Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2012, 4(6):2340-2346
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Chemical modification of glycidyl methacrylate copolymers with oximes containing pyridine groups

Sahar Sattarzadeh* and Hassan Golipour

Department of Chemistry, Ardabil branch, Islamic Azad University, Ardabil, Iran

---

ABSTRACT

In this work the homopolymer and copolymers of glycidyl methacrylate (GMA) with methyl methacrylate (MMA), ethylmethacrylate (EMA), methylacrylate (MA) and ethylacrylate (EA) were synthesized by free radical polymerization using azobis (isobutyronitrile) (AIBN) as initiator at 70 ±10C. Then, copolymers of glycidyl methacrylate have been modified by incorporation of highly sterically hindered demanding 2-pyridinecarbaldehyde oxime through the ring opening reaction of the epoxy groups. The polymers were characterized by 1H-NMR and FT-IR. Presence of bulk the 2-pyridinecarbaldehyde oxime groups in polymer side chains leads to an increase in the rigidity and glass transition temperature of polymer as shown by DMTA analysis. The metal ion uptake by the functional groups of membranes was determined by the use of atomic absorption (AA) and SEM-EDAX and X-Ray Mapping techniques. The research demonstrated that the synthesized modified polymer could successfully remove heavy metals from solution. With the incorporation of the 2-pyridinecarbaldehyde oxime groups in the polymer side chains, a series of novel modified polymer containing new properties are obtained, that can find some applications in polymer industry.

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

---

INTRODUCTION

Chemical modification of glycidil Meta carylate polymers

Caycaretal have synthesized poly glycidil Meta carylate by suspension polymerization technique and then modification of this polymer has performed by imido di acetonitrile (IDAN) and thus modified chains are modified by (IDAN) and hydroxyl amin. The modification of (IDAN) groups and conversation of nitrile groups to amidooxim are followed by FT-IR spectromy. Surface morphology and modified thermal behavior PGMA is definite by scanning elecrtronic microscope and thermal gravimetrytechniques [1].

General properties 2- pirydincarbaldehydeoxim

2-pirydin carbaldehydeoxime is a compound of aromatic heterocyclic containing a pirydinring. Paoh is a white powder in room temperature that it solves easily in solvents such as ethanol, methanol chloro form, diethyl ethroaceton [2].

The synthesis of 2-pirydin carbaldehydeoxim

There are various wags for synthesis of 2- pirydincarbaldehydeoxim from 2- pirydincarbaldehyde that have synthesized by chemists. Youuswani et.al provided a solution fo an equivalent gram from 2-pirydin carbaldehyde and 1.25 gr equivalent from hydroxyl amin hydro chloride for synthesis in water 5ml , then they provided a solution of equivalent 1.25 gr from sodium bi carbonate in water 10ml and next gradually added into first solution .

The solid precipitation, E -2-priydin carbaldehydeoxim had filtered and dried with 0.83 efficiency [3]. Ahmetkocak et.al had performed this reaction using hydroxyl amin hydrochloride, so sodium bi carbonate in benzene and (E)-2-pirydin carbaldehydeoxime in 60 -80.c temperature [4].

MATERIALS AND METHODS

Providing copolymer (glycidil Meta crylate – methyl Meta carylate) poly (GMA-VI-MMA)

In a balliin100ml , the initiator (6.50×10-2g, 0.4mmol) and glycidil Meta crylate (2.84 g, 20mmol) and methyl meta crylate (2000g , 20 mmol) is solved in tetrahydro furan (THF) the solution is de – oxygenated by nitrogen gas flow. Then it is stirred in 70.c temperature for 24 hours .The resulted sticky solution is poured into a beaker containing cold methanol 125ml, while it is stired by a magnetic stirrer.Gradually polymeric precipitations are formed .The polymeric precipitations are separated by decantation of methanol and is washed by cold methanol and is dried in room temperature and under vacaum the resulted polymer's weight is 4.16gr and reaction yield is 86.32%

Providing copolymer (glycidil Meta crylate – methyl Meta crylate) containing 2-pirydin carbaldehydeoxim.

