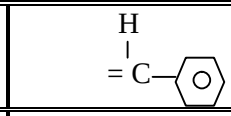
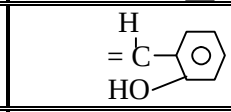
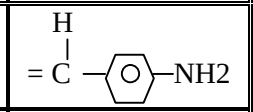
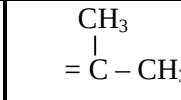
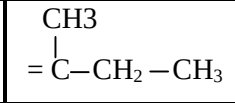
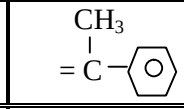
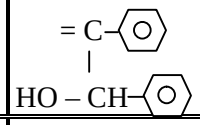
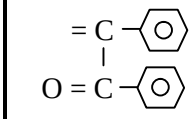
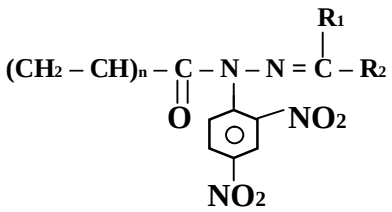
Comp. No.	*Nomencalture of new Polymers*	*R1 | = C – R2*	*Conversion %*	*Color*	*S. P. c°*	*M. P. c°*
1	Poly [(N – acryl) benz – 2, 4 – dinitro phenyl hydrazone]		80 %	Orange	270 – 290	290 – 295
2	Poly [(N- acryl) – 0 – hydroxyl benz – 2, 4 – dinitro phenyl hydrazone]		85 %	Brown	218 – 238	238 – 241
3	Poly [(N – acryl) – p – amino benz – 2, 4 – dinitro phenyl hydrazone]		70 %	Red	205 – 225	225 – 230
4	Poly [(N – acryl) dimethyl – 2, 4 – dinitro phenyl hydrazone]		50 %	Red	256 – 276	276 – 281
5	Poly [(N – acryl) methyl ethyl – 2, 4 – dinitro phenyl hydrazone]		60 %	Red	265 – 283	285– 288
6	Poly [(N – acryl) methyl benz – 2, 4 – dinitro phenyl hydrazone]		65 %	Orange	263 – 280	283 – 288
7	Poly [(N – acryl) benz hydroxy benzyl – 2 – 4 – dinitro phenyl hydrazone]		82 %	Orange	198 – 220	222 – 230
8	Poly [(N – acryl) benz phenoxy – 2, 4 – dinitro phenyl hydrazone]		88 %	Brown	255-276	276-280

Table (3)
FT – IR & UV spectra of poly [(N – acryl) substituted hydrazone].



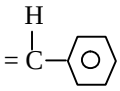
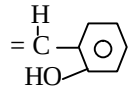
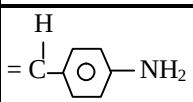
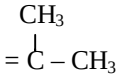
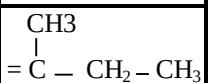
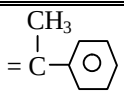
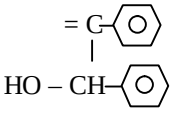
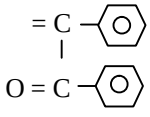
Comp. No.	*R1 | = C – R2*	*υ C – H aromatic*	*υ C – H aliphatic*	*υ C = N*	*υ – NO2*	*υ C = O*	*υ C – O*	*υ C – N*	*υ C = C*	*υ Other*	*UV l max (nm)*
1.		3120	2930	1588	1520	1660	1112	1320	1620, 1590	—	390
2.		3139	2923	1590	1512	1710	1140	1334	1620, 1590	υ – OH 3427	480
3.		3132	2923	1620	1512	1680	1134	1350	1620, 1500	υ – NH_2 3409	540
4.		3271	2923	1589	1504	1666	1114	1319	1666, 1589	—	310
5.		3120	2923	1596	1504	1650	1064	1350	1670, 1596	—	358
6.		3116	2923	1581	1512	1710	1110	1303	1620, 1581	—	380
7.		3101	2928	1620	1512	1720	1118	1334	1620, 1590	υ – OH 3440	410
8.		3120	2923	1618	1512	1620	1134	1311	1620, 1600	υ C = O 1735	402

Table (4)
Solubility of prepared poly [(N – acryl) substituted hydrazone].

