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Synthesis of New Poly (Subs- Vinyl Malonate Amide) from Malonic Acid

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Abstract: ***New polymers were prepared by modification of malonic acid, these polymers were prepared by several steps. The first step was included reaction of poly vinyl alcohol with malonyl chloride to produce poly vinyl malonate. Second step was included reaction of poly sodium vinyl malonate with different alkyl halide. Bromine in was added to produce polymers in third step, and then added ammonia to prepared polymers to form poly amino alkyl vinyl malonate. The last step was reacted poly amino malonate with acid chloride [(acetyl, benzoyl) chloride] in DMF. All the prepared polymers were characterized by FT-IR, H-NMR, and measured some of different physical properties as, solubility and softening point.***

Keywords: malonic acid, polyvinyl alcohol, polyester-amide

1. Introduction

Malonic acid (also called propanedioic acid) is a dicarboxylic acid with structure CH_2 (COOH) $_2$.It's a white crystalline with melting point 135-136 C; readily soluble in water, alcohol and ether. Malonic acid itself is rather unstable and has few applications[1]. Malonic acid was converted to malonyl dichloride which can be prepared from reaction of malonic acid with thionyl chloride. Malonyl dichloride converted into polyester. Malonic acid and its esters[2] contain active methylene groups which have relatively acidic alpha-proton due to H atoms adjacent to two carbonyl groups. Malonyl chloride was reacted with PVA to prepare ester polymers. Polyesters are one of the most versatile synthetic polymers. They are widely used commercially as fibers, plastics, and coatings[3, 4, 5]. On the other hand polyamides which prepared in this paper. Polyester-amide represent a class of high performance usually formed by the reaction of polyester which is prepared with acid chloride. These polymers have found use in a wide variety of applications since they possess many desirable characteristics, such as good process ability, good mechanical properties, good thermal stability, and chemical resistance[6, 7].

In this research includes preparing of ester –acid chloride polymers through the reaction of acid chloride with polyvinyl alcohol, the produced polymers were modified to ester –amide by reaction with acetyl chloride and benzoyl chloride to yield ester – amide polymers. As shown in scheme (1).

2. Experimental

A-Instruments

1) Melting points were determined on Gallenkamp capillary melting point apparatus.
2) FTIR spectra were recorded using KBr discs on Shimadzu FTIR-8400 Fourier Transform Infrared spectrophotometer in Ministry of Science and.
3) ^{1}H-NMR spectrum were recorded on near magnetic resonance Bruker, Ultrashield 300 MHz in Iran, using tetramethylsilane as internal standard and deuterated dimethyl sulfoxide (DMSO-d_6) as solvent.

B-Procedure of prepared compounds.

1-Preparation of malonyl chloride (8)

In 250 round bottom flask with a reflux condenser and dropping funnel was dissolved (2.5 g) of malonic acid (1mol) in 10 ml of dioxanethen added to the flask (5ml) of thionyl chloride (2mol) its added gradually by dropping funnel , A mixture was stirred and refluxed for (0.5-1) hrs.

2-Preparation ofpoly (vinyl malonate) (9)

In 250 round bottom flask was dissolved (2g)(1mol.) of poly vinyl alcohol in 20 ml DMF, [4ml (1mol.)]of the malonyl chloride was added to the polyvinyl alcohol with (1 ml) Et_3N to remove salt.The mixture refluxed for 4-5 hrs. The product was purified by dissolved in DMSO and reprecipitating from another solvent such as (water, ethanol, acetone, THF).

3-General preparation ofpoly [(2-alkyl)vinyl malonate] (10)

In 250 round bottom flask was dissolved [0.8 g (0.1 mol)] sodium metal in (30 ml) absolute methanol.Sodium methoxidewas product and added to poly (vinyl malonate) to prepared poly(sodium vinyl malonate), Then added different alkyl halide [0.5-1.2 ml (1 mol)] to poly (sodium vinyl malonate) [4 g (1 mol)] with (1 ml) Et_3N to remove the salts, the product wasrefluxed for (8-10) hrs. The mixture was purified bydissolved in DMSO and reprecipitating from another solvent such as (water, ethanol, acetone, THF).

