

Synthesis of new poly (acryl amido - N - oxo – hydrazones derivatives) from poly acryloyl chloride

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Abstract :

In this work , different aldehyds and ketones were reacted with the amino compound (semi-carbazide) to produce the corresponding Schiff bases , and then these bases were reacted with poly acryloyl chloride to produce a new polymers containing imine group in their chains. polymers that prepared were characterized by FTIR spectra and physical analysis via measuring melting points and solubility . The results showed that the prepared polymers , have good physical properties .

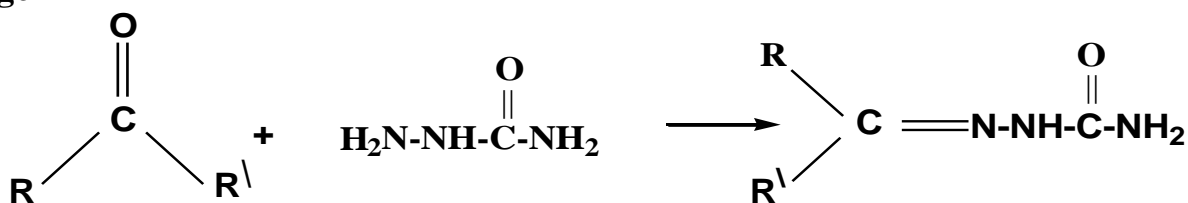
الخلاصة :

في هذا العمل تم مفاعلة الديهايدات وكيتونات مختلفة مع مركب الامين (الكاربازيد المتماثل) فتم الحصول على قواعد شيفف المقابلة ، ثم مفاعلة هذه القواعد مع متعدد الاكريلويل كلورايد فتم الحصول على بوليمرات جديدة تحتوي سلسلتها البوليمرية على قواعد شيفف وتم تشخيص البوليمرات المحضرة باستخدام مطيافية (FTIR) وكذلك تحليلها فيزيائياً عن طريق قياس درجات الانصهار والذوبانية وقد دلت النتائج المستحصل عليها ان البوليمرات المحضرة ذات خواص فيزيائية جيدة .

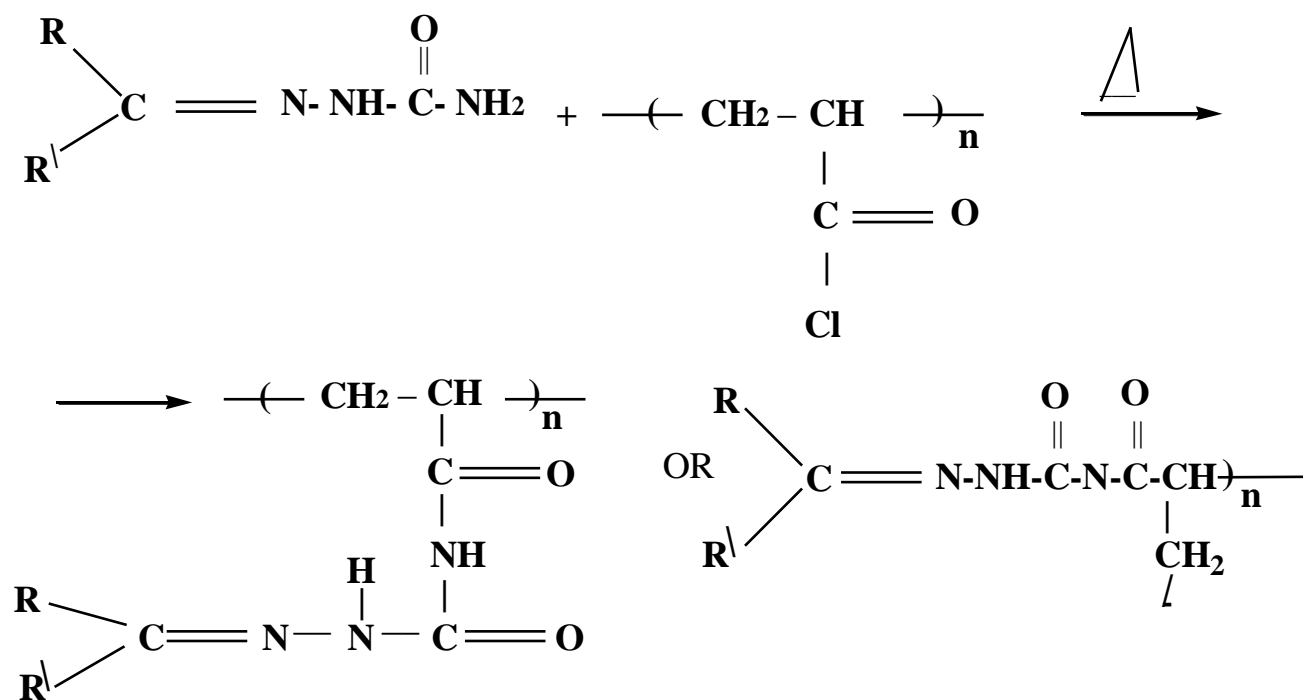
Introduction :

Acryloyl chloride can be polymerized easily to linear polymer at room temperature by exposure to other violet light in quartz tubes⁽¹⁾ poly acryloyl chloride can also be prepared by treating poly (acrylic acid) with thionyl chloride⁽²⁾ . ultra root to prepare poly (acryloyl chloride) is by photo initiated polymerzaion of acryloyl chloride⁽³⁾ . from which poly amide (PA) was prepared which is known by the trade name nylon, and it consists of highly ordered molecules of high tensil strength . Amides , can also be prepared from acids by treatment with thionly chloride and then with ammonia⁽⁴⁾ . The acryl amide 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 ethylene diamine tetra acetic acid (EDTA)^(7,8,9) sulfate salt of acryl amide can be used as a base on an ion exchange column⁽¹⁰⁾ and N-substituted acryl amides⁽¹¹⁾ so poly amides were synthesized as the same root of amide , many main routs have been mentioned to prepare these compounds⁽¹²⁻¹⁷⁾ one of these roots which was used in this paper was from aldehyde or keton carbazone poly acryloyl chloride to give poly acryl amido-N-oxo carbazone.

