

Synthesis and characterization of poly (vinyloxy -4-yl - amino) with Phenyl acetonitrile

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Abstract : A new synthesis of poly adipoyl chloride with vinyl alcohol under refluxed for 6 hr. to give poly (vinyloxy acid chloride) then the product reacted with N-methoxyphenylamino)-2-phenyl acetonitrile under refluxed for 6 hr. in presence of boron at 61°C to give Poly N-vinyloxyphenylamino-2-phenyl acetonitrile. According to the obtained product the coordinate of N2- donor atoms in the compound. N-H group in the compounds was very effective and can enter many reactions. NMR identified the prepared polymer and FT-IR, Solubility and thermal stability were study.

Keyword : poly amino nitrile, N-methoxyphenylamino)-2-phenyl acetonitrile.

Introduction:

Poly amino acids are important compounds in medicinal and pharmaceutical field. They show biological activities including antibacterial^(1,4), anticancer^(7,9). Furthermore, this new amino polymer has been widely used as protective group of amino group in organic synthesis^(11,12).

Strecker reaction provides one of the most efficient method for the synthesis of aminonitrile since 1850 when used an aldehyde, amine, and HCN, addition of (CN) to imines provides direct reaction of aminonitrile derivatives have elevated fungi static activity more than commercial fungicide kaptan⁽¹⁾. aminonitriles are useful for *synthesis of* amino acids^(2,3) among many other applications which are importance as ligand for Zinc (II) complex with potential antitumor properties^(7,8). aminonitrile has often been used as chelating ligand through two nitrogen atoms in amino coordination chemistry.

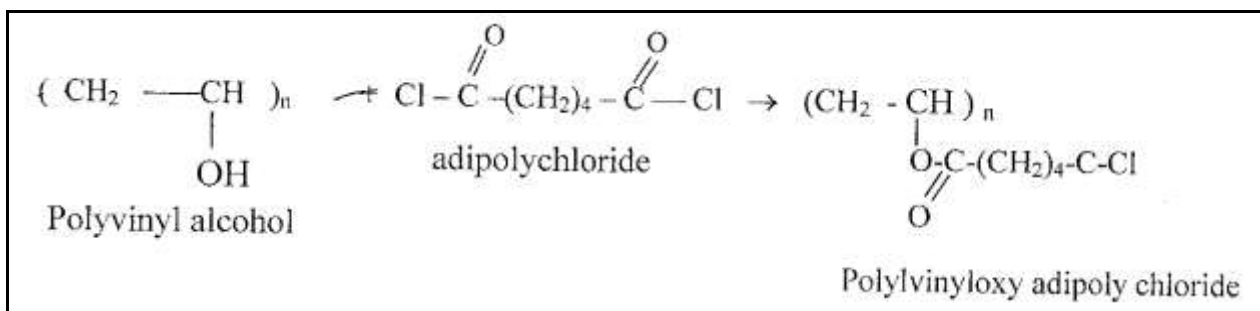
Experimental:

All chemicals used were highest purity available from B.H.D. company. The prepared ligand N-methoxyphenylamino)-2- phenyl acetonitrile was synthesized and characterized according to published work. Melting points were fixed by Gallenkamp melting point apparatus(MFB-600).