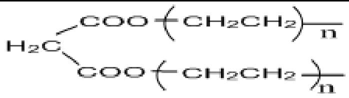
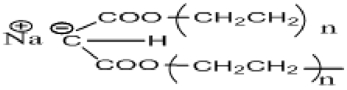
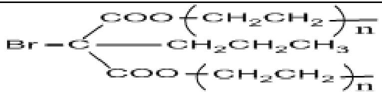
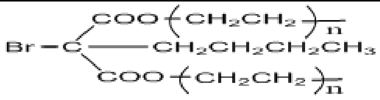
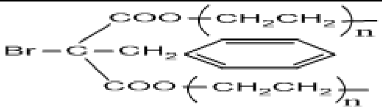
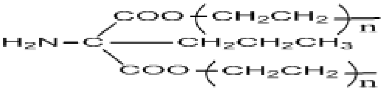
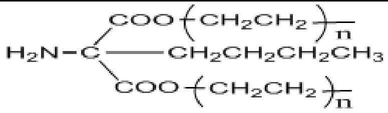
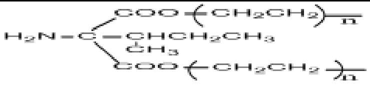
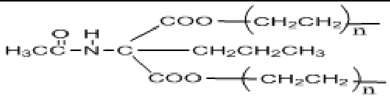
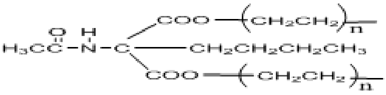
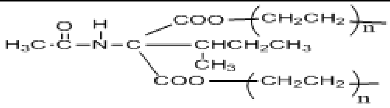
4- General preparation of poly [(2-amino-2-alkyl) vinyl malonate] (11)

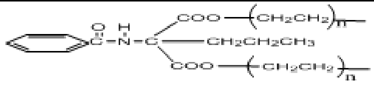
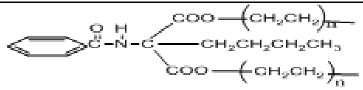
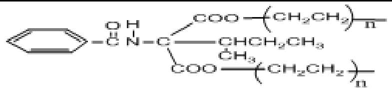
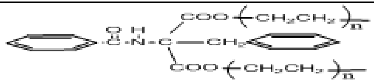
In 250 round bottom flask was dissolved (4 ml) of bromine in CCl_4 then added to poly [(2-alkyl) vinyl malonate] (1 mol) and (1ml) of Et_3N, Then mixture was refluxed for 4 hrs. The product was filtered and purified by dissolved in DMSO and reprecipitating from another solvent such as (water, ethanol, acetone, THF). (1 mol) of product was added to (1mol) ammonia with (1ml) Et_3N. The mixture was refluxed 4 hrs.Finally the product was filtered and purified by dissolved in DMSO and reprecipitating from another solvent such as (water, ethanol, acetone, THF).

5-General preparation of Poly (Subs- vinyl malonate amide) (12)

In 250 round bottom flask was dissolve (1mol) of poly [(2-amino-2-alkyl) vinyl malonate]in 10ml DMF and (1mole) acid chloride [(acetyl and benzyl) chloride] with (1 ml) ofEt_3N was added and refluxed for (4-6) hrs. .The product was purified by dissolved in DMSO and reprecipitating from another solvent such as (water, ethanol, acetone, THF.

Table 1: Physical Properties of the prepared Compounds (1-22)