Stage 1



Stage 2



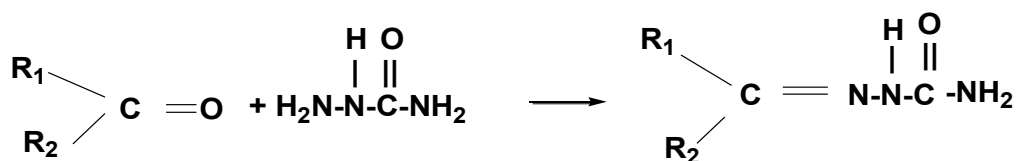
The compound semicarbazide (H₂N-NH-CO-NH₂) was condensed with various carbonyl compounds to prepare Schiff bases that containing pendent NH₂group which it treatment with poly acryloyl chloride to prepare a new poly acryloyl amido carbonyl carbazone which contain (-C=N-) imin group that poly amido which containing Schiff bases which known to posses biological activity behavior⁽¹⁸⁻²⁴⁾

Experimental :

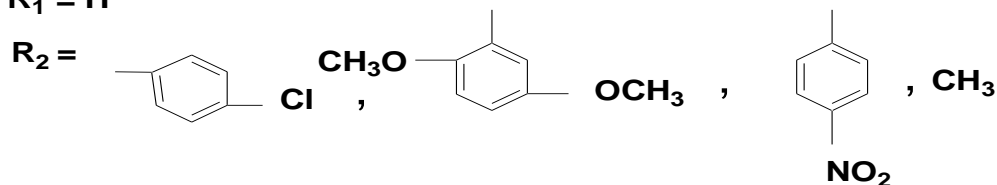
Melting points were determined on Gallenkamp melting point apparatus (MFB-600) , FTIR were prefomed using (FTIR) absorption spectra , KBr disks were used an a (FTIR-84005) FOURIER transform infrared spectrophotometer . SHIMADZU

Preparation of Schiff bases :

A solution of carbonyl compound (1mole) in the minimum amount of ethanol added to solution of semi carbazide hydrochloride (1mole) and hydrated sodium acetate (3g) in distilled water (10ml) in a reflex flask . refluxed the mixture an hour . after that the product was filtered and recrystallized from absolute ethanol.



Which R₁ = H



Which R₁ = CH₃

R₂ = - C₂H₅ , - CH₃

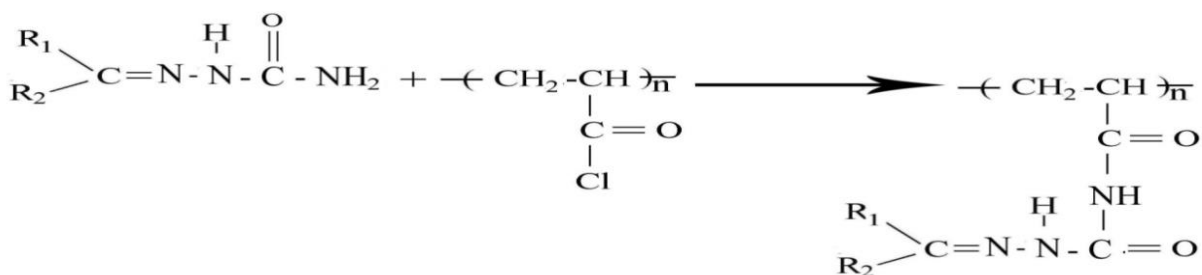
Which

R₁, R₂ = 

schem(1):Synthesis of Schiff bases by reaction of some carbonyl compounds with semicarbazide

Preparation of poly acryl amido carbonyl semi carbazone :

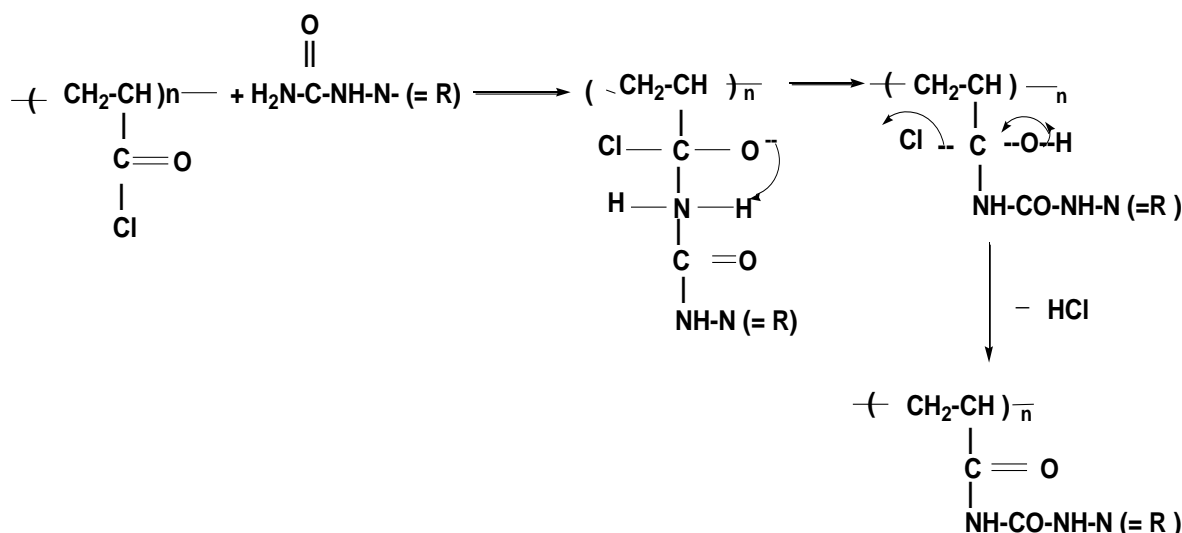
Poly acryloyl chloride (0.02 mole) was dissolved in 20ml of (DMF) , the prepared Schiff bases (0.02 mole) were added to the mixture , that has been refluxed for (8-7) hours , then poured the reaction mixture into(50 ml) distilled water and the separated soild was filtered and dried the polymer purified by dissolving at (DMF) and precipitate from water.Physical properties an *d FTIR* absorption for all polymers prepared were listed intables (1-3)



Schem(2):Synthesis of new poly (acryl amido-N-oxo-hydrazones)by reaction of the prepared Schiff bases with poly acryloyl chloride

Results and discussion :

Although there are several procedures for the prepare of N-substituted amides ^(7,8,9) one of them was found suitable for the prepare of Schiff bases by condensing semi carbazide compounds with various carbonyl compounds that shown in schem (1) and suitable for the prepare new polymers from the reaction of poly acryloyl chloride with prepared Schiff bases schem (2) . the mechanism of the reaction is shown in schem (3) :



