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Chemical modification of 4-chloromethyl styrene polymers with oximes containing pyridine groups

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ABSTRACT

In this research, 4-chloromethyl styrene copolymers synthesized with various monomer such as methyl Meta crylate, ethyl Meta crylate, methyl acrilat and 4-metoxy styrene by polymerization of free radical in presence of Azobis – iso – botiro – nitril (AIBN) initiator in 70±ic tempera ture. Substiturions of 2- pridincarbaldehidoxim and phenyl-2-pyridyl ketonoxim connected obtained copolymers up to substituting all chlorine atoms in CMS units. Obtained polymers identified with a good efficiency rate by FT-IR, HNMRspectromy techniques.

Keywords: chemical modification, 4-chlor methyl styrene 2-pyridin caraldehidoxim.

INTRODUCTION

Examining into the traits, syntheze, reactions, and monomer chemical modification of parachloro methyl stayren.
Para – chloro – methyl styrene (CMS) orpara – vinyl – benzyl –chloride (VBC) is one of the important functionalized monomer. Commercial synthesis first has performed 1957 year. Since 1972, there have been studied about physical and chemical properties and its polymers and the uses of these polymers [1].

Chemical modification of monomer 4-chlro –methyl styrene (CMS). The synthesist of nono – particle composite heat and ph sensitive using polymerization of free radical by 4- chlro methyl styrene.
Hapykfeng et .al presented a syntheric way for the synthesis of nono particle composite heat and ph sensitive using controlled polymerization of free radical. First, cross links of a random copolymer had taken by polymerization of mini emulsion in acqueus solution including methyl mera acrylate (MMA), 4-vinyl benzyl chloride (VBC) and di-vinyl – benzene (DVB). Then, they generated photosensitive and PH – sensitive polymers influenced by nano particle of two kind of photosensitive and ph sensitive compound in organic solution of this random copolymer. Fluorescence emission spectrum (TEM) and H-NMR had investigated traits of these polymers [2]. In American patent, for providing o xim, 2-pyridin carbaldehid 18.69 mmol in methanol 20 ml added into stat sodium 22.44mmol. While stirring, hydroxyl amin hydro chloride 20.56mmol added into this solution of reaction in 20-30.c temperature. After two hours, the product obtained efficiency 85% and dried under vacuum. Obtained product organized by H- FT- IR, GC- MASS, MMR spectrum [3].

MATERIALS AND METHODS

Providing copolymer (4-chlromethyl styrene methyl Meta crylate)
Poly (4-chloromethyl styrene – co – methyl methacrylate) 1:3 in a balloon 100ml, initiator AIBN (65% g, 4% mmol) and 4-chlromethyl styrene (1.53g, 10mmol) and methyl Meta crylate (3g, 30mmol) solve in dry tollen solvent 15. The solution de – oxygenates under nitrogen gas and preserve from humidity with a shield tube for calcium chloride (caclz). Then this solution stires in oil bath in 70.c temperature for 30 hours .the resulted solution stires and pours in a beaker containing a cool methanol 15ml drop by drop using a magnetic stirrer. Gradually, copolymer precipitation (4-chlromethyl – styrene – methyl – Meta crylate) occurs. Whits polymer precipitations separates' by decantation of methanol and the resulted precipitation dryes under room temperature and vaccum. End product is as a white powder and the weight of resulted copylemer is 35gr and reaction yield is 77%.