Comp. No.	*$CHCl_3$*	*H_2O*	*THF*	*DMF*	*Acetone*	*EtOH*	*MeOH*
1.	–	–	+	+	+	–	–
2.	–	–	+	+	+	+	–
3.	–	–	+	+	+	+	–
4.	–	–	+	+	+	–	–
5.	–	–	+	+	+	+	+
6.	–	–	+	+	+	–	–
7.	–	–	+	+	+	+	+
8.	–	–	+	+	+	–	–

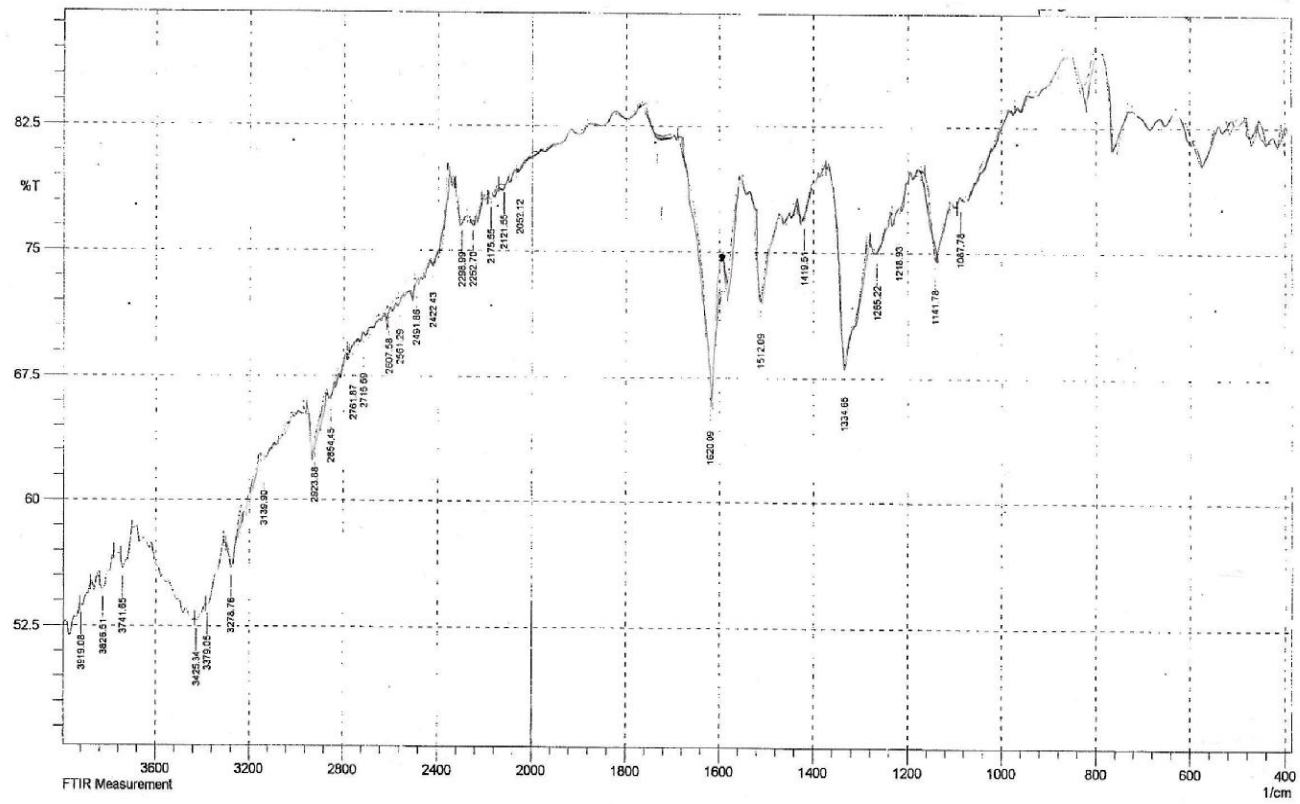


Figure (1) FT – IR spectrum of poly [(N – acryl) – o – hydroxy benz – 2,4 – dinitro phenyl hydrazone].