In a balloon 100ml equipped with a bromvial, 2- pirydincarbaldehydeoxim (0.26g, 2.1 mmol) is solved in dried DMF solvent 20ml under nitro gen gas and guard tube of chloride calcium. After 30 minutes , k2co3 (0.88g , 6.3mmol) is added into the balloon .After one hour, BTAC (3.2mmol , 0.72g) is added into the balloon containing oxim and potassium carbonat . then , in a simple balloon 100ml , copolymer (GMA – CO -MMA) 1.4mmol , 0.2g is solved in dried DMF solvent 20ml , next , the simple balloon contents that conaining solved copolymer are added into two top balloons by a brom vial during one hour. There action solution is stirred in room temperature for 24 hours .for precipitation of balloon contents, cold ethanol 150ml is added in to a beaker. Then , polymeric precipitation is formed in the bottom of beaker , next it is preserved in a refrigerator for one night to formed alkoxide is conversed to hydoxid .Polymer is filtered by helping a funnel and fitlterpaper. For washing of oxim , the resulted precipitation is continued with ethanol 50ml twice and with water 50ml twic. Also , for washing of potassium carbonat , we continue washing with water and the resulted whit precipitation .Is dried under vacuum for one hour and in room temperature for 48 hours .The resulted weight is 21% gr and the reaction yield is 45.5%

Providing copolymer (glycerin Meta crylate – methyl acrylate) poly (GMA – CO- MA)

IN a balloon 100ml, new crystal initiator (0.4mmol, 6/500×10-2g) and methyl acrylate (20mmol, 1.730g) is solved in tetrahydro furan THF solvent 20ml. The solution is de – oxygenized by nitrogen gas flow. Then, it is stirred in 70 temperatures for 24 hours. The resulted sticky solution is poured into a beaker containing cold methanol 125 ml, while it is stirred by a magnetic stirrer. Gradually, polymeric precipitations are formed polymeric precipitations are seprated by decantation of methanol and is washed by cold methanol and is dried under vacuum in room temperature. The resulted polymer weight is 2.5gr and reaction yield is 55%

Providing copolymer (glycidilmetacrylate methyl acrylate) containing 2-pirydin carbaldehydeoxim group

In a balloon 100ml, new crystal initator (0.4mmol, 6.500×10-2g) and glycidil Meta crylate (20mmol, 2.840g) and ethyl acrylate 20mmol, 2.560g are solved in tetrahydrofurrun (THF) solvent 20ml. The solution is de oxygenated by nitrogen gas flow .then; it is stirred in 70 temperatures for 24 hours. The resulted sticky solution is pourd into a beaker containing cold ethanol 125 ml .while it is stirred by a magnetic stirrer .Gradually, polymeric precipitations are formed, the polymeric precipitations are separated by decantation of methanol and are washed by methanol and are dried under vacuum in room temperature .The resulted polymer weight is 2.75 gr and reaction yeile is 48.71%.

RESULTS AND DISCUSSION

Examining into copolymer IR pectrumPoly (GMA –CO - MMA)

Symmetric and asymmetric stretch vibration of aliphatic C-H bonds have seen in 3002.61cm-1 and 2991.59cm-1.The stretch vibration of carbonil ester has seen in 1732.08 cm-1.The prak of 908.47cm-1 is related to asymmetric stretch vibration of epoxy C-O bonds. The peaks in 1269.16 and 1149.57cm -1 are related to stretch vibration of ester C-O bonds Figure 1.

Examining into copolymer IR spectrumPoly (GMA –CO - MA)

Symmetric and asymmetric stretch vibrations of aliphatic C-H bonds have seen in 3061.03 cm-1 and 3007.02cm-1. The stretch vibration of carbonyl ester has seen in 1732.09cm-1 the peak of 906.54 cm-1 range is related to asymmetric stretch vibration of epoxy ring C-O bonds. The peaks in 1261.45cm-1.And 1114.88cm-1 are related to stretch vibration of ester C-O bonds Figure 2.