Providing copolymer (para vinyl benzyl 2-pirydine carbdidehydeoxime co methyl methacrylate):
Simple 100ml, 2-pirydine carbaldehydeoxime (4% gr, 3.27ml) is solving in DMF solvent 20ml.
This reaction is performing under nitrogen gas and under preservation of calcium chloride. After half hour, potassium carbonate (K2co3) slowly is adding into balloon contains in room temperature amount (1.33gr, 9.7ml). After one hour, we are adding amoun (1.47 gr, 6.5 ml) of benzyl tre ethyl – ammonium chloride (BTAC) into the balloon. Then, the balloon content is stiring in room temperature for 30 minutes. Next , it is solving in two top ballon 100ml equipped with a wial of brom under nitrogen gas and guard tube) of calcium chlorik , copolymer 5% gr (4-chloro methystyrenemethyle – meta cyrelate) in dried DMF solvent 20ml. and then we are adding simple balloon contents into this homo polymere .(While stirring) by a brome wial during one hour and reaction solution is stirring in room temperature for 24 hours. For precipitation, the ballon contents are adding into a beaker containing cold ethanol 150 ml. gradually, polymeric precipitation is formed in the botton of beaker and polymer is filtered using funnel and filter paper. In order to washing of pirydin car baldehy de oxim, the resulted precipitation is washed with ethanol 50% twice and with distilled water 50ml. the resulted milky precipitation is dried for 48 hours in room temperature and for one hour under vacuum . The weight of product is 6% and reaction yield is 68%.

Providing copolymer (4-chloromethyl styrene – co –methyl acrylate).
In a balloon 100ml, AIBN initiator (1065gr, 0/4 ml) and 4-chloromethyl styrene (1.53gr, 10ml) and methyl acrylate. (2.59 g, 30ml) is solved in dried tollen solution 15ml. This solution id se oxygenated under nitrogen gas and is preserved with guard tube of calcium chloride (cacl2) from humidity , then it is stired in an oil bath for 30 hours in 70.c temperature , The resulted solution is poured into a beaker containing cold methanol 150 ml. Gradually, copolymer precipitation (4-chloromethyl styrene methyl acrylate) is formed, white polymeric precipitations is separated by overflowing of methanol and the resulted precipitation is dried room temperature and under vacuum. The end product is as a white powder and the weight of resulted copolymer is 3.2 gr and reaction yield is 77%

Providing copolymer (paraviny benzyl 2-prirydine carbaldehydeoximemethyl acrylate).
Simple 100 ml, 2-pirydine car baldehydeoxime (0.4gr, 3.27ml) is solved in dried DMF solvent 20ml. This reaction is performed under nitrogen gas and under the preservation of calcium chloride. After 30 minutes, the amount of (1.35gr, 9.7 mmol) potassium carbonat (k2co3) slowly is added into bollon contents in room temperature after one hour. The amount of (1.47gr, 6.5 mmol) benzyl tre ethyl ammonium chloride (BTAC) is an added into balloon. Next, the balloon contents is stirred in room temperature for 30 minutes. Then, in two top balloon 100ml equipped with bromwial, chloride calcium, copolymer 0.5 gr (4-chloromethy) styrene methyl Meta crylate is solved in dried DMF solvent 20ml under nitrogen gas and guard tube and then simple balloon contents is added into this homopolymer solution by brom vial during one hour. Reaction solution is stired in room temperature for 24 hours .for precipitation, ballon contents is added into a beaker containing cold litra ethanol 150 ml. gradually, polymeric precipitation is formed in the bottom of beaker and polymer is filtered using a funnel and a paper filter. For washing 2-pirydin carbaldehydeoxime, resulted preciprtation is washed with ethanol 50 ml wice and with distilled water 50ml twice. The resulted milly precipitation is dried in room temperature and under vacuum for 48 hours. The weight of product is 0/5 gr and the reaction yield is 55%

RESULTS AND DISCUSSION

Examining into copylomerIR spectrum (4-chloromethyl styrene methyl metaacrylate)

IR spectrum with dilution by KBr and in copolymer IR spectrum, the band of aromatic stretch vibration and asymmetric stretch vibration of aliphatic bonds (C-H) have seen in 2949cm -1 and 2993cm-1 .Weak band related to C-C of aromatic , Also , there has seen a band related to (c-cl) in 685 cm -1 range .