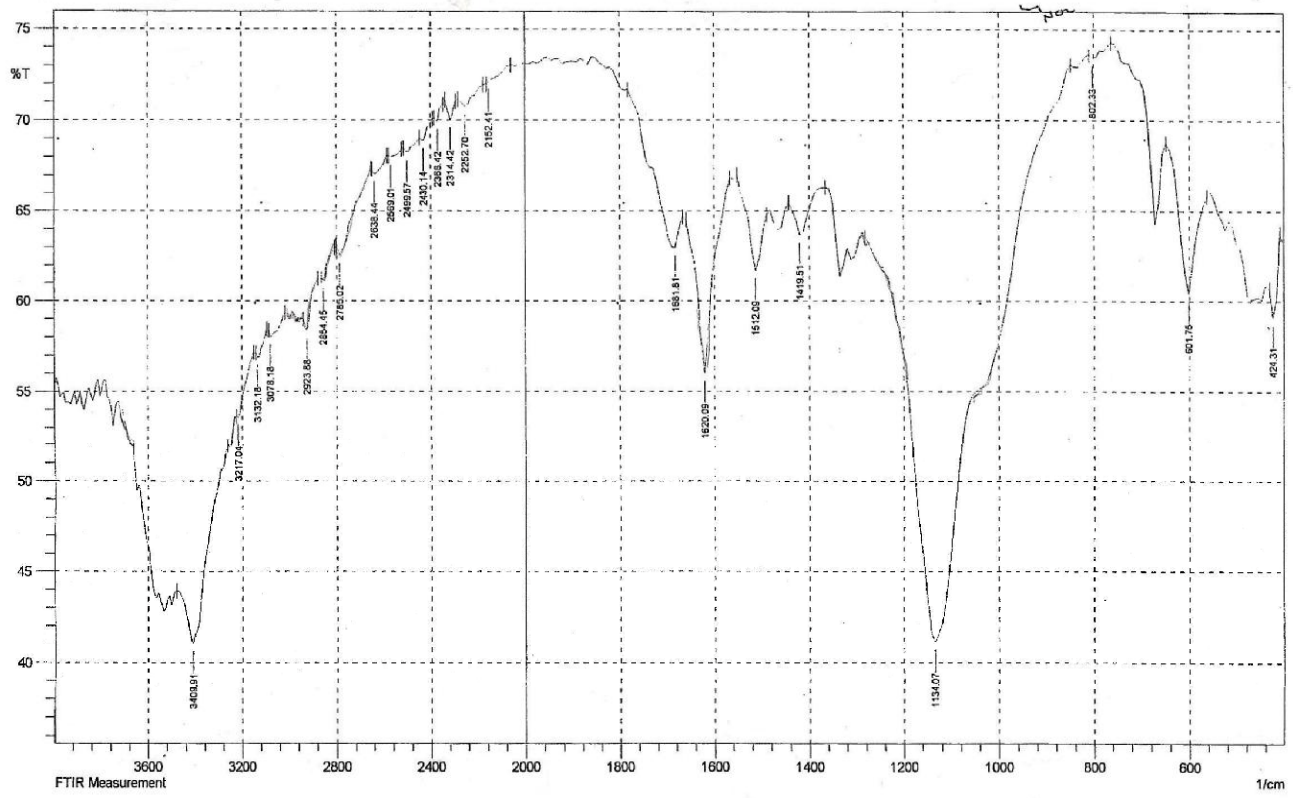


Figure (2) FT – IR spectrum of poly [(N – acryl) – p – amino benz – 2,4 – dinitro phenyl hydrazone].