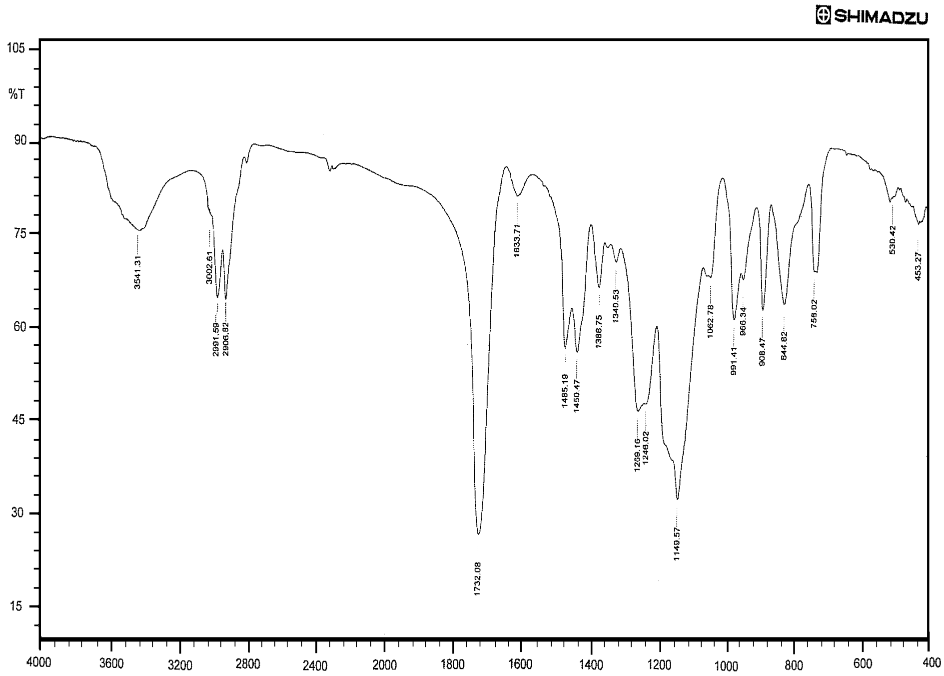

Figure 1. Copolymer IR pectrum Poly (GMA –CO - MMA)

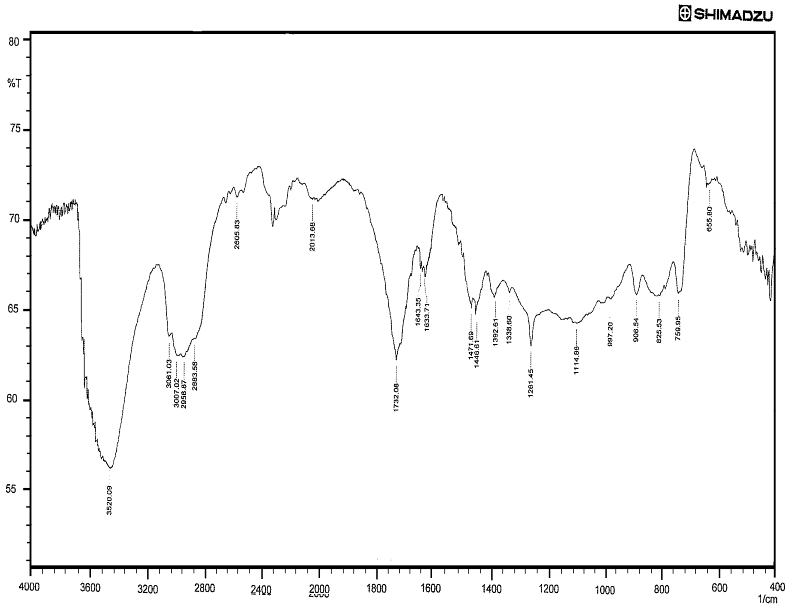

Figure 2. Copolymer IR spectrum Poly (GMA –CO - MA)