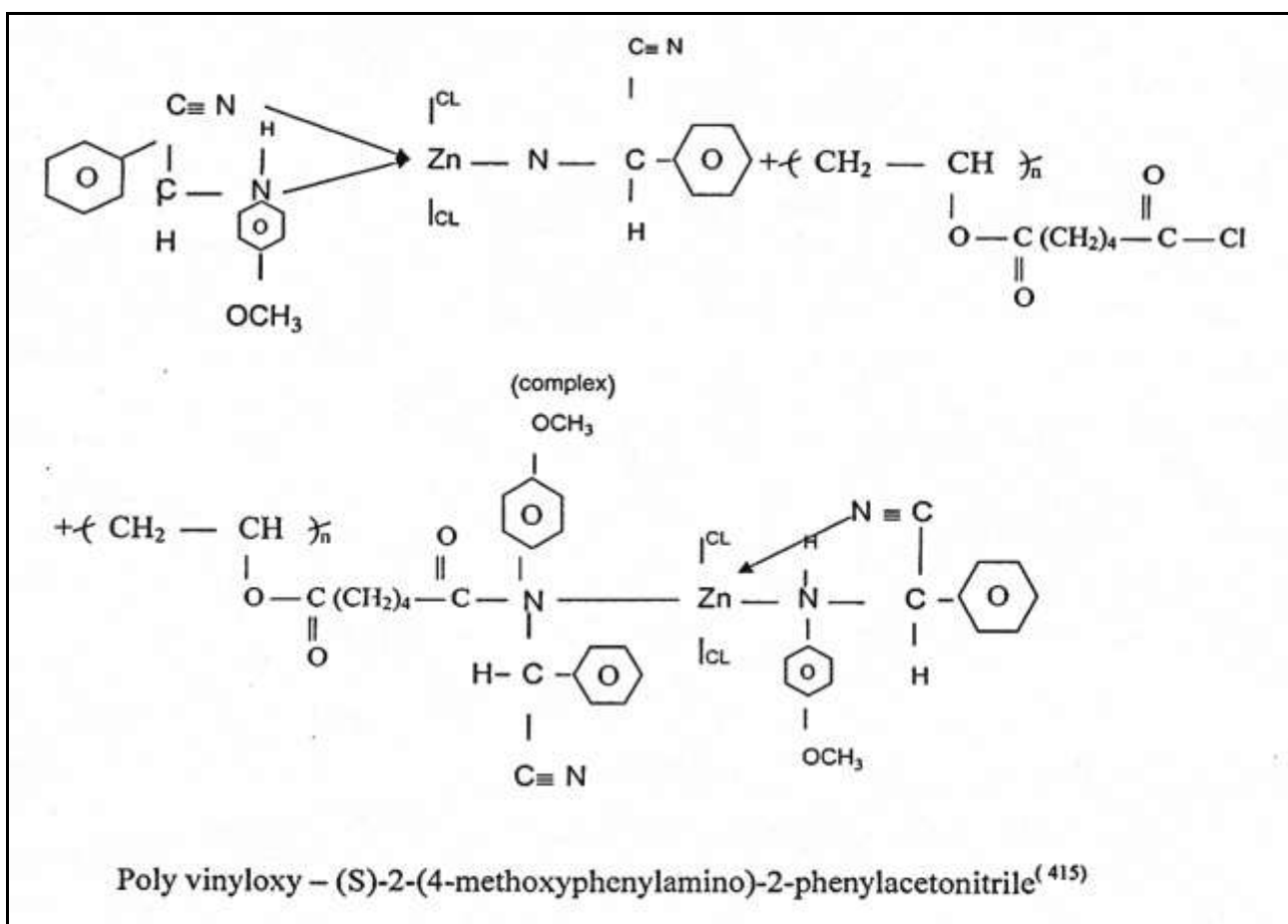
Structures conformation of new prepared polymer and ligand were proved by FT-IR spectroscopy using CsI disk on shimadzu and other physical properties including solubility, melting points of polymer were calculated.

1) Preparation of Softening point (189-201) °C

Poly(vinyloxy adipoyl chloride (0.011 mole) of polyvinyl alcohol (PVA) and (0.011 mole) of adipoyl dichloride dissolved in 7ml of benzene and refluxed at 61°C for six hrs. Filtered and purified with T.H.F. conversion of yield = (81%). Melting point (203-205)°C. The reaction was clarify below:

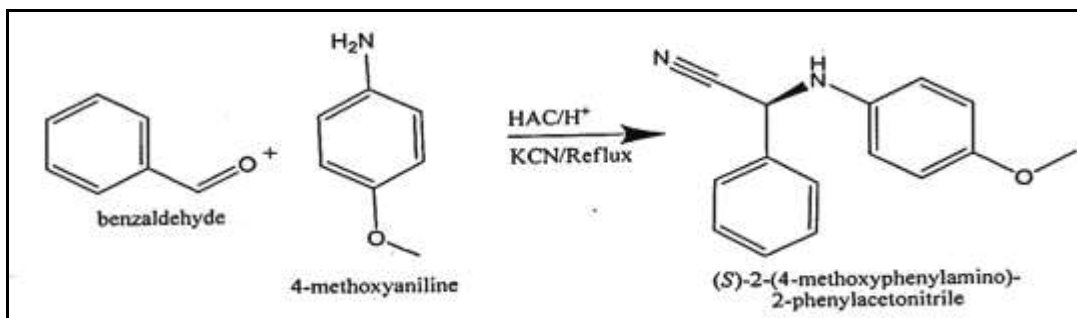


The 0.011 mole of poly vinyloxy with complex of (0.011 mole) dissolved in 7 ml benzene heated under reflux for six hrs. Filtered and purified with THF the reaction clarified below:



2) Preparation of N-methoxyphenylamino)-2-phenylacetone nitrile ligand (L) (A13)

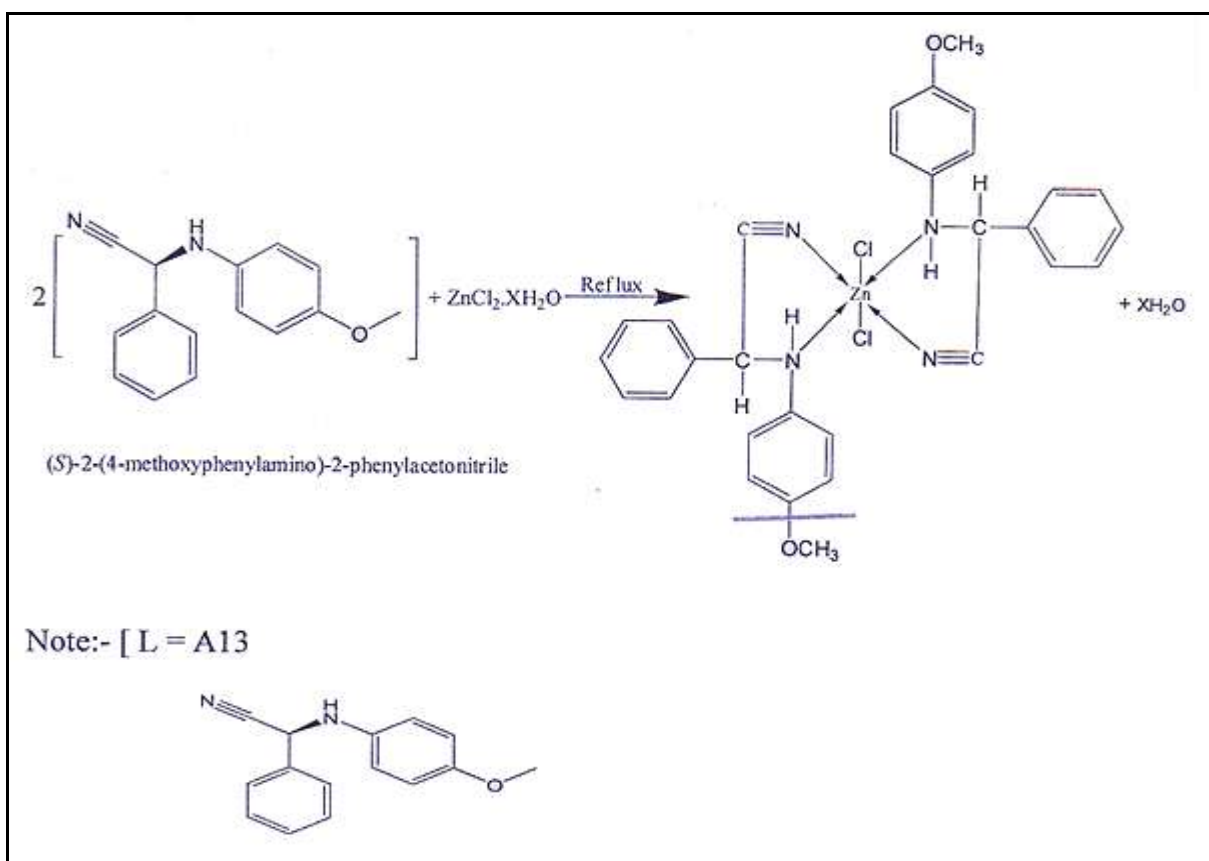
A common method [15, 16] can be adopted for [L] preparation which can be described as follows: (20 ml) glacial acetic acid was added to benzaldehyde (1 mmol), p-toluene sulphonic acid was added in very little portion as catalyst, followed by adding (1 mmol) p-methoxy aniline. The pH was change to about 4 by addition of concentrated sulfuric acid drop wise to obtain Schiff base which stirred for 30 min. Potassium cyanide (2 mmol) was added to the mixture and set aside stirring for 4 days. The reaction mixture was poured into ice and then made slightly alkaline with (NH₄OH) solution. The solid yield, was filtered, washed with water and air dried. The presence of nitrile group in the prepared aminonitrile was indicated.