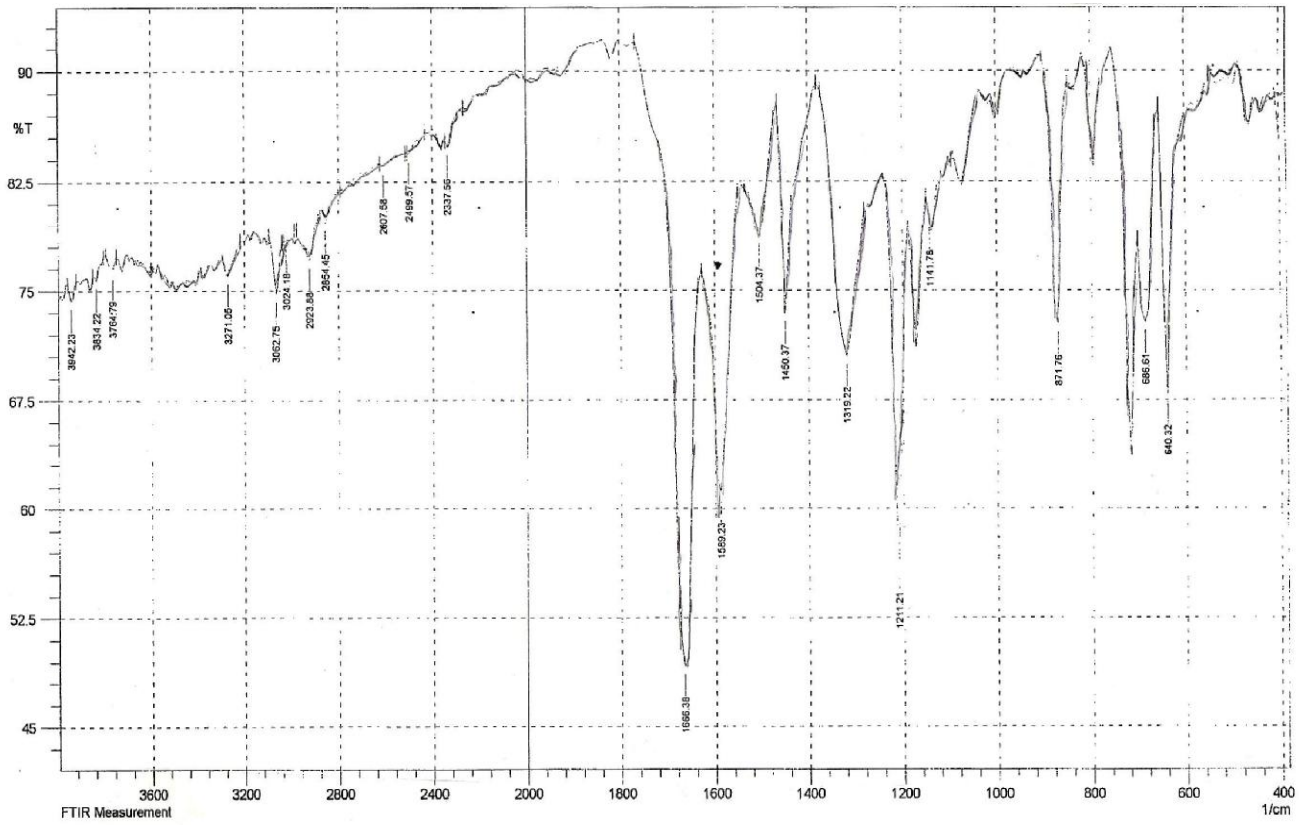


Figure (3) FT – IR spectrum of poly [(N – acryl) dimethyl – 2,4 – dinitro phenyl hydrazone].