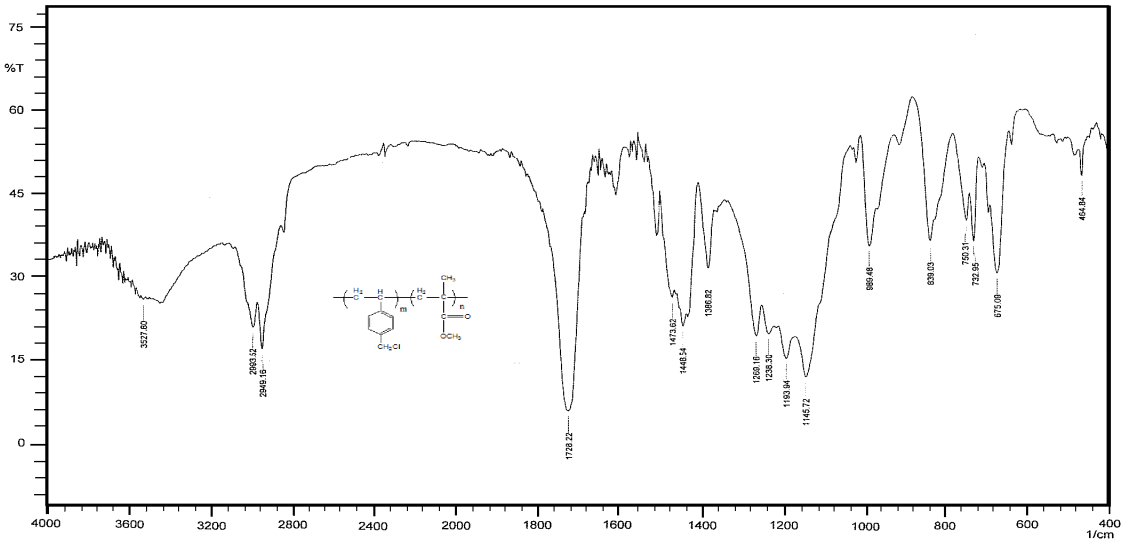

Figure 1. Copylomer IR spectrum (4-chloromethyl styrene methyl metaacrylate)

Examining into copolymer HNMR spectrum (4-chloro methyl styrene – methyl Meta crylate) in CDcl3 solvent.

In ' HNMR spectrum of this copylemer, there is a peak related to (-CH2-CH-) and (C-CH3) hydrogen's in 2.95 and 0.7ppm range . There are two protons related to benzyle chloride (CH2CL) bond in 4/5 ppm range. The peaks in 6.6-7.2 ppm indicate that velatedhydrogens to ring are aromatic.