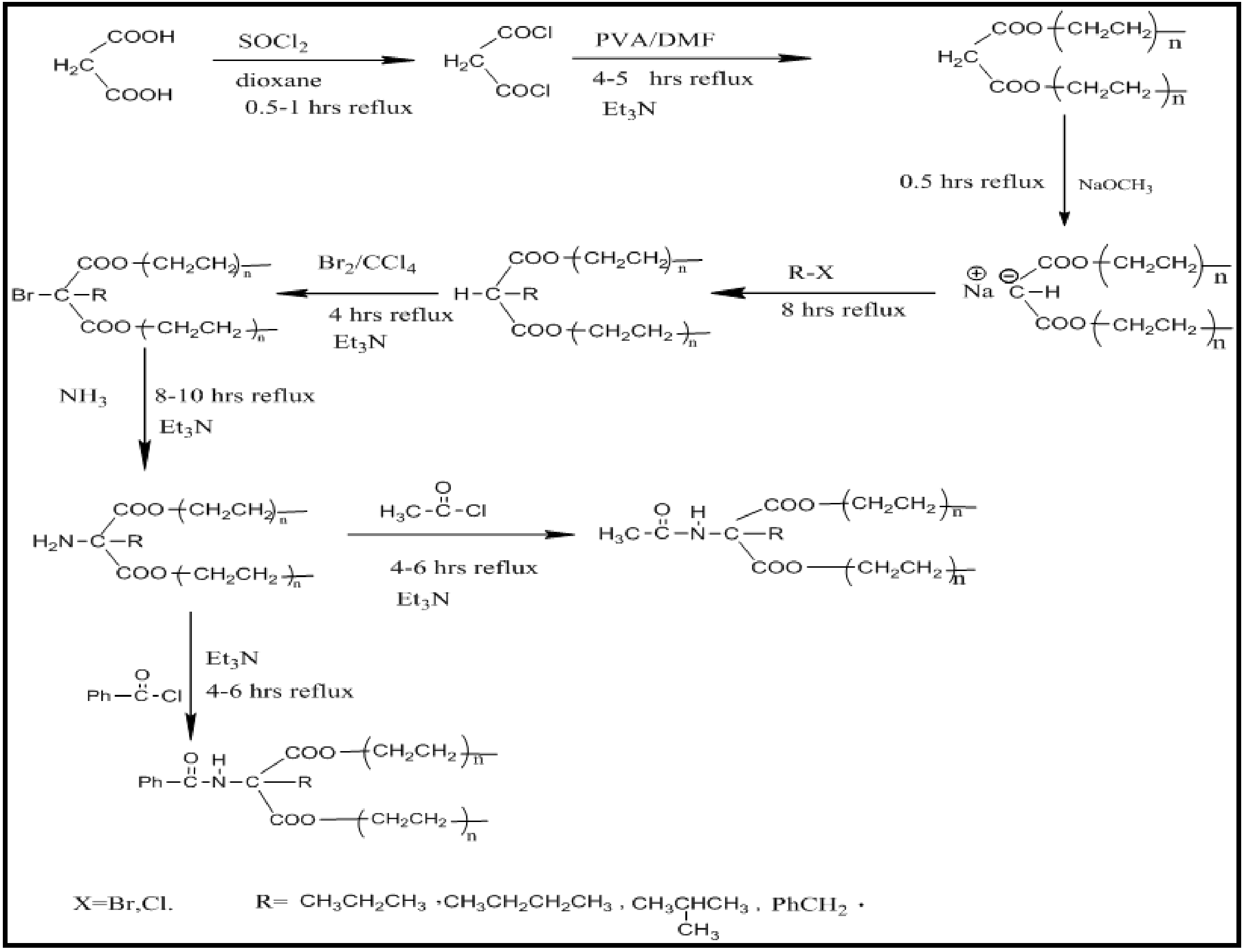
NO.	Structure	Colour	S.P	Conversion %
1		Yellow	141-156	57
2		Yellow	146-160	78
3		Deep yellow	176-186	89
4		Brown	181-196	79
5		Deep orange	187-203	68
6		Black	198-213	79
7		Light yellow	203-211	78
8		Yellow	209-223	75
9		Orange	217-230	80
10		Deep orange	229-242	54
11		Black	232-247	69
12		Brown	237-286	73
13		Deep brown	241-253	87
14		Black	253-268	78
15		Brown	274-286	93
16		Deep orange	278-291	75
17		Deep yellow	285-297	96

18		Black	303-312	81
19		Deep orange	306-319	89
20		Light brown	313-325	95
21		Brown	325-337	73
22		Black	337-348	87

3. Results and Discussion

In the current study of synthesis of the targeted compounds Synthesis of New Poly (Subs- vinyl malonate amide) were obtained by series reactions. Malonic acid was the starting material. All product have conversions ratioranges {54-96} %. The synthesis of compounds (1-22) are outlined in scheme (1).