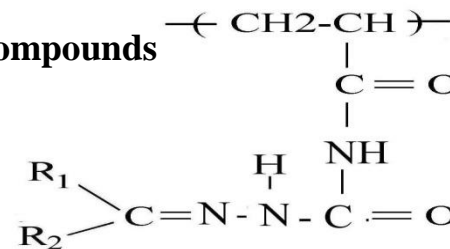
Schem(3):The Mechanism of The Reaction

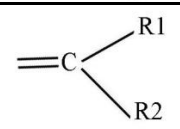
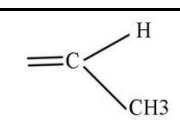
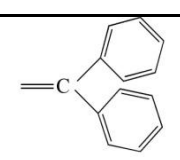
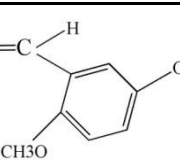
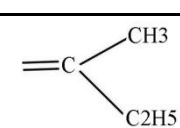
All physical properties and solubility for prepared polymers are listed in tables (1-2).The *FTIR* spectrum for prepared schif bases shown absorption band at (3400-3450) cm^{-1} due to NH_2 group and at (3317-3200) cm^{-1} for N-H group due to stretching vibration ⁽²⁵⁾ .The *FTIR* spectrum showed strong absorption band in the region (1700-1681) cm^{-1} which is typical for the (C=O) stretching vibration of carbonyl amide .The chemical reactivity of the NH_2 group in prepared schiff bases plays a significant role in using this compounds as a good synthon in the synthesis of new polymers by reaction of Schiff bases prepared with poly acryloyl chloride in DMF . The *FTIR* spectra of polymers (1-7)

showed strong absorption band in the region $(1620-1680)\text{cm}^{-1}$ which are typical for the $(\text{C}=\text{N})$ stretching vibration of polymers^(25,26). In the spectra of the N-acryl semi carbazones the absorption band of these group are shifted to higher frequency and appear at $(1700-1701)\text{cm}^{-1}$ ⁽²⁷⁾. In the *FTIR* spectra⁽²⁸⁾ of the poly N-substituted imine which contain N-acryl semi carbazone the stretching vibration of the $(\text{C}=\text{O})$ group appear as doublet absorption in the region $(1700-1660)\text{cm}^{-1}$ (table 3). Associates with an intermolecular hydrogen bonding type $\text{C}=\text{O} \dots \text{H}-\text{N}$ are absent in solution since the appearance of spectrum is not changed with dilution. These poly semi carbazones acrylate were characterize by using physical properties and structures and *FTIR* spectraray these characterized listed in table (1-3) and in fig (2-8). schem (2) summarized all the performed reactions in this work and ketones because steric hindrance and electronic effect. the solubility and melting points of all prepared polymers indicate the formation of high thermal stable polymers.

Table (1)

Physical properties of prepared compounds



No. comp.	Name of polymers		Conversion	T.m C°	colour
1	Poly acryl amido -N-oxo -methyl hydrazone		40%	270-280	Brown
2	Poly acryl amido -N-oxo - dipheyl hydrazone		30%	244	Brown
3	Poly acryl amido -N-oxo -2,5-dimethoxy phenyl hydrazone		40%	158-160	yellow
4	Poly acryl amido -N-oxo -Methyl ethyl hydrazone		40%	240-250	yellow

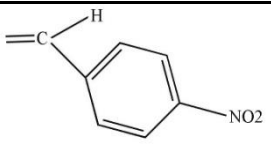
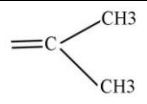
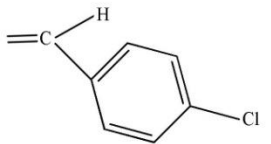
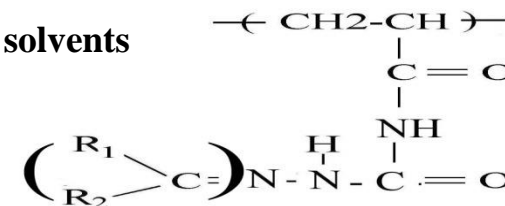
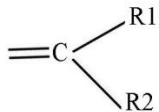
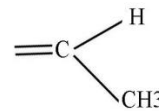
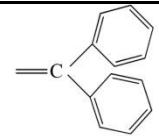
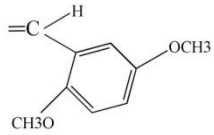
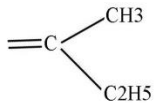
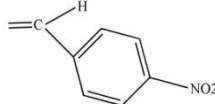
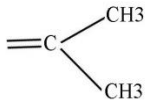
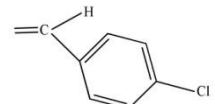
5	Poly acryl amido –N-oxo –p-Nitro phenyl hydraone	 <p>The structure shows a benzene ring with a nitro group (-NO₂) at the para position relative to a hydrazone group (-C(=O)-NH-). The hydrazone group is attached to the ring at the 1-position, and the nitrogen atom is double-bonded to the ring.</p>	30%	270	yellow
6	Poly acryl amido –N-oxo –dimethyl hydrazone	 <p>The structure shows a central carbon atom double-bonded to a nitrogen atom. The nitrogen atom is also double-bonded to another carbon atom, which is bonded to two methyl groups (-CH₃).</p>	40%	250	Brown
7	Poly acryl amido –N-oxo –p-chloro phenyl hydrazone	 <p>The structure shows a benzene ring with a chlorine atom (-Cl) at the para position relative to a hydrazone group (-C(=O)-NH-). The hydrazone group is attached to the ring at the 1-position, and the nitrogen atom is double-bonded to the ring.</p>	30%	260-267	Brown

Table (2)

The solubility of prepared compounds in different solvents



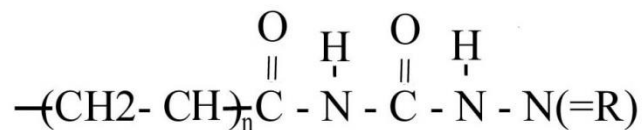
No. comp.		H ₂ O	EtOH	MtOH	CCl ₄	CHCl ₃	Toluene	Petroleum spirit (60 - 80)	DMF	DMSO	Acetone	ether
1		÷	+	-	-	-	-	-	÷	÷	÷	-
2		-	-	÷	-	-	-	-	÷	÷	-	-
3		-	+	+	+	+	+	-	+	+	+	+

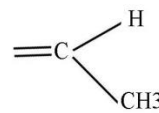
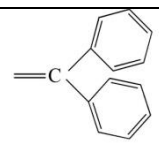
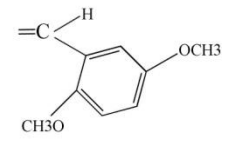
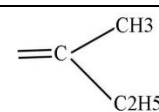
4		-	÷	-	-	-	-	-	-	÷	-	-	
5		-	-	-	÷	÷	-	-	-	÷	÷	÷	-
6		÷	-	-	-	-	-	-	-	÷	+	-	-
7		-	-	÷	-	-	-	-	-	÷	+	-	-

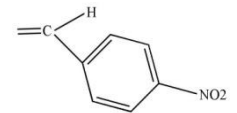
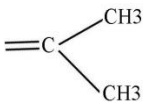
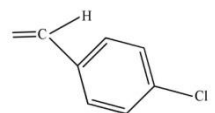
(+) soluble , (-) Insoluble , (÷) sparingly