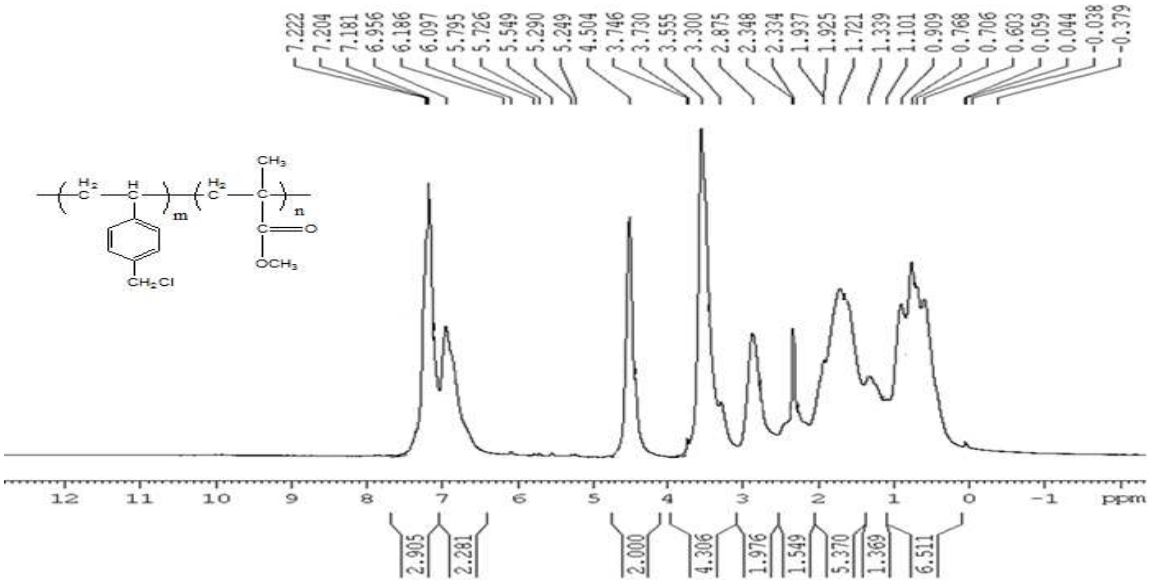

Figure 2. Copolymer HNMR spectrum (4-chloro methyl styrene – methyl Meta crylate) in CDcl3 solvent

Examining copolymer IR spectrum (4-vinyl benzyl 2-pirydin carbaldehidoxime – methyl Meta crylate)

IR spectrum and in resulted copylemer spectrum of related band (C-H) to aromatic has seen in 3051 cm-1. Symmetric stretch vibration and asymmetric stretch vibration of aliphatic (C-H) bonds has seen in 2948cm-1 and 2991cm-1. Also , there has seen weak and average band related to aromatic rings C=C in 1469 cm-1 , 1566 cm-1 , 1676cm -1. The bond band related to (c-o) has seen in 1145 cm-1.

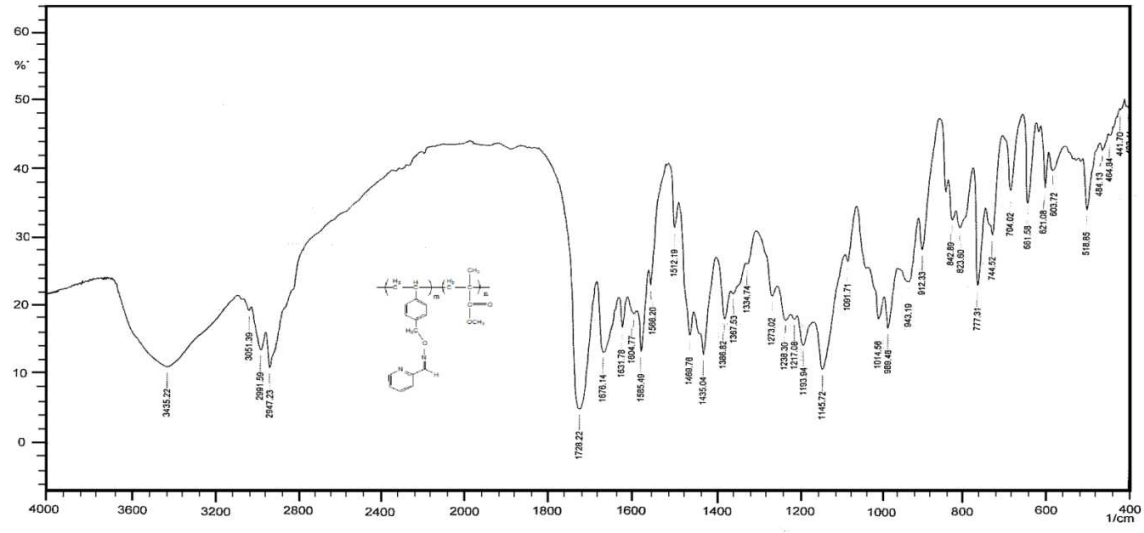

Figure 3. Copolymer IR spectrum (4-vinyl benzyl 2-pirydin carbaldehidoxime – methyl Meta crylate)