Scheme (1).



Compounds {1, 2, 3, 4, 5, and 6} were prepared by reaction of malonyl chloride with PVA and different alkyl halides in DMF. The softening point's ranges were {141-213} and conversions ratio were {57-89} %. All the physical properties of the compounds are listed in the Table (1).

FTIR of Compounds {1, 2, 3, 4, 5, and 6} showed appearance of the absorption band of (νC=O) ester at (1724-1740) cm$^{-1.}$ Absorption band of (νC-H) aliphatic at (2817-2990) cm^{-1}.And the other associations are listed in Table (3). H-NMR of preparedpolyester compound (1) show 0.47 ppm (t, 4H, CH2); 3.4 ppm (t, 4H, S-CH2-O); 3.9 ppm(s, 2H, CH2) show in fig.(1)

H-NMR of prepared compound (3) show 0.52 ppm (t, 4H, CH2); 0.87 ppm (t, 3H,); 1.3 ppm(tq, 2H,) show in fig.(2). Compounds {7, 8, 9, and 10} were prepared by reaction of poly [(2-alkyl) vinyl malonate] with bromine. The softening point's ranges were {203-242} and conversions ratio were {54-80} %. All the physical properties of the compounds are listed in the Table (1).

FTIR of Compounds {7, 8, 9, and 10} showed appearance of the absorption band of (νC=O) ester at (1733-1749) cm^{-1}. Absorption band of (νC-H) aliphatic at (2780-2981) cm^{-1}.FTIR spectra showed the formation of a new absorption region at (622-773) cm^{-1} of (νC-Br). And the other associations are listed in Table (3).

H-NMR of prepared compound (10) show 0.5ppm (t, 4H, CH2); 3.12 ppm (s, 2H, S-<u>CH2</u>-O); 7.6 ppm(s, 2H, CH2 aromatic ring) show in fig.(3)
Compounds {11, 12, 13, and 14} were prepared by reaction of poly [(2-bromo-2-alkyl) vinyl malonate] with of poly [(2-amino-2-alkyl) vinyl malonate]in DMF.The softening point's ranges were {232-268} and conversions ratio were {69-87} %. All the physical properties of the compounds are listed in the Table (1).

FTIR of Compounds {11, 12, 13, and 14} showed appearance of the absorption band of (νC=O) ester at (1734-1750) cm^{-1}. Absorption band of (νC-H) aliphatic at (2775-2990) cm^{-1}. FTIR spectra showed disappearance of (νC-Br) and formation of new absorption region at (3360-3490) cm^{-1} of (νC-NH_2).And the other associations are listed in Table (3).

H-NMR of prepared compound (11) show 0.53ppm (t, 4H, CH2); 4.9 ppm (s, H fr NH2,); 7.6 ppm(s, 2H, CH2) show in fig.(4)

Compounds {15- 22} were prepared by reaction of poly [(2-amino-2-alkyl) vinyl malonate]with acid chloride [(acetyl and benzyl) chloride] in DMF.The softening point's ranges were {274-348} and conversions ratio were {73-96} %. All the physical properties of the compounds are listed in the Table (1).

FTIR of Compounds {15- 22} showed appearance of the absorption band of (νC=O) ester at (1726-1750) cm^{-1}. Absorption band of (νC-H) aliphatic at (2779-2998) $cm^{-1}$and Absorption band of (νC-H) aromatic at (3020-3116) cm^{-1} and Absorption band of (νC=C) at (1514-1590) cm^{-1}. FTIR spectra showed appearance of the absorption band of (νC=O) amide at (1662-16) cm^{-1}.FTIR spectra showed disappearance of(νC-NH_2) and formation of new absorption region at (3149-3386) cm^{-1} of (νC-NH). And the other associations are listed in Table (3).