Table (3)

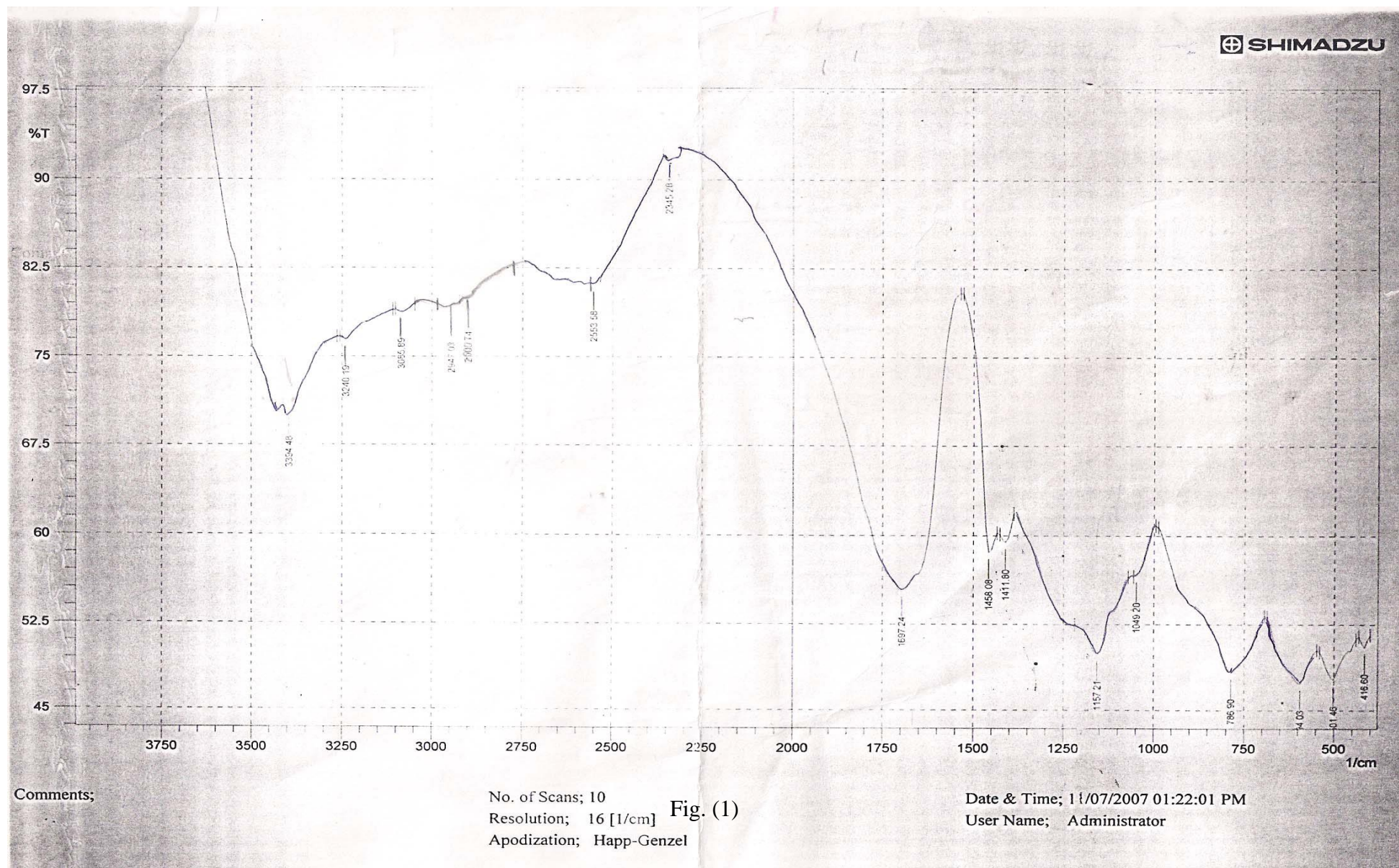
FTIR spectra of poly acryl semi carbazide and its derivatives in cm⁻¹



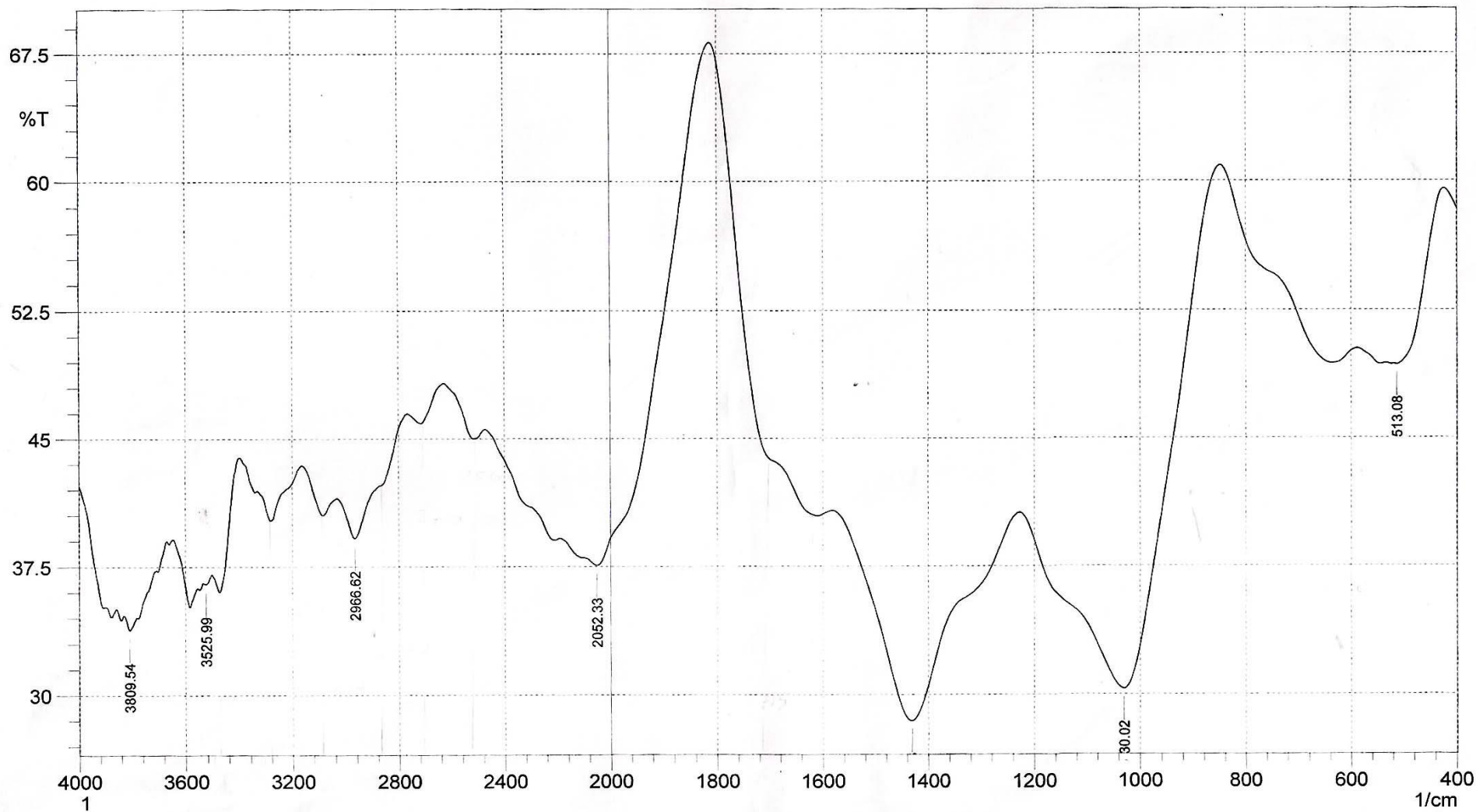
Comp. No.	(=R)	ν (N-H)	ν (C-H) ar.	ν (C-H) vinyl	ν (C-H) aliph.	ν (C=O)	δ (N-H)	ν (C-C) ar.	ν (C-N-N) ν (O-C-N)	ν (C=N)	Others
1		3480 (m)	-	3080 (w)	2966 (br) 2870 (w) 2710 (w)	1715 (w)	2530 (w)	-	1430 (br)	1620 (w)	ν (C-O-C) 1030 (br)
2		3460 (br) 3350 (m)	3100 (br)	-	2760 (w)	1631 (br)	2407 (br)		1437 (br)	1631 (br)	ν (C-O-C) 1047 (br)
3		3420 (br)	3000 (s)		2960 (s) 2900 (s) 2820 (s)	1670 (w)		1465 (s) 1496 (s) 1590 (s)	1420 (s) 1320 (s)	1620 (s)	ν (C-OC) 1050 asym. ν (C-O-C) 1265 ¹ asym.
4		3409 (br)		3024 (br)	2792 (w)	1704 (br)	2453 (br)		1465 (s) 1388 (w)	1665 (br)	