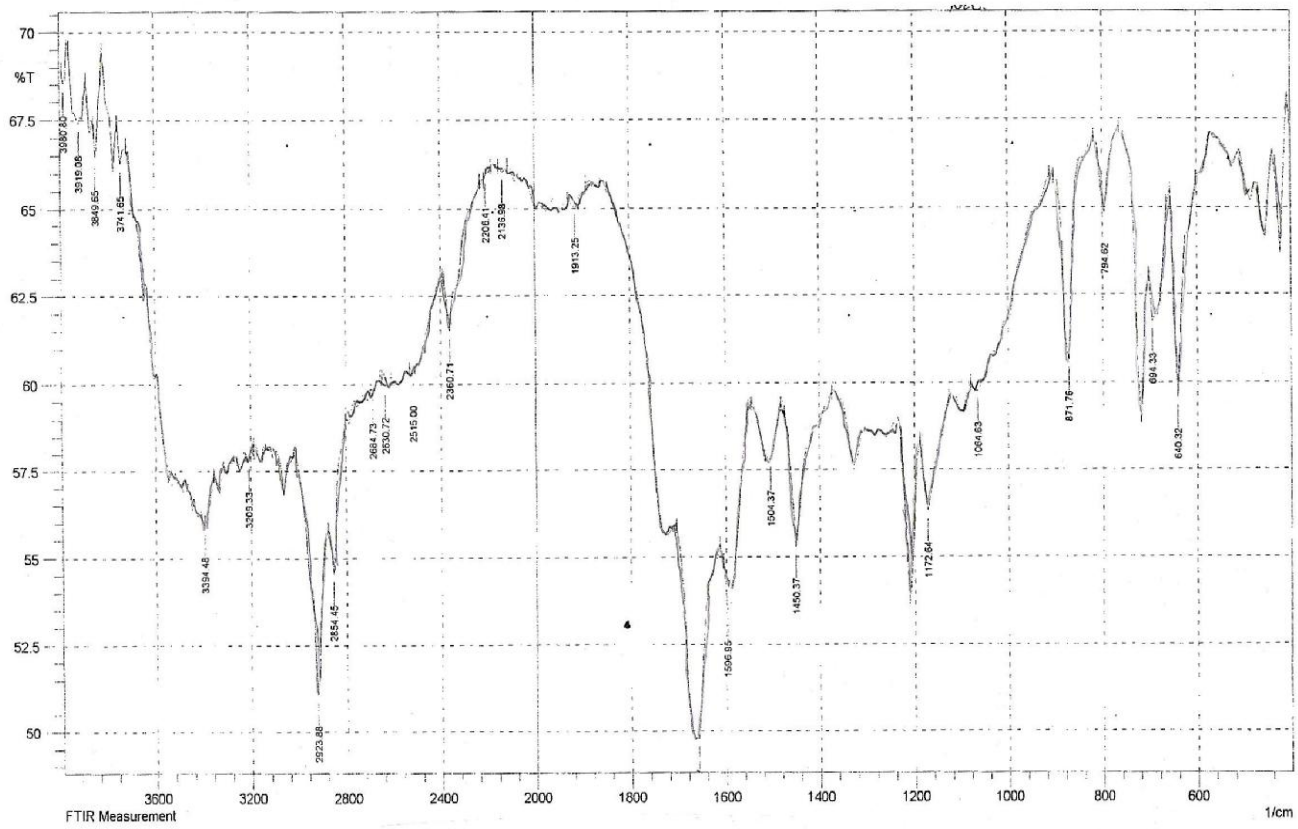


Figure (4) FT – IR spectrum of poly [(N – acryl) methyl ethyl – 2,4 – dinitro phenyl hydrazone].