Examining into copolymer H-NMR spectrum Poly (GMA –CO - MMA) in CDCL3

In 'H NMR , copolymer Glycidilmetacrylate, CH hydrogen's, the main chain of polymer and the main chain of CH2 hydrogen's have seen in 0.84-1.88ppm.Methylen protons of epoxy rings have seen in 2.61ppm and 2.81 ppm.3.19ppm peak caused by epoxy ring methyl hydrogen. Two methyl protons through the COOCH2 ester groups in polymer GMA unite have seen in 4.24-4.29ppm and 3.76 -3.74ppm. The absorption of 3 methyl proton through the COOCH3 ester group related to MMA have seen in 3.56 ppm range Figure 3.

Examining into copolymer H-NMR spectrum Poly (GMA –CO - MA) in CDCL3

In H-NMR spectrum , copolymer glycidil meta crylate – methyl acrylate , CH3 hydrogen's of the main polymer chain and CH3 hydrogen's of the main chain and CH methyl acrylate have seen in 0.88 -2.14ppm. Methyl protons of epoxy rings have seen in 2.58ppm and 2.78ppm.3.1ppm peak is caused by methynhydrogroup in polymer GMA unit have seen in 4.03 ppm and 4.26ppm .The absorption of three methyl proton through – cooch3 ester group related to MA units have seen in 3.58 -3.68 ppm Figure 4.