5		3394 (br)	3008 (w)		2965 (w) 2918 (w) 2875 (w)	1700 (br)	2420 (br)	1596 (br) 1519 (s)	1342 (s) 1415 (w)	1680 (br)	ν (C-N) 840 (br) ArNO ₂ out plane
6		3210 (br)			2955 (br) 2800 (w)	1700 (br)			1458 (br) 1373 (w)	1655 (br)	
7		3471 (br)	3039 (br)		2780 (w)	1716 (br)	2420 (w)	1640 (w)	1431 (br)	1640 (w)	ν ((N-H) 3153 sym. ν (C-O-C) 1058 (br)

(FTIR) spectrum for poly acryloyl chloride



(FTIR) spectrum for compound no. (1)



Comment;
1

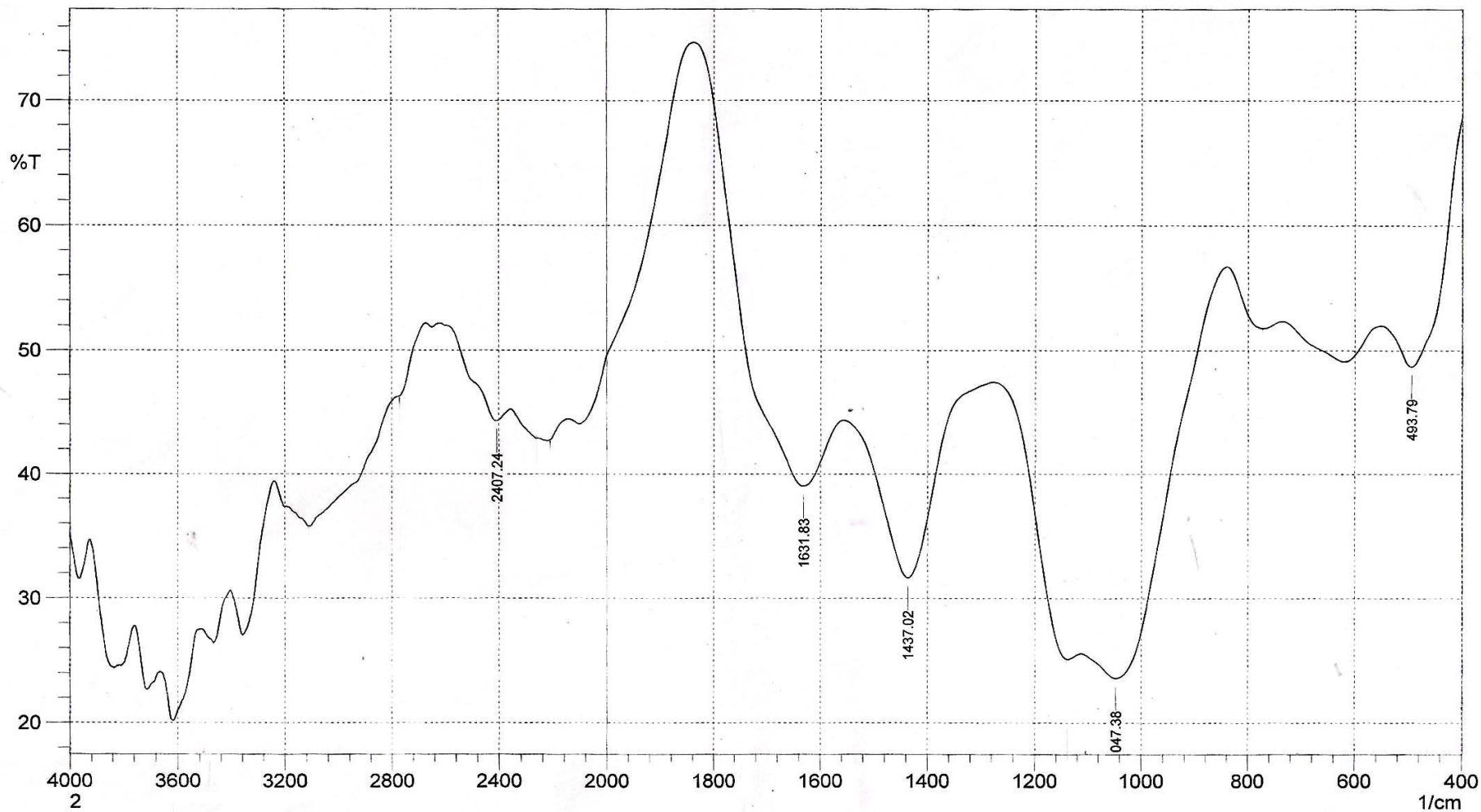
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Fig. (2)