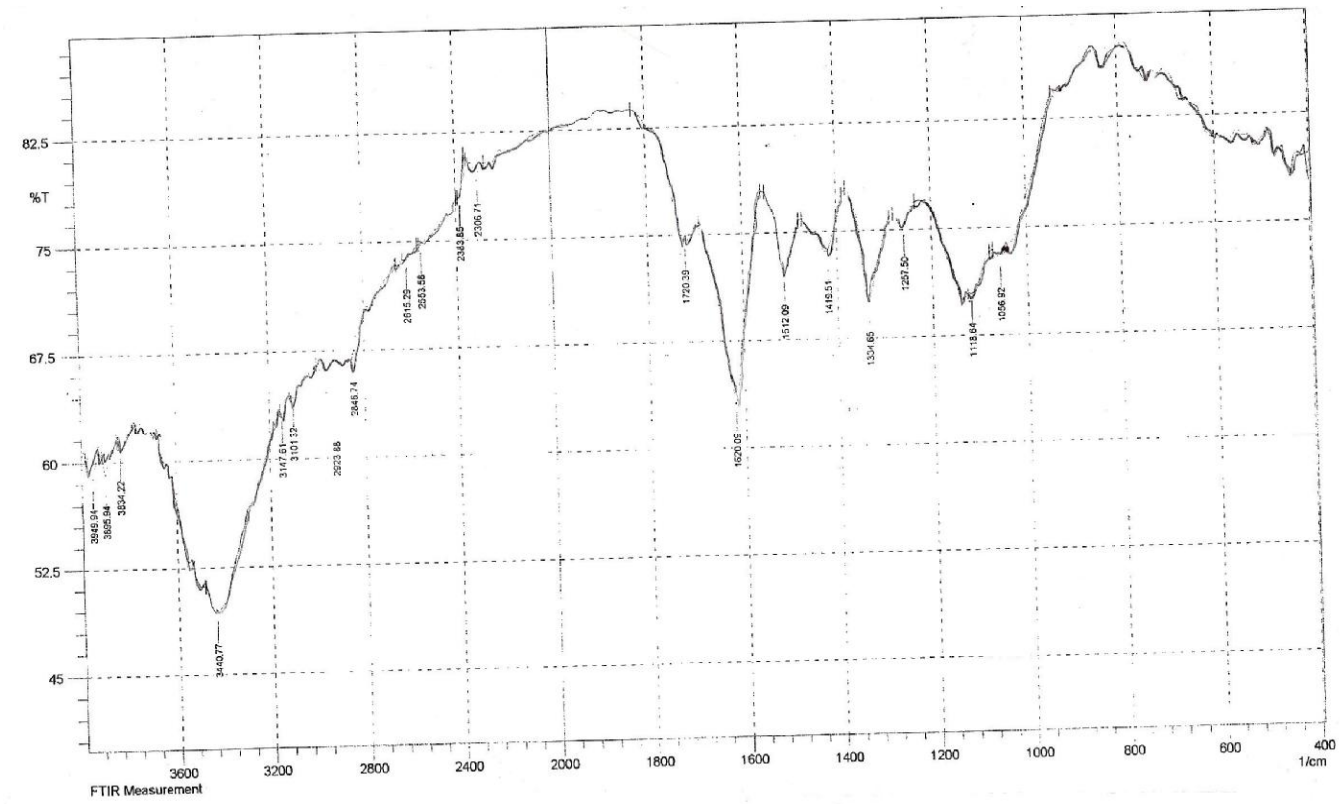


Figure (5) FT – IR spectrum of poly [(N – acryl) benzhydroxy benzyl – 2,4 – dinitro phenyl hydrazone].

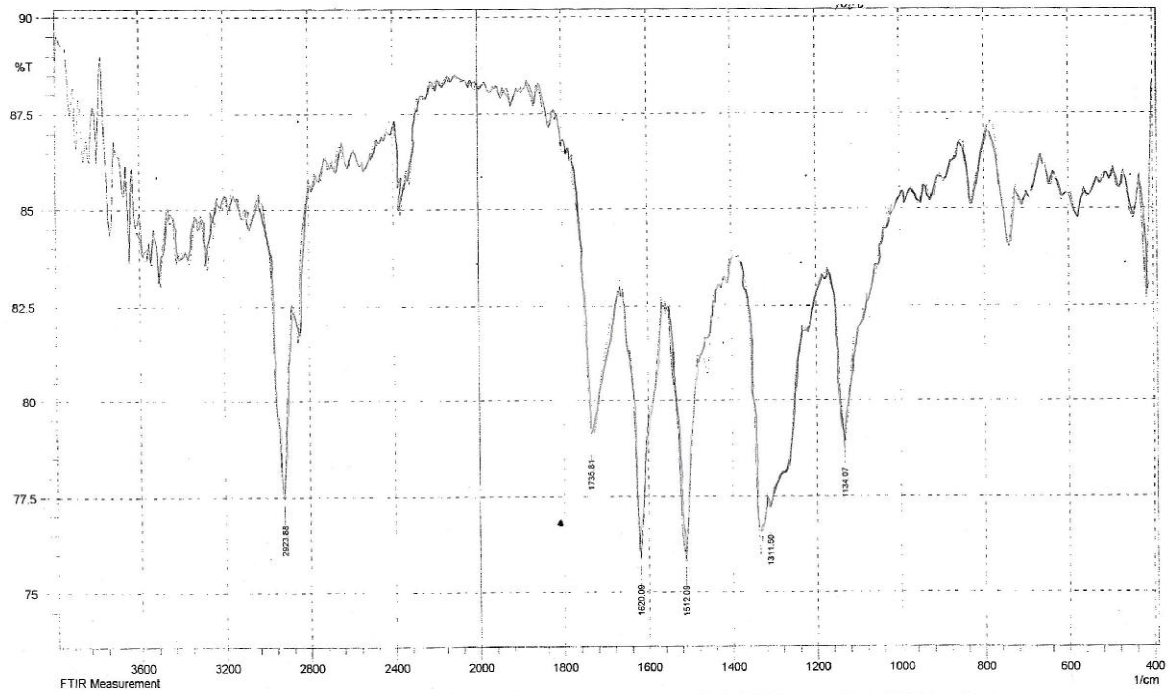


Figure (6) FT – IR spectrum of poly [(N – acryl) benz phenoxy – 2,4 – dinitro phenyl hydrazone] .