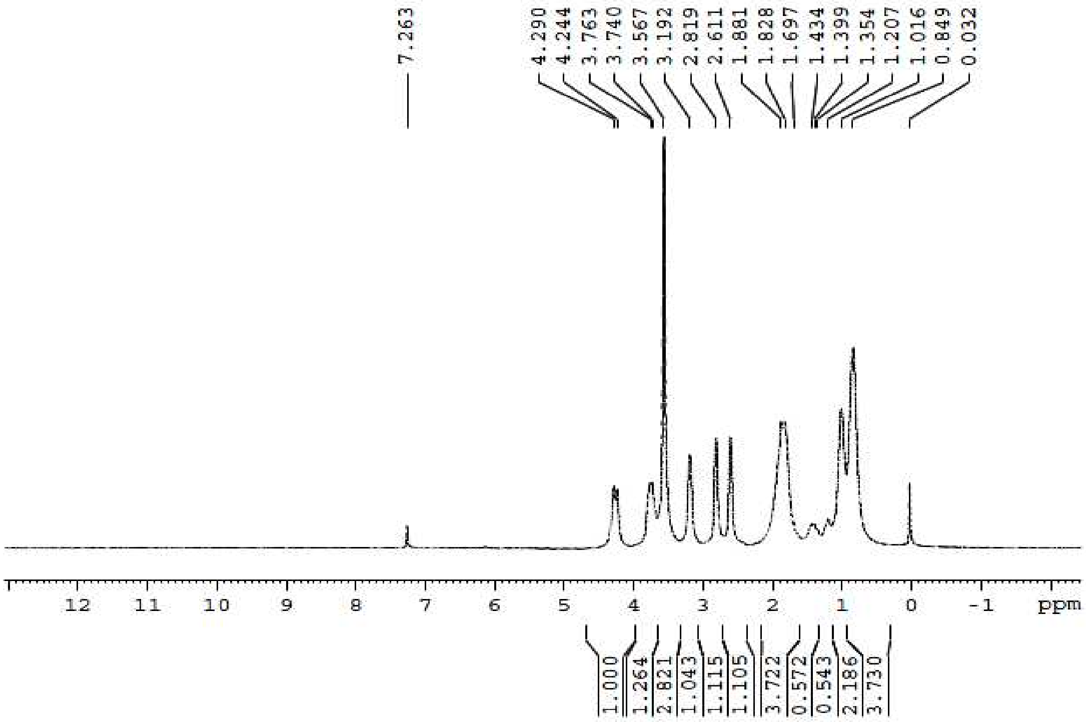

Figure 3. Copolymer H-NMR spectrum Poly (GMA –CO - MMA) in CDCL3

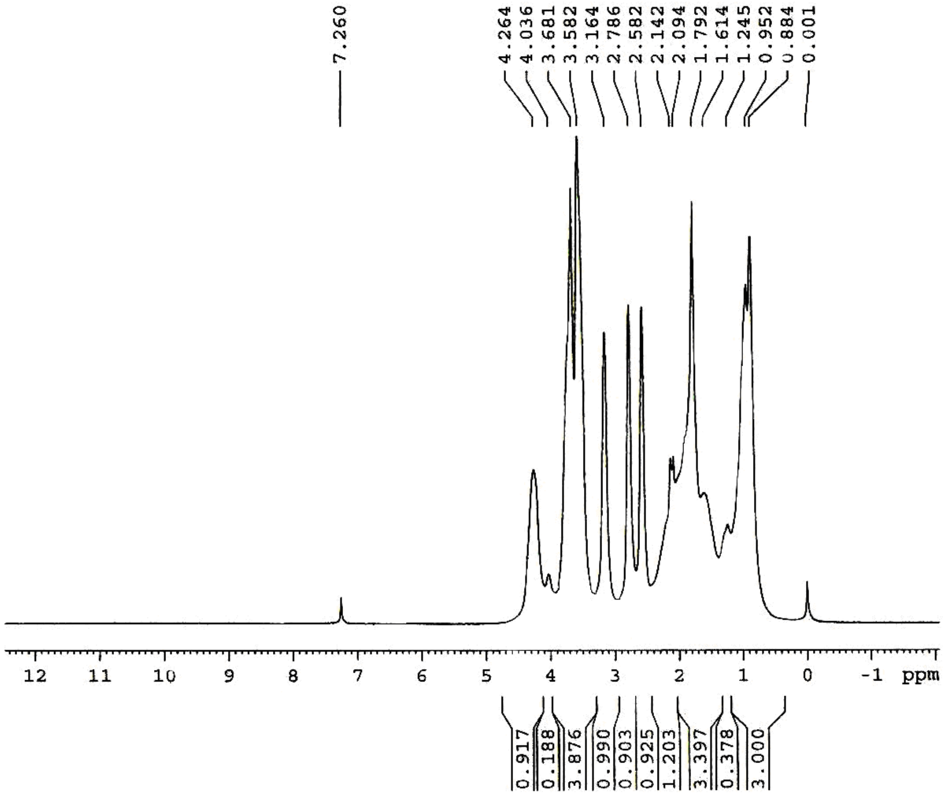

Figure 4. Copolymer H-NMR spectrum Poly (GMA –CO - MA) in CDCL3

Examining into copolymer IR spectrum Poly (GMA –CO - MA) containing 2-pirydine carbaldehydeoxime

IN IR spectrum, modified polymer of peak related to C-O epoxy ring has been reduced due to spatial inhibition of 2-priydin carbaldehydeoxime but it is not destroyed perfectly. The hand in 3431.36cm-1 related to the presence of secondary alcohol 1 functional groups is in polymeric chain and it indicates that ring opening reactions in polymer are fundamental. The peak related to carbonyl ester group has stretched from 1732.08 to 172cm-1, probably it is formed with OH that generated in hydrogenise bond .the peaks with average intensity have seen in 1564.27cm and 1585.49 that are related to aromatic ring C=C after throghtoxime the rest peaks of IR spectrum is similar with not reacted polymer peaks .The peak related to oxime N-O bond has seen after through in 941.92cm-1 Figure 5.