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(FTIR) spectrum for compound no. (2)

SHIMADZU



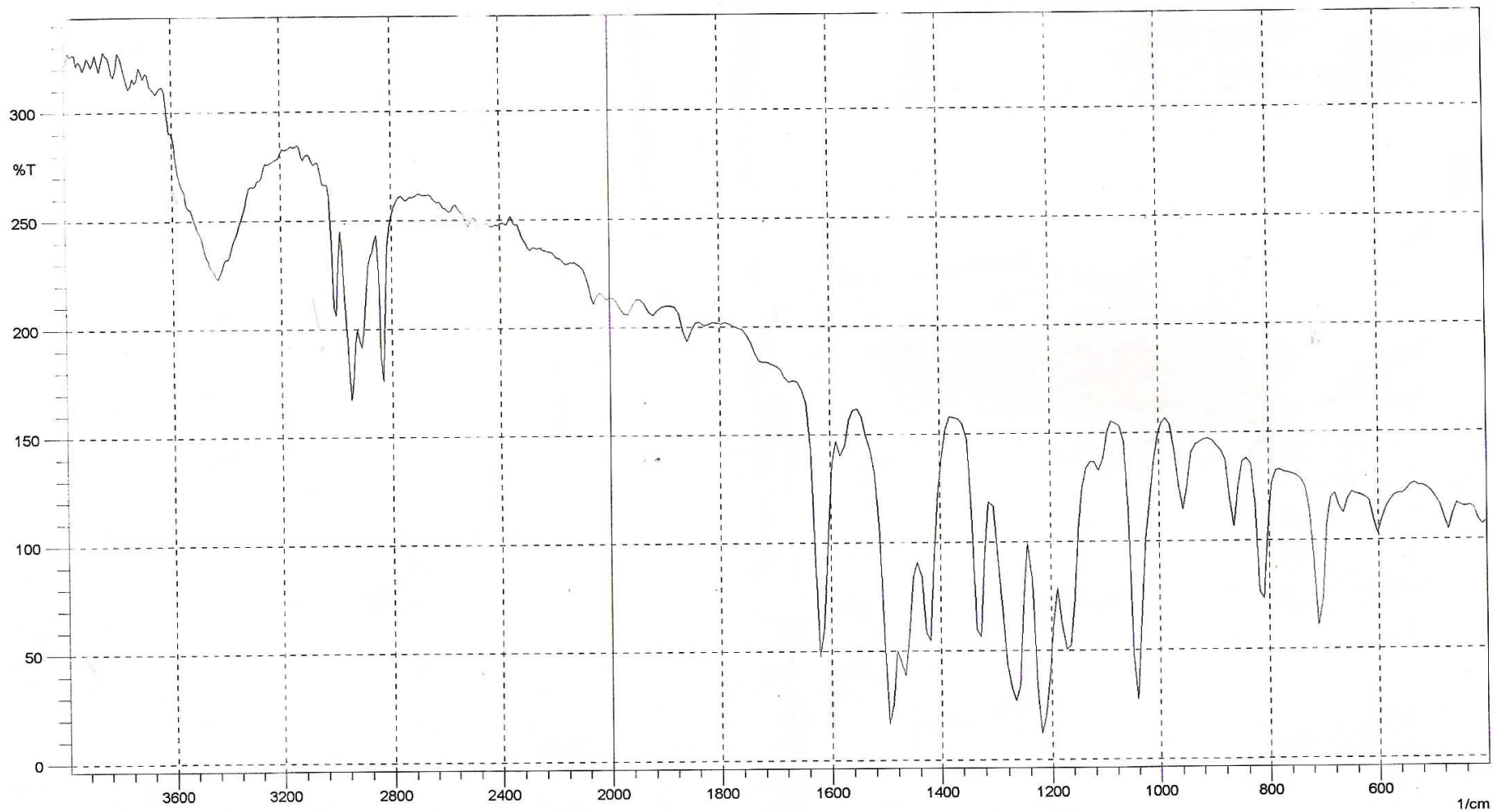
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Fig. (3)

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(FTIR) spectrum for compound no. (3)