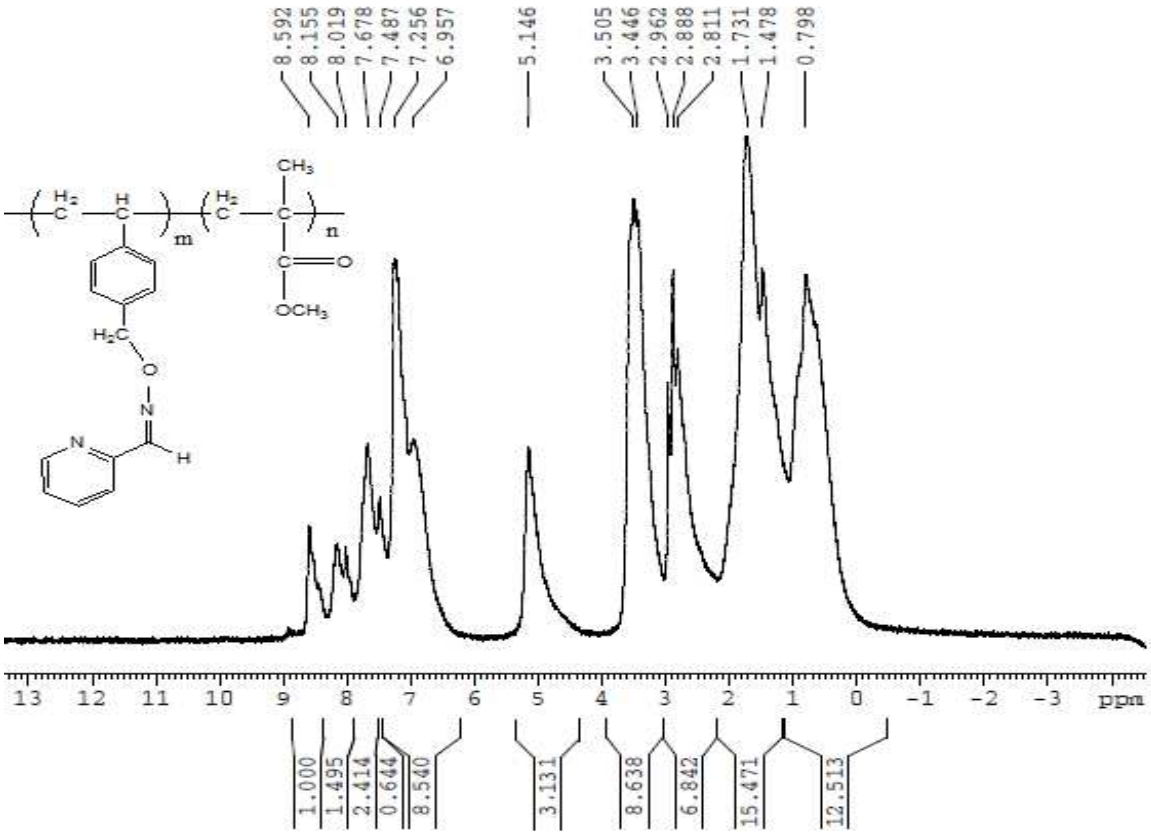

Figure 4. Copolymer HNMR spectrum (4-vinyl benzyl 2-pirydin carbaldehydeoxime methyl Meta crylate) in CDcl3 solvent

Examine into copolymer HNMR spectrum (4-vinyl benzyl 2-pirydin carbaldehydeoxime methyl Meta crylate) in CDcl3 solvent.

jinCD cl3 solvent In HNMR spectrum, it seems that modified copolymer (4-vinyl benzyl 2-pirydin cabaldehydeoxim methyl meta crylate) 2-pyridin carbaldehidoxim reacted with all groups of chloride benzyl and 2-pyridine carbaldhydeoxime groups and the peak that related to hydrogen's (CH2cl) destroyed in 4.5 ppm and the peak that related to hydrogen's (CH2o) has seen in 5.14 ppm range. Also there has been aromatic (C-H) in 6.9 and 8.6 ranges.

Examining into copolymer IR spectrum (4-chloro methyl styrene – methyl acrylate).