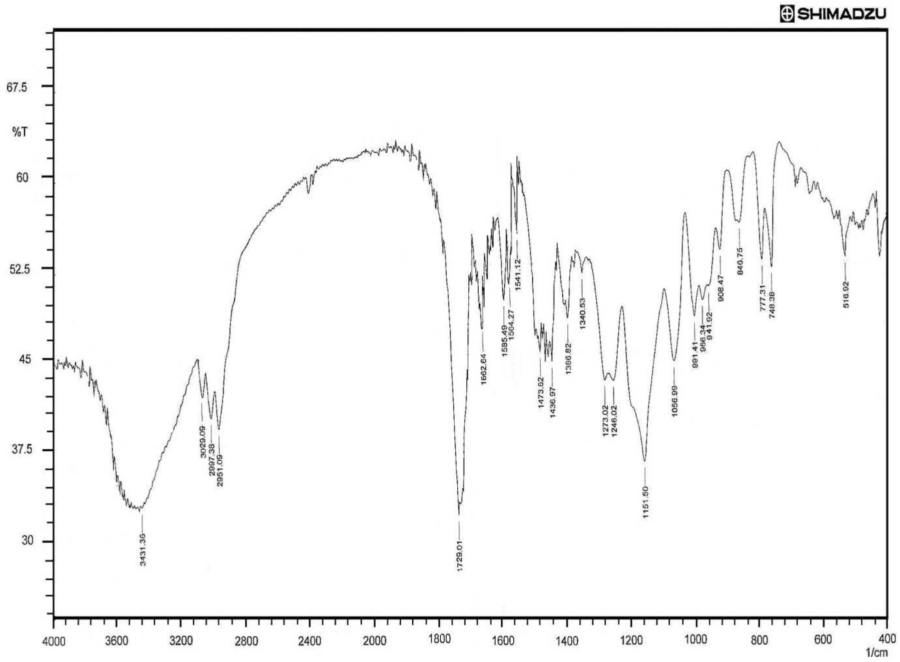

Figure 5. Copolymer IR spectrum Poly (GMA –CO - MMA) containing 2-pirydine carbaldehydeoxime

Examining into copolymer IR spectrum Poly (GMA –CO - MA) containing 2-pirydin carbaldehyleoxime groups.

In IR spectrums of modified polymer, related peak to epoxy ring of C-O in 906 cm-1 has destroyed perfectly. The present band in 3412.08cm-1 range is related to the presence of secondary alcohol functional group in polymeric chain that it is indicative of opening –ring reactions in fundamental polymer. The peak related to carbonyle ester has stretched from 1732 cm-1 to 1724cm-1Probably it is formed with generated OH of hydrogenise bond .the peaks with average intensity that have seen in 1560.41 and 1587.42 cm-1 are related to aromatic ring C=C after through the oxim .The related peak to oxime N-O bond has seen after through in 93.19cm-1. The remain peaks of IR spectrum similar with polymer peaks haven't reacted Figure 6.