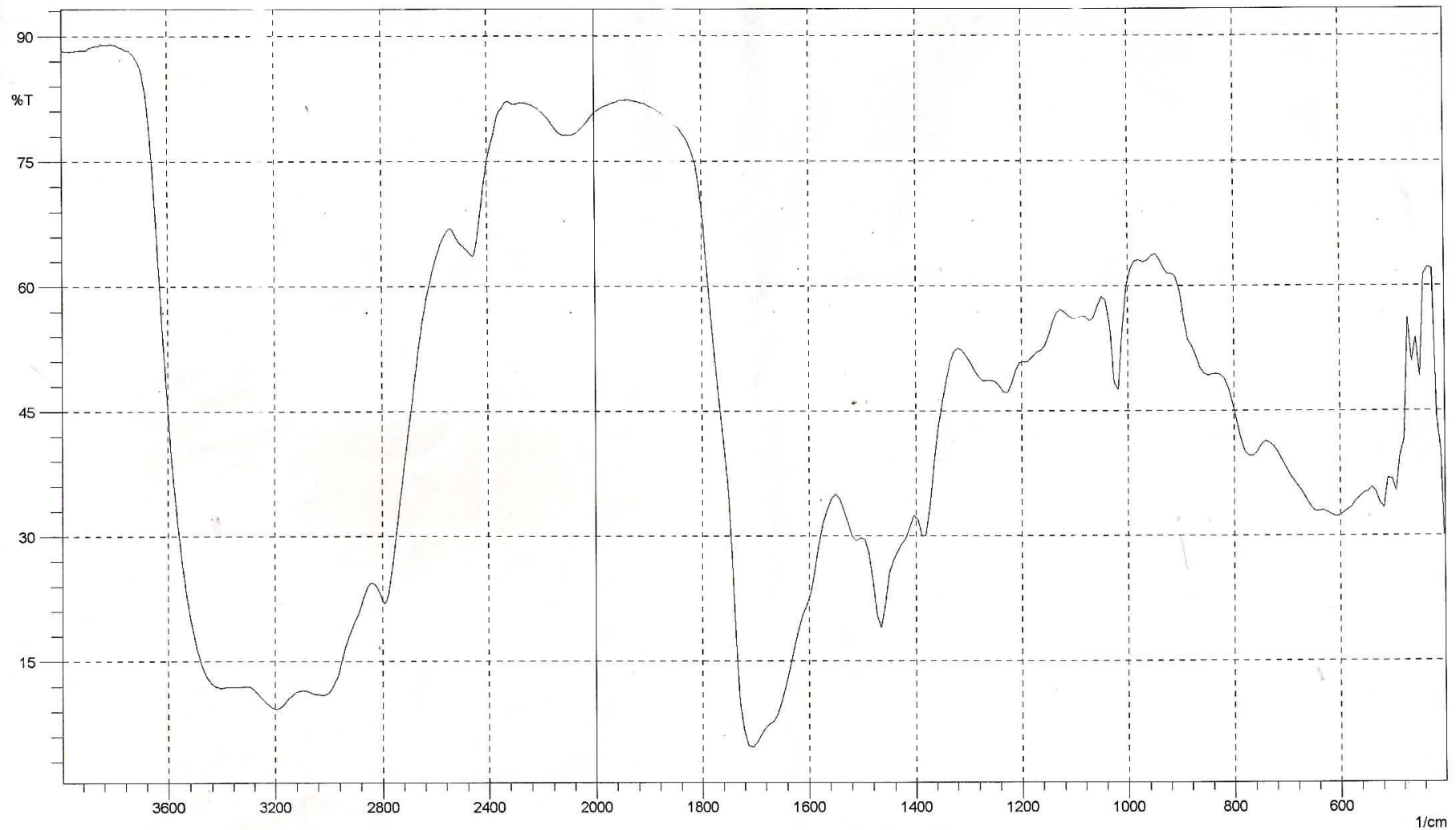


Comments;

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(FTIR) spectrum for compound no. (4)



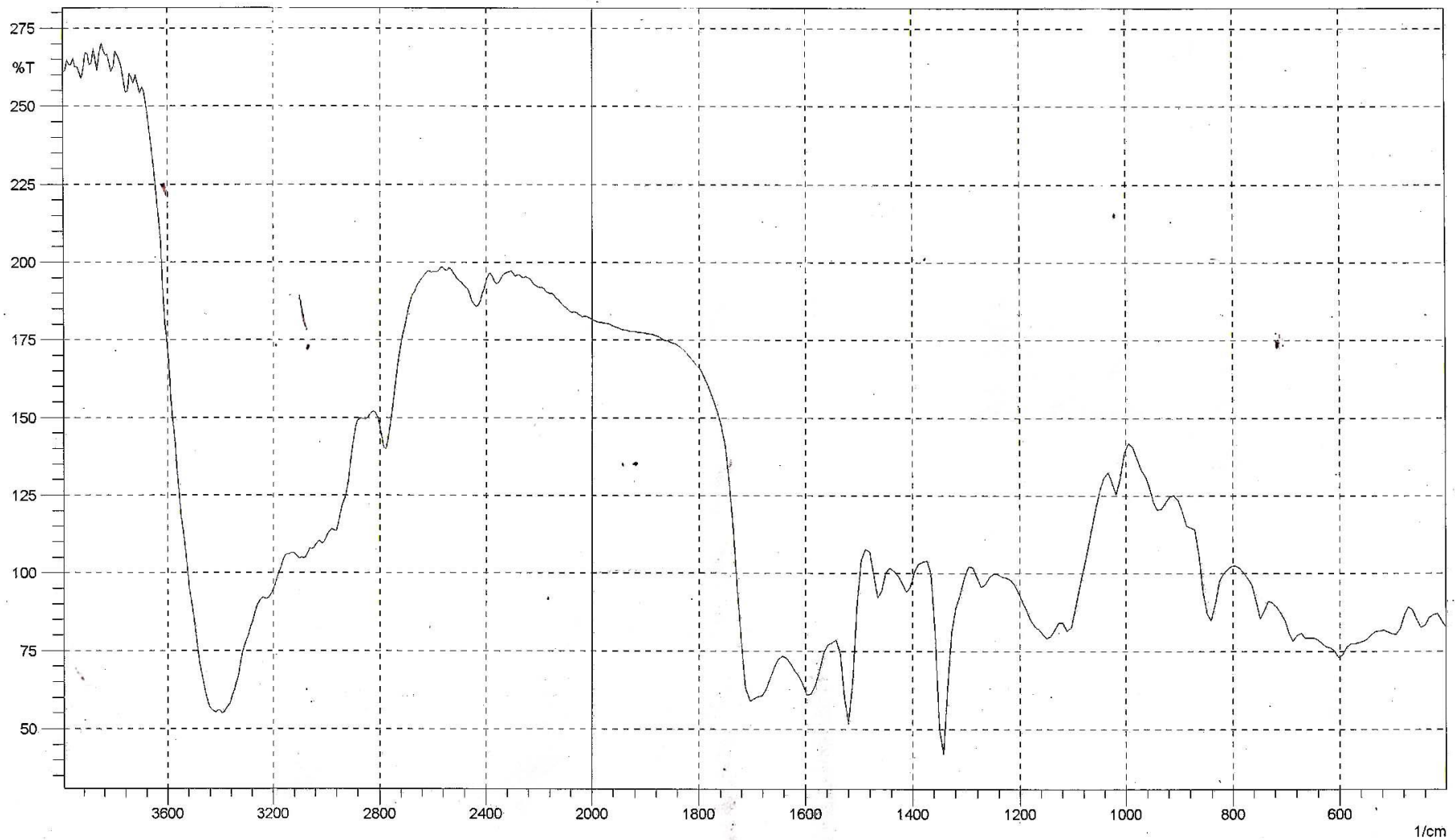
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Fig. (5)

(FTIR) spectrum for compound no. (5)