IR spectrum with resulted copolymer IR spectrum that is related to aromatic (C-H) has seen in 3001 cm -1. Symmetric and asymmetric stretch vibration of aliphatic (c-h) bonds has seen in 2991 cm -1. The related band to (C=O) in 1732 cm-1 and weak and average band related to aromatic ring c=c have seen in 1512 cm-1 and 1442. We have seen a band for (c-cl) bond in 683 cm -1

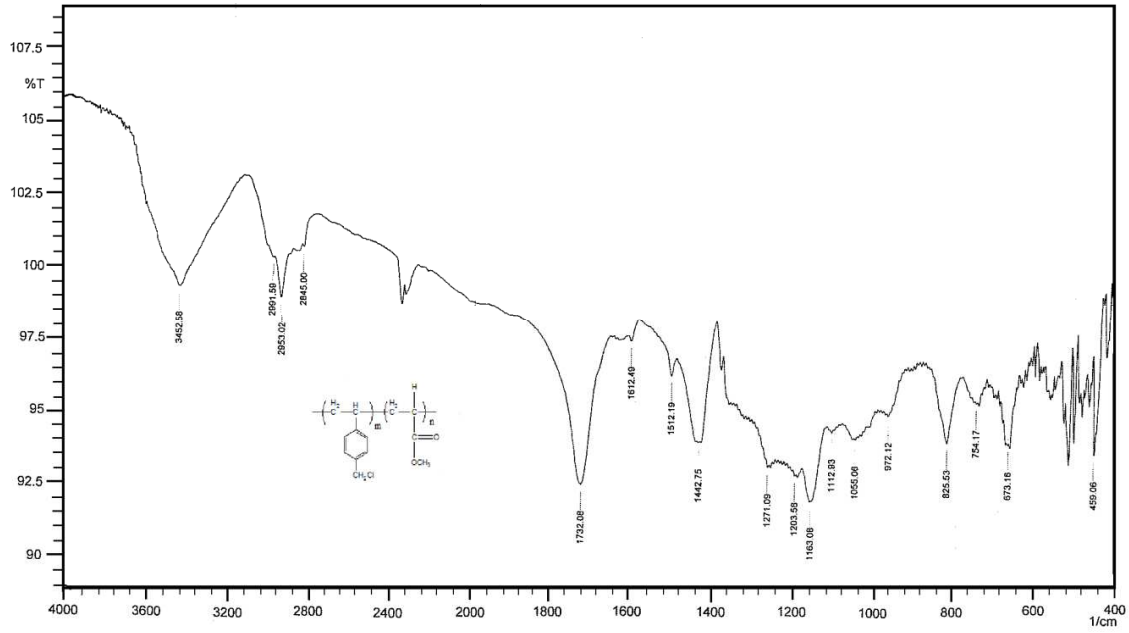

Figure 5. Into copolymer IR spectrum (4-chloro methyl styrene – methyl acrylate)

Examining into copolymer HNMR spectrum (4-chloro methyl styrene – methyl acrylate)

In HNMR spectrum of this copolymer, there is a peak related to (-CH2-CH-) hydrogen's in 0.9 ppm to 2.7 ppm. There are two protons related to benzyl chloride (CH2CL) bond in 4.5 ppm. The peaks in 7.2 and 6.8 ppm indicate hydrogen's related to aromatic ring.

Examining copolymer IR spectrum (4-vinyl benzyl 2-pyridin carbaldehydeoxime methyl acrylate)

IR spectrum in resultelcophymer spectrum of related band (C-H) to aromatic has seen in aromatic. Symmetric and asymmetric stretch vibrations of aliphatic (c-h) bonds have seen in 2949 cm-1. There have been a peak related to (C-O) bond in 1734 cm -1 and a weak band related to aromatic rings C=C in 1585 cm -1 and 1566 . The band related to (C-O) bond is emerged in 1197 cm -1. The peak related to (C=N) is in 1676 cm -1.