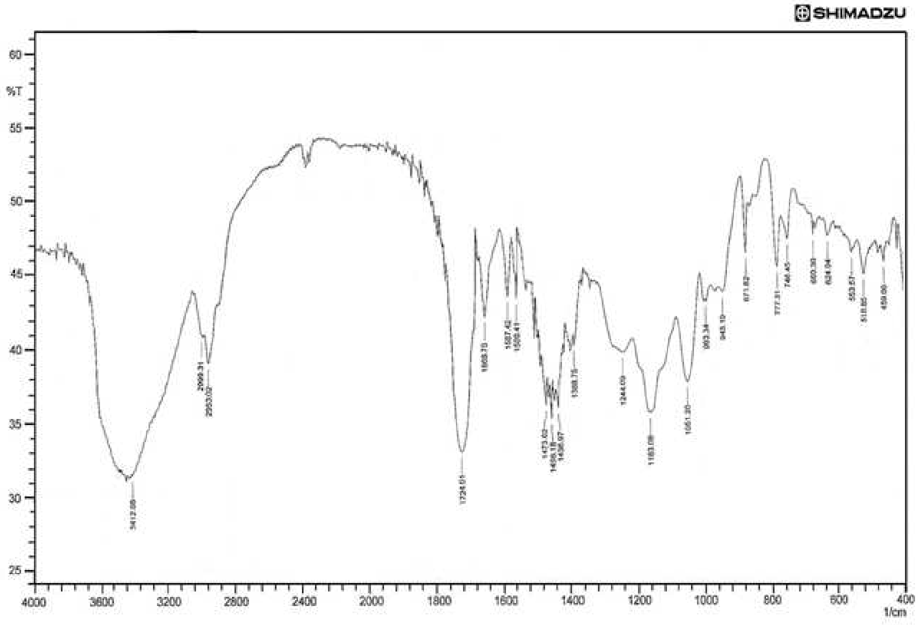

Figure 6. Copolymer IR spectrum Poly (GMA –CO - MA) containing 2-pirydin carbaldehyleoxime groups

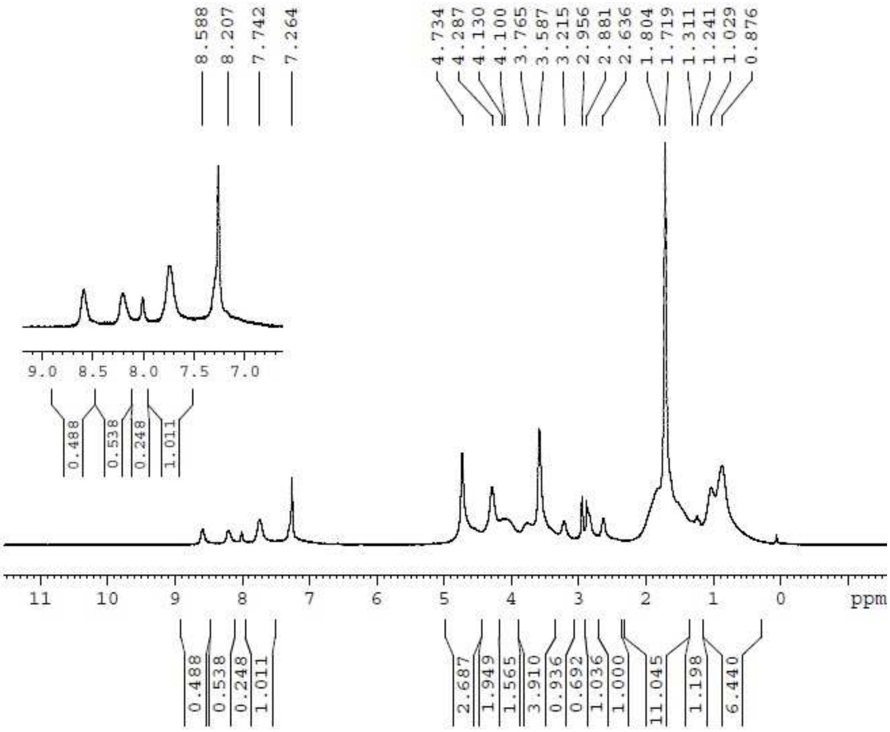

Figure 7. Copolymer H-NMR Poly (GMA –CO - MMA) containing 2-pirydin carbaldehyleoxime groups in chloroform