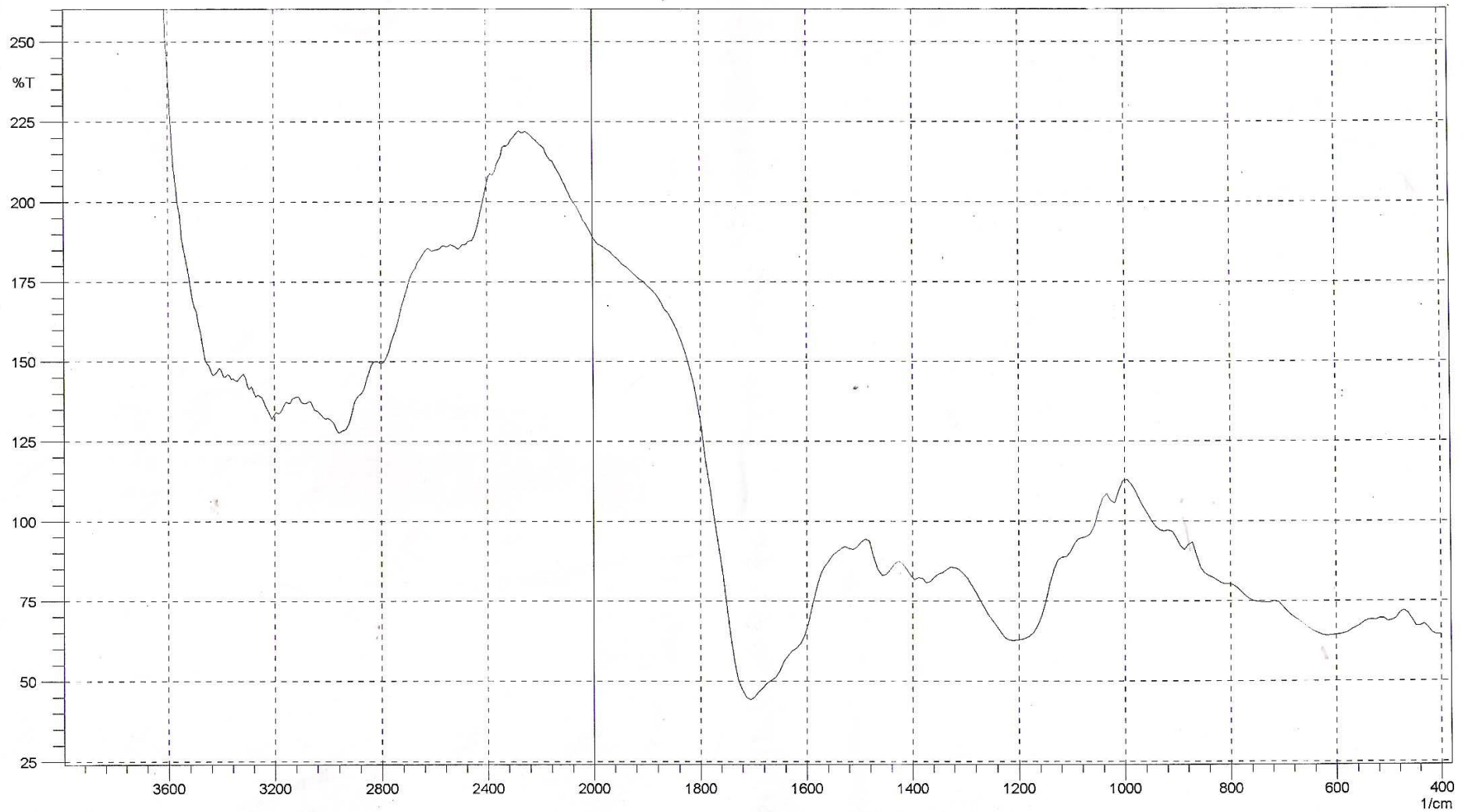
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Fig. (6)

(FTIR) spectrum for compound no. (6)



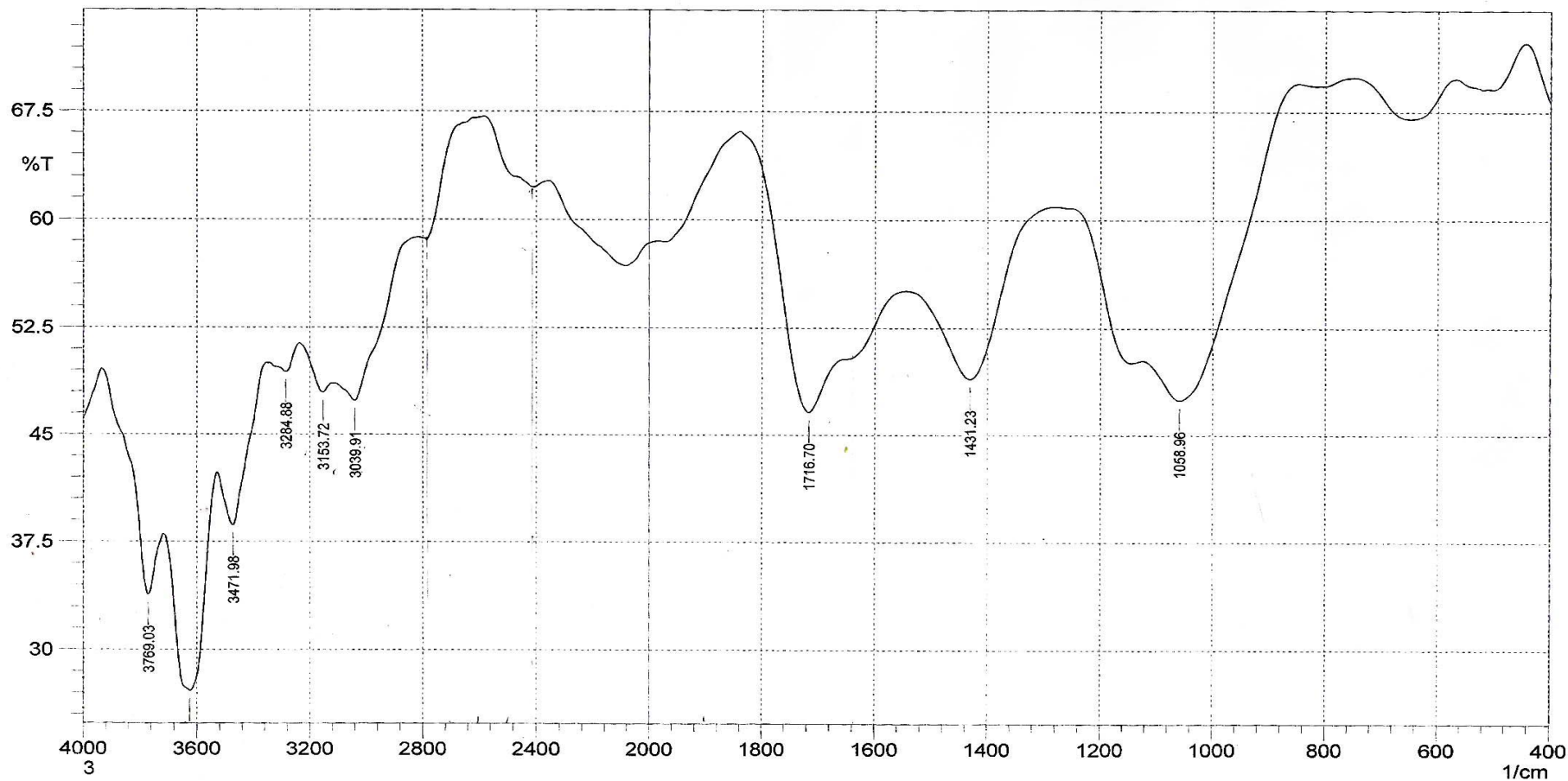
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Fig. (7)

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(FTIR) spectrum for compound no. (7)



Comment;
3

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