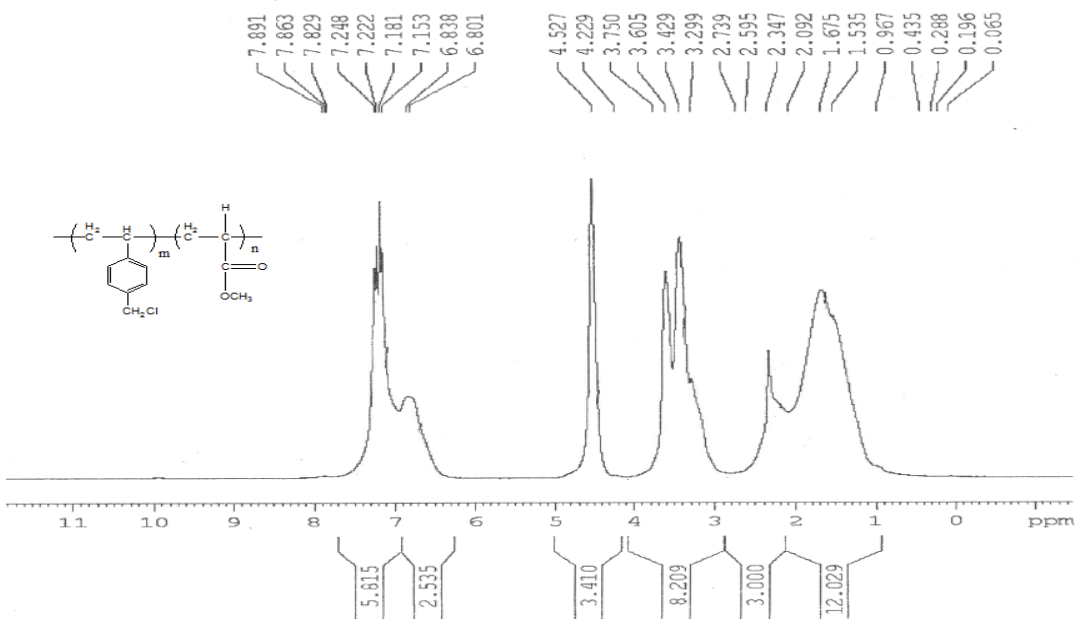

Figure (6) copolymer HNMR spectrum (4-chloro methyl styrene – methyl acrylate)