By treating little amount of the sample with 10% sodium hydroxide solution, the releasing of ammonia after hydrolysis of nitrile group, which was detected by wet red litmus paper, indicating the presence of nitrile group. Purity of the obtained compound was chequered by TLC, using chloroform and ethyl acetate (1:1) as eluent. The product color was faint green and the yield percentage was (85.23 %) and the melting point was (58-60 °C). The reaction was clarified below:

3) Preparation of metal complex:-

The complexes [Zn] have been prepared by the reaction of (0.476 gm) (2 mmol) of (L) with (Immol) of Zinc chloride (0.136 gm of ZnCl) dissolved in (20 ml) absolute ethanol and refluxed with stirring under anhydrous conditions using Na₂SO₄ (anhydrous) for 24 hours. The obtained complex was obtained after evaporation of ethanol and triturated with petroleum ether (60-80 °C) then filtered and the product was left in the desiccators to be dried under P₂O₅. The general reaction was clarified below:



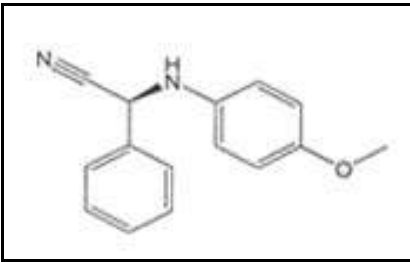
4) Preparation of poly (vinyl-oxo- -4-yl amino)phenyl acetonitrile ^(4,5)

20ml of glacial acetic acid was added to(1 mmole) of benzaldehyde, P- toluene sulphonic acid was added as catalyst, adding (1 mmole) P- methoxy aniline at PH=4 by addition of conc. Sulfuric acid drop wise to obtain Schiff base which stirred for 30min. finally Potassium cyanide (2mmole) was added to the mixture and set aside stirring for 4 days. Mixture was poured into ice and then made slightly alkaline with ammonium

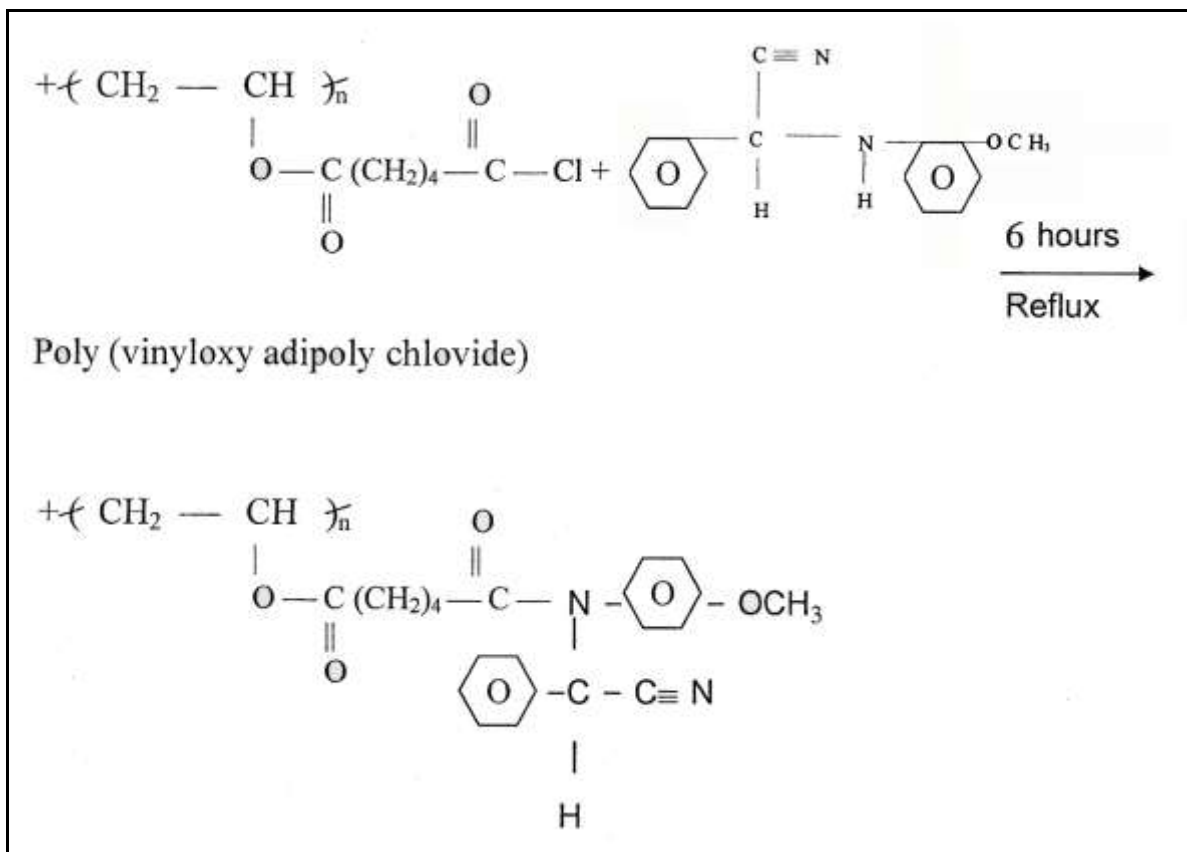
hydroxide solution precipitate was formed and filtered, washed with water and air dried.