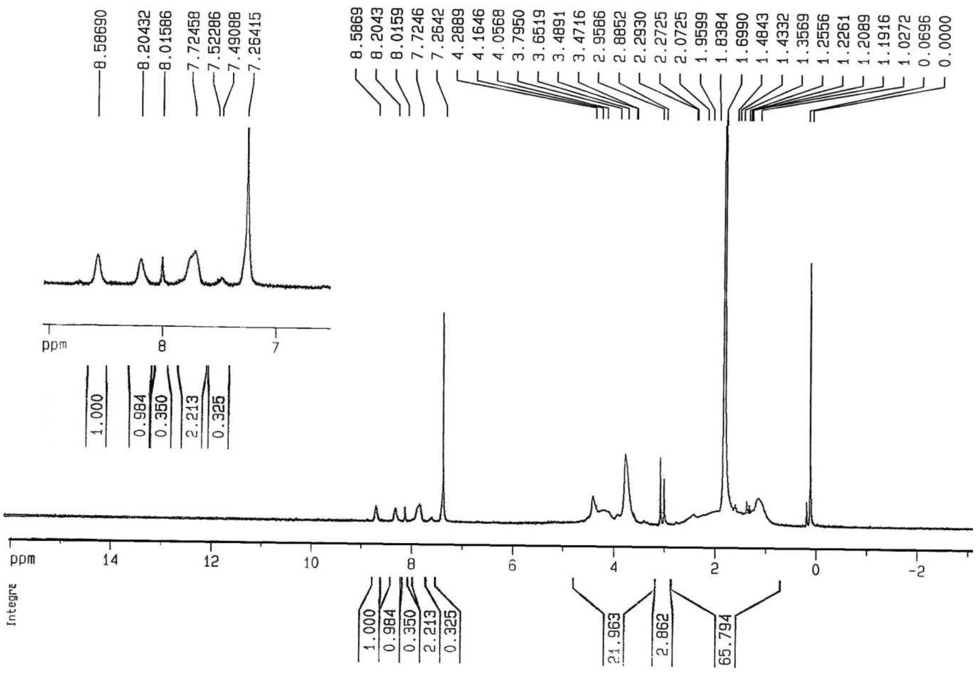

Figure 8. Copolymer H-NMR Poly (GMA –CO - MA) containing 2-pirydin carbaldehyleoxime in chloroform solvent

Examining into copolymer H-NMR Poly (GMA –CO - MMA) containing 2-pirydin carbaldehyleoxime groups in chloroform

In H-NMR copolymer glycidilmetacrylate modified methyl metacrylate , have not destroyed due to spatial inhibition of 2- pirydincarbaldehydeoxime, two CH2 hydrogen of epoxide ring in 2.6ppm and 2.8ppm and CH hydrogen of epoxide ring in 3.21ppm perfectly. The present peak in 3.58 is related to protons of COOCH3 ester group in MMA unit. IN 4.1-4.73 ppm range, the peaks of CH hydrogen and CH2 epoxide ring have overlapped after opening the amounts of epoxide with related peak to COOCH2 two hydrogen in GMA unit. The peaks in 7.74-8.58 ppm are indicative of 2-pirydine carbaldehydeoximehydrogens. Other protons in copolymer structure have remained in %87-1.8ppm range Figure 7.

Examining into copolymer H-NMR Poly (GMA –CO - MA) containing 2-pirydin carbaldehyleoximein chloroform solvent

In H-NMR, modified copolymer glycidil Meta crylate methyl acrylate CH2 hydrogen of epoxide ring in 2.63 ppm and 2.88 ppm and CH hydrogen of epoxide ring in 3.21 ppm have remained. Three hydrogen are related to COOCH3 of MA unit in 3.79-4.05 ppm. Two hydrogen COOCH2 in GMA unit with related peak to CH, CH2 hydrogen's of epoxide ring overlapped after opening the amount of epoxides and related peak to oh group that caused by opening epoxide ring. The peaks in 7.26-8.58 ppm are indicative of 2-pirydin carbaldehyleoximehydrogens. Other protons in copolymer structure have remained in 0.06-2.29ppm ranges Figure 8.

REFERENCES

[1] T Caykara T, S.S Alaslan, J. Appl. *Polym*. Sci. **2007**, 106, 2126-2131.
[2] J Smith, A Limprich, B Romer, *Organic Synthesis Archive Book*, **2004**, 12.
[3] Y.M Wani, A Fareeda, A.S Attar, A Amir, A.S Mohan, Ch Inho, R.A Bhat, Eur. J. *Med. Chem*. **2011**, 46, (9), 4742 – 4752.
[4] A Kocak, S Malkondu, A Yaylaci, S Kurbanli, G Ahmetli, N Kocak, **2011**, *Synth*. *Comm*. **2011**, 41, (11), 1629 – 1637.