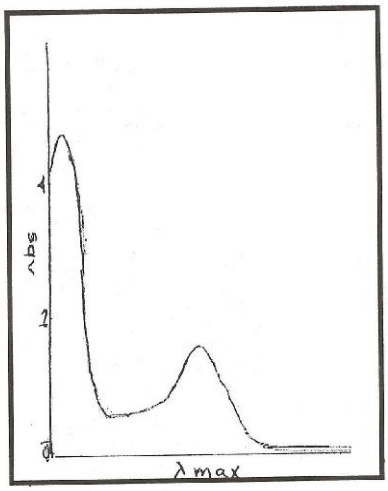


Figure (7) UV Spectrum of comp. (2).

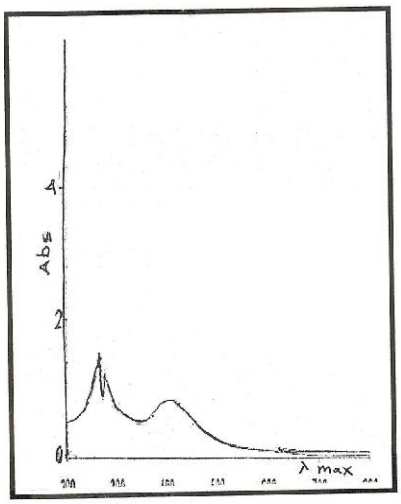


Figure (9) UV Spectrum of comp. (6).

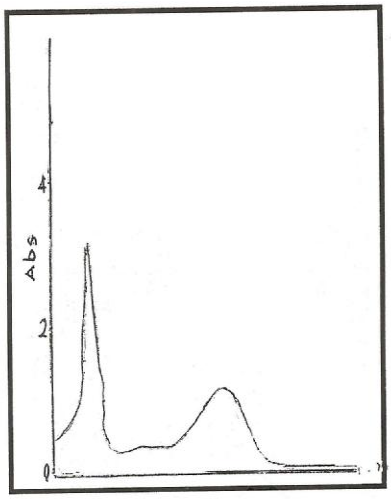


Figure (8) UV Spectrum of comp. (3).

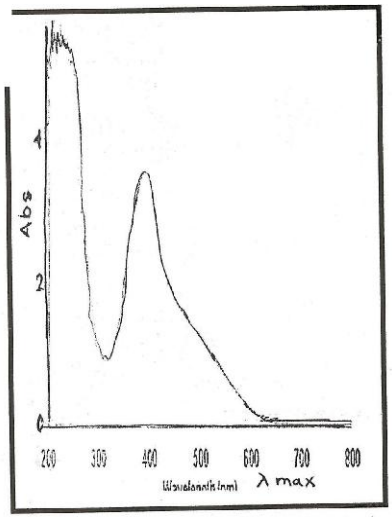


Figure (10) UV Spectrum of comp. (7).

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الخلاصة

تم في هذا البحث تحضير ثمانية بوليمرات جديدة من تحوير بوليمر كلوريد الاكريلويل (acryloyl chloride), حضرت هذه البوليمرات بخطوتين, الخطوة الأولى تضمنت تحضير مركبات الهايدرازونات المعروفة بقواعد شيف (Schiff bases) وذلك من تفاعل الالديهايدات والكيتونات المختلفة مع 4, 2– ثنائي نايتروفينيل هيدرازين ((2, 4–dinitro pheny hydrazine الخطوة الثانية من التفاعل تضمنت تفاعل قواعد شيف مع بوليمر كلوريد الاكريلويل في مذيب الـ DMF ليعطي بوليمرات جديدة من نوع [poly (N– substituted hudrazone] (acryl).

تم تشخيص هذه البوليمرات المحضرة باستخدام اطياف الـFT-IR والـUV وقياس درجات الانصهار والتلين والذوبانية وكذلك دراسة الفعالية البايولوجية لبعض هذه البوليمرات المحضرة.