Nitrile group in the prepared aminonitrile was indicated by treating with little amount of 10% NaOH solution releasing ammonia after hydrolysis of nitrile group. Which was detected by wetted litmus paper indicating the presence of TLC, using CHCl_3 and $\text{CH}_3\text{CH}_2\text{C}-\text{OCH}_3(1:1)$ as eluent. The product color was faint green and percentage yield was (85.23%), melting point was (58-60) $^\circ\text{C}$. The reaction was clarified below-

Reaction of 0.01 Imole poly (vinyl oxy adipoyl chloride) with 0.011 mole of (N -3- methoxy phenylamino)Phenylacetonitrile



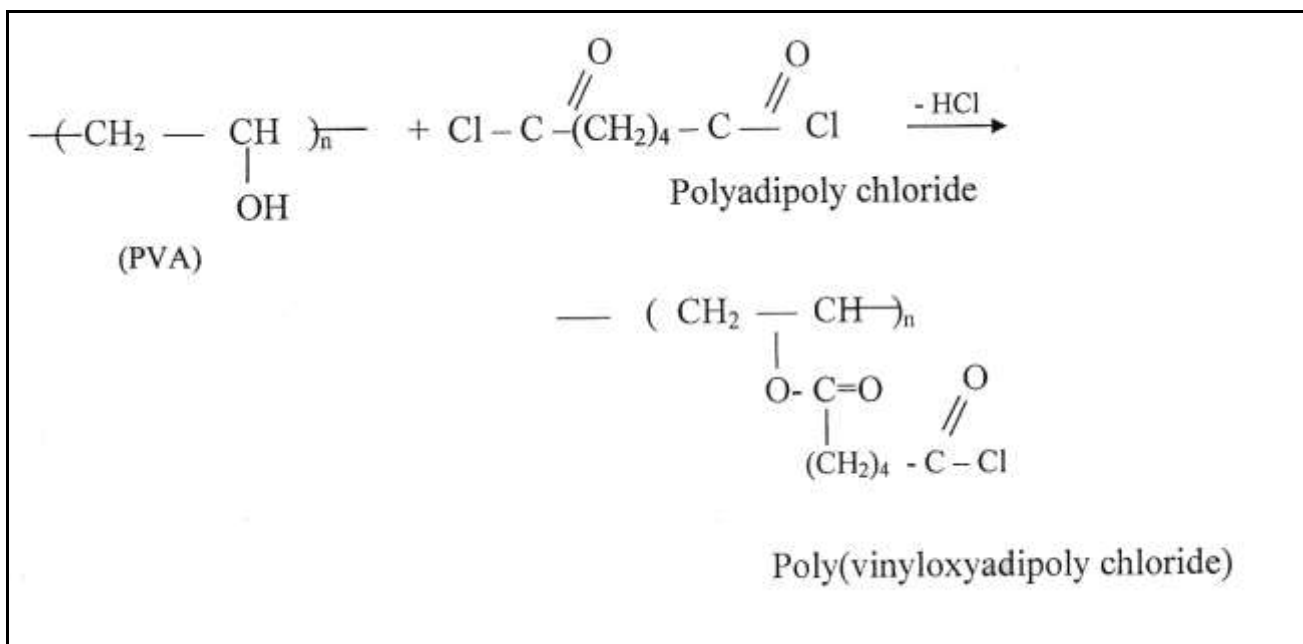
In 7 ml of benzene under refluxed with tetrahydroformamide, conversion yield (75%) softening point (189- 201) $^\circ\text{C}$ and melting point (203 -205) $^\circ\text{C}$. The reaction was clarified below:



Results and discussion:

One of appropriate procedure for synthesis of poly (vinyl alcohol from vinyl acetate) via hydrolysis in acidic medium with acetone under reflux. Physical properties in table (1-1).

The FT-IR spectrum show absorption band at (3500- 3600) cm^{-1} for OH- group and at 1250 cm^{-1} for O-C-O alcohol and for - CH aliphatic at 2990 cm^{-1} . The FT- IR spectra for poly (vinyl oxy adipoyl chloride), show absorption band at 1280 cm^{-1} for o-c-o ester group and at 1697 cm^{-1} for C=O group and at 2916 for - CH group and at 617 cm^{-1} for (C- Cl), mechanism reaction in schem(1).



All compounds reported in this work in table (1) which demonstrate physical properties, along with molar conductivity at room temp.

Metal and elemental analysis of all compound are represented in table (2). (N-4- methoxy phenyl) aminophenyl acetonitrile was prepared as reported in literature (17). It was characterized by elemental analysis and infrared spectral data.

The complexes have been prepared under anhydrous conditions to stay away from any hydrolysis of nitrile group to amide duo to the presence of metal ion [18] CO- amino are useful inter mediates for synthesis of amino acid [2,3] , and N- containing heterocycles such as thienopyrimidine derivatives which have antibacterial and antifungal activities higher than the corresponding antibacterial (ampicillin and antifungal nystatin) [4-6]. Besides, they are readily hydrolyzed to diamine , which are interest as ligands for pt(II) complexe with potential antitumor properties oc- aminonitrile have been used as chelating ligand through two nitrogen atoms in discipline of amino coordination chemistry. This is new study of coordination field as lighand with metals ions. These complexes were stable in solid state and regarded as molar conductivity, metal and elemental analysis, magnetic susceptibility, FTIR and UV- visible spectroscopy , it's suggested that all complexes have- struchure with coordination (6) No. that includes two atoms of coordinate chlorides. Conductivity for the complexes 10^3M in absolute ethaol in rang (4-12) indicating non- electrolytic nature of complexes (20).

Moleration used to calculate the ratio of metal ion to liqand complexes at $T_{\text{max}}(T_{7\text{naz}} = 571 \text{ nm for } [\text{Co}_2\text{cl}_2]\text{ and } \lambda_{\text{ma}^*} = 460\text{nm for } [\text{Cu}_2\text{cl}_2 \cdot 2 \text{H}_2\text{O}]$ in alcoholic solution

Table (2): Infrared absorption band (cm)⁻¹ of new prepared polymers

comp ound No.	compound name	ν_{C-O} ν_{C-O} acid - OH	$\nu_{C=O}$ ν_{acid} ester	ν_{C-OC} cm ⁻¹	ν_{C-H} bendig cm ⁻¹	ν_{C-C} aram atic	ν_{C-H} aliph atic cm ⁻¹	ν_{C-H} aroatic cm ⁻¹	Other s bands cm ⁻¹ - OH	ν_{C-Cl}
1	Poly (vinyl alcohol)	— 1250	-	-	1459	-	2990	-	3250- 3600	
2	poly adipoly chloride	1218	1650	1280			2916			617