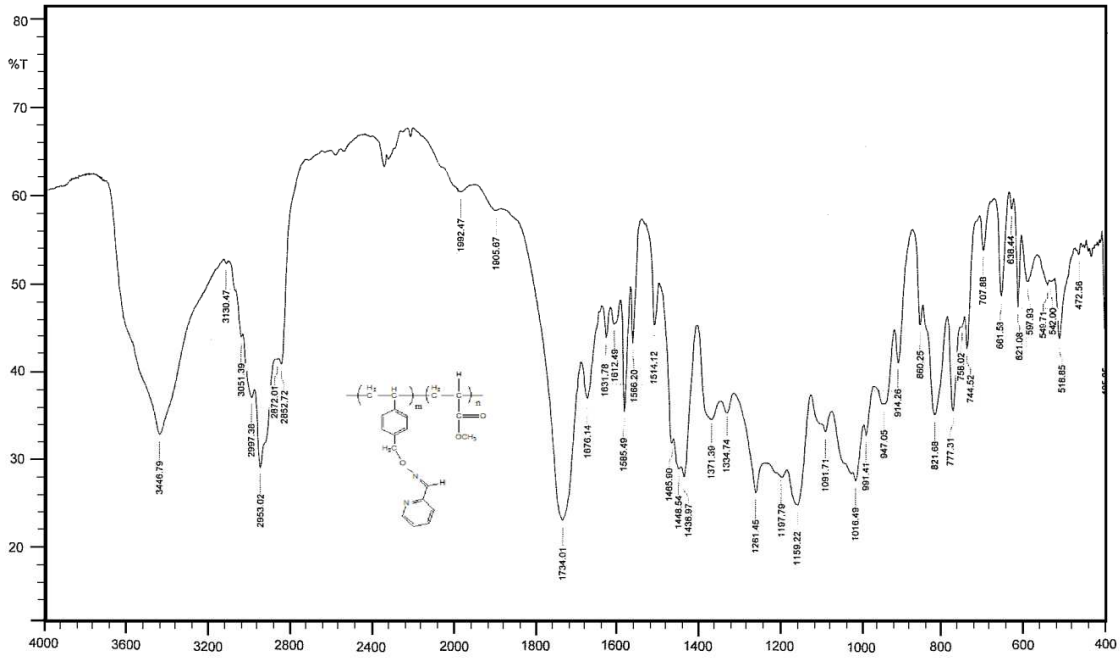

Figure 7. Copolymer IR spectrum (4-vinyl benzyl 2-pyridin carbaldehydeoxime methyl acrylate)

Examining into copolymer HVMR spectrum (4-vinyl benzyl 2-pirydin carbaldhydeoxim – methyl acrylate)

IN HNMR spectrum , modified coplymere (4-viny) benzyl 2-pirydin carbaldehydeoxime – methyl acrylate) with cyclohexanoloxime , it seems that all chloride benzyle groups reacted with 2- pirydinecarbaldehydeoxime groups and related peak to (CH2CL) hydrogen's had destroyed in 4.5 ppm range and there is a peak related to (CH2O) hydrogen's in 5.2 ppm.

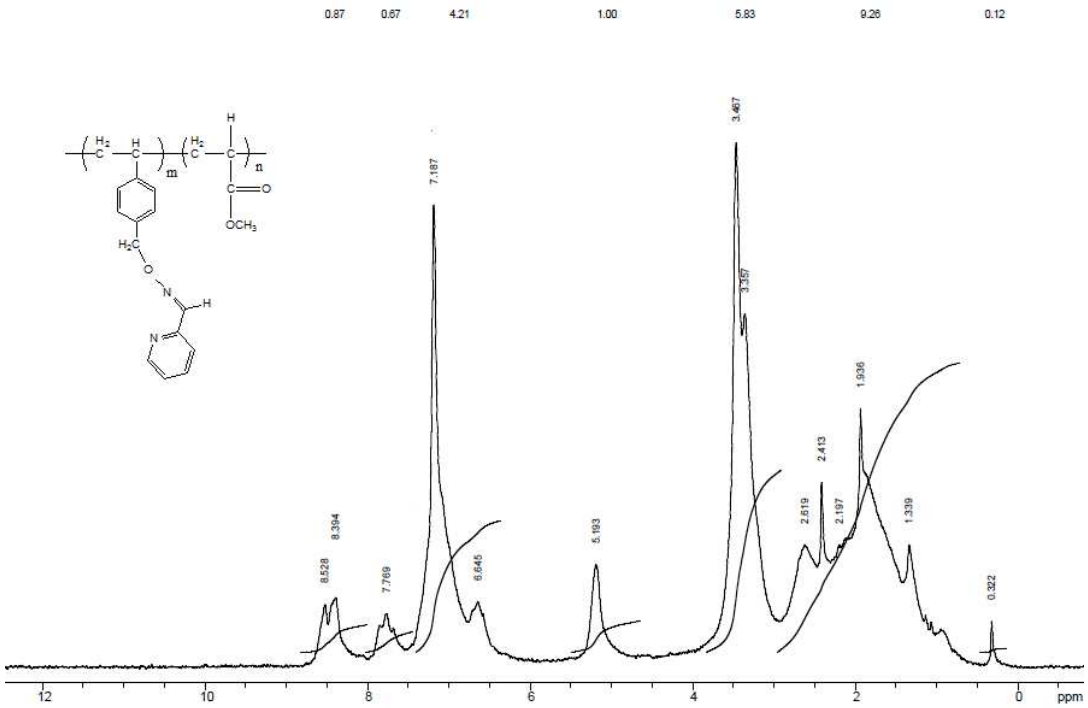

Figure 8. Copolymer HVMR spectrum (4-vinyl benzyl 2-pirydin carbaldhydeoxim – methyl acrylate)

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