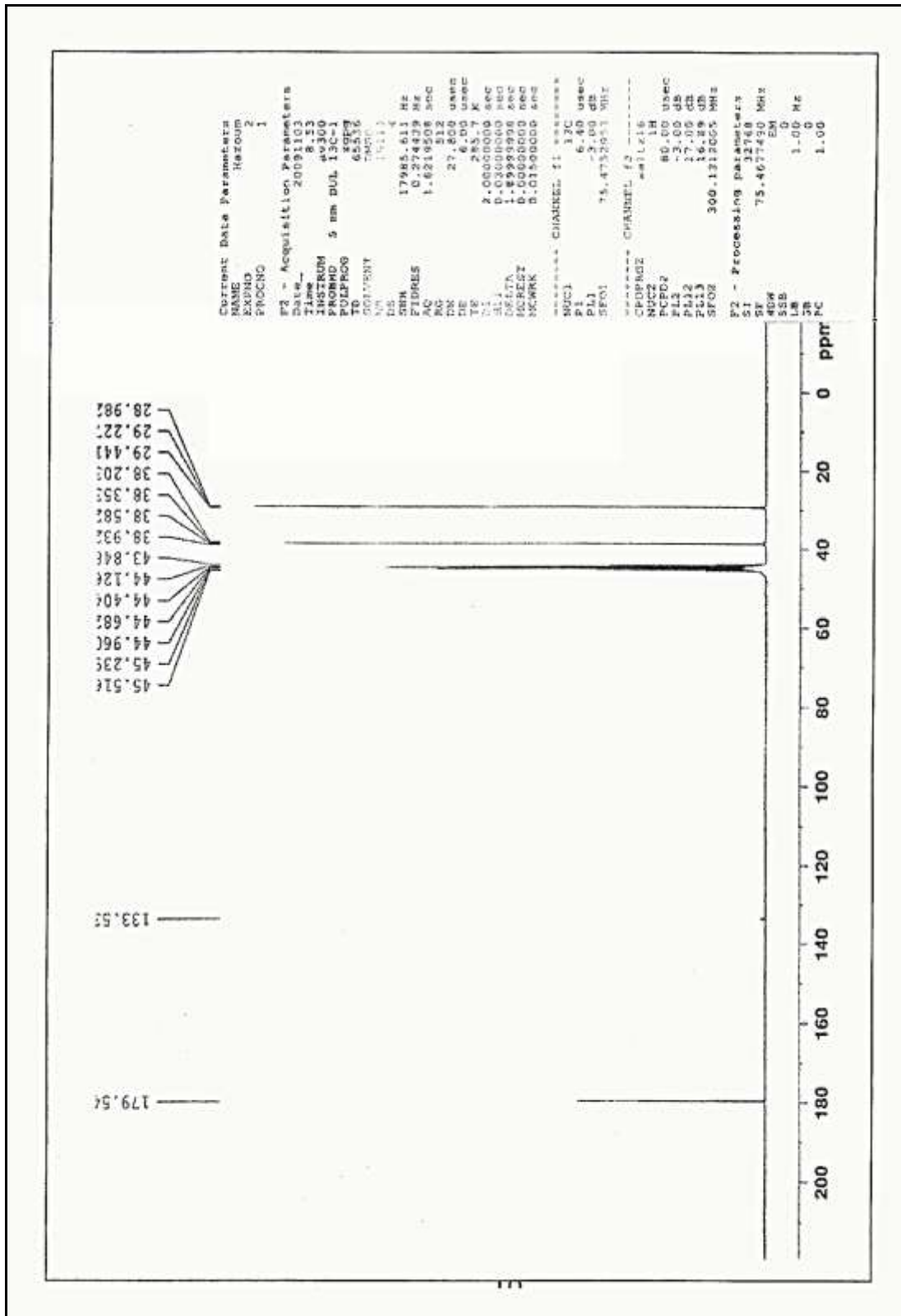
Table (3): Solubility of new polymer

No.	Benzene	DMF	DMSO	THF	Water	CCl4	Acetone	EtOH
poly (vinyl alcohol)	VS.	VS.	VS.	VS.	ps.	ps.	VS.	VS.
poly (vinyloxy- adipoly chloride)	VS.	VS.	VS.	VS.	ps.	ps.	VS.	VS.

vs. = very soluble ps. = partial soluble

Table (4): ¹H-NMR spectra of selected polymers

Comp. No.	¹ H-NMR parameters (ppm) δ -H
poly (vinyl alcohol)	3.2 (t, 2H, -CH ₂); 2.5 (m, 1H, -CH), 10.1 (OH)



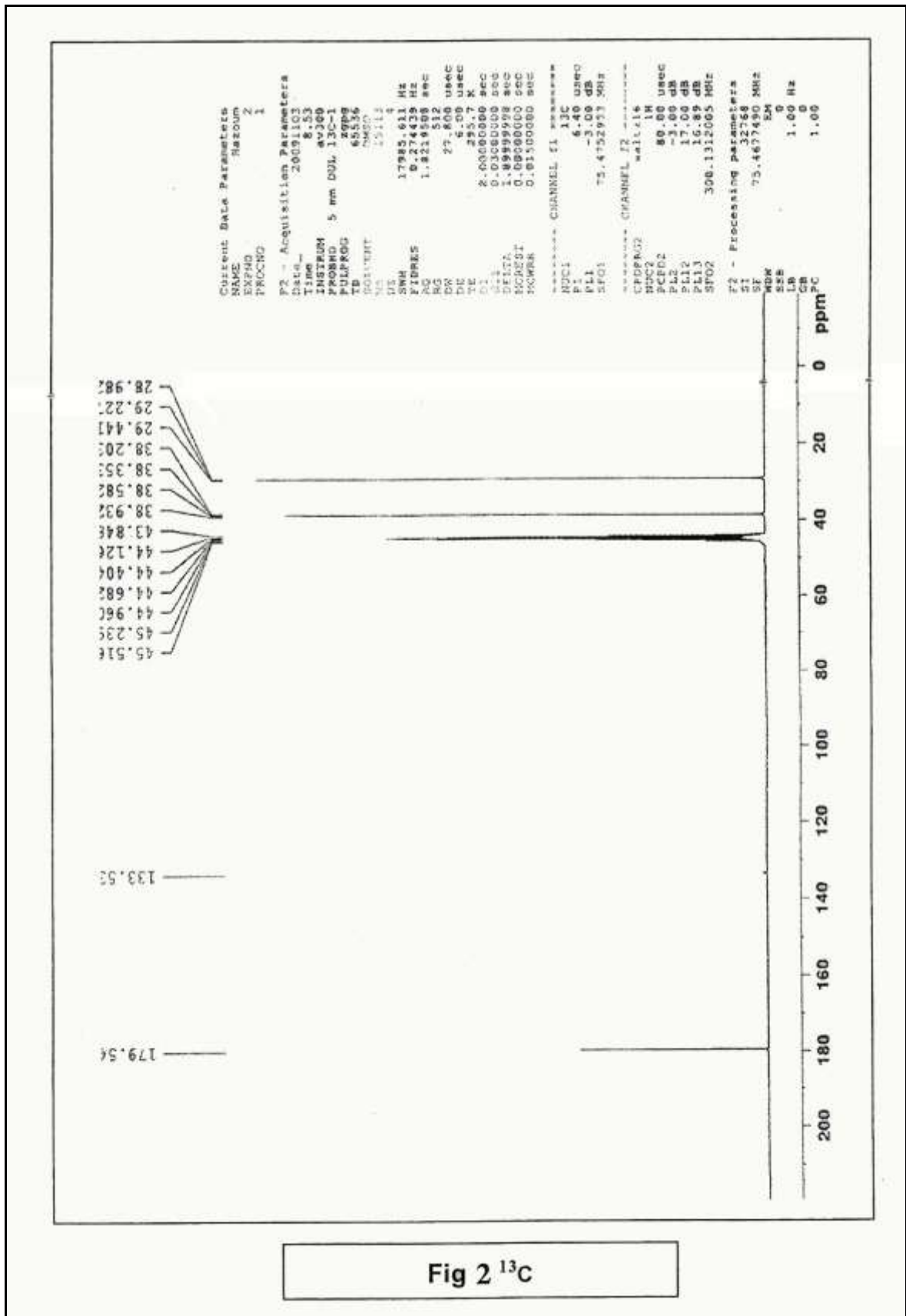


Fig 2 ¹³C

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