H-NMR of prepared compound (18) show 0.5ppm (t, 4H, CH2)); 7.6 ppm(s, 2H, CH2 aromatic ring) 8.7 ppm (s, H for NH,); show in fig.(5)

H-NMR of prepared compound (21) show 0.52ppm (t, 4H, CH2)); 6.5 ppm(s, 2H, CH2 aromatic ring) 9.3 ppm (s, H for NH,); show in fig.(6)

Table 2: Solubility of the prepared polymers**.**

Comp. No.	$CHCl_3$	CCl4	Water	DMF	Acetone	DMSO	Benzene	THF	CH_2Cl_2	Dioxane
1.	Ins.	P.S	S.	S.	P.S	S.	Ins.	P.S	P.S	Ins.
2.	Ins.	P.S	S.	S.	Ins.	S.	Ins.	P.S	P.S	Ins.
3.	Ins.	P.S	P.S	S.	P.S	S.	Ins.	P.S	P.S	Ins.
4.	Ins.	P.S	P.S	S.	Ins.	S.	Ins.	P.S	P.S	Ins.
5.	Ins.	P.S	P.S	S.	Ins.	S.	Ins.	P.S	P.S	Ins.
6.	Ins.	P.S	P.S	S.	P.S	S.	Ins.	S.	P.S	Ins.
7.	Ins.	P.S	P.S	S.	Ins.	S.	Ins.	S.	P.S	Ins.
8.	Ins.	P.S	P.S	S.	Ins.	S.	P.S	P.S	P.S	Ins.
9.	Ins.	P.S	P.S	S.	Ins.	S.	P.S	P.S	P.S	Ins.
10.	Ins.	P.S	P.S	S.	Ins.	S.	Ins.	P.S	P.S	Ins.
11.	Ins.	P.S	Ins.	S.	P.S	S.	Ins.	P.S	P.S	Ins.
12.	Ins.	P.S	Ins.	S.	Ins.	S.	Ins.	P.S	P.S	Ins.
13.	Ins.	P.S	Ins.	S.	Ins.	S.	Ins.	P.S	P.S	Ins.
14.	Ins.	P.S	P.S	S.	P.S	S.	Ins.	P.S	P.S	Ins.
15.	Ins.	Ins.	Ins.	S.	Ins.	S.	Ins.	P.S	Ins.	Ins.
16.	Ins.	Ins.	P.S	S.	Ins.	S.	Ins.	P.S	Ins.	Ins.
17.	Ins.	Ins.	Ins.	S.	Ins.	S.	P.S	P.S	Ins.	Ins.
18.	Ins.	Ins.	Ins.	S.	Ins.	S.	Ins.	P.S	Ins.	Ins.
19.	Ins.	Ins.	Ins.	S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.
20.	Ins.	Ins.	Ins.	S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.
21.	Ins.	Ins.	Ins.	S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.
22.	Ins.	Ins.	Ins.	S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.

s. =soluble, p.s=partiallysoluble, Ins. =insoluble

Table 3: FTIR absorption (cm^{-1}) of the prepared compound.

+No.	ν(C=O) Ester	ν(C-H) Aliphatic.	ν(C-H) Aromatic.	ν(C=C) Aromatic	ν(NH2)	ν(N-H)	Other band
1.	1739	2985 2941	–	–	–	–	–
2.	1740	2987 2939	–	–	–	–	–
3.	1724	2950 2990	–	–	–	–	–
4.	1731	2943 2817	–	–	–	–	–
5.	1724	2987 2910	–	–	–	–	–
6.	1739	2977 2945	3024	1580 1545	–	–	–
7.	1733	2972 2844	–	–	–	–	ν(C-Br)=622
8.	1741	2921 2845	–	–	–	–	ν(C-Br)=638
9.	1739	2981 2830	–	–	–	–	ν(C-Br)=773
10.	1749	2960 2780	3028	1590 1550	–	–	ν(C-Br)=682
11.	1750	2990 2914	–	–	3360 3470	–	–
12.	1745	2964 2906	–	–	3490 3448	–	–
13.	1741	2985 – 2880	–	–	3435 3419	-	_
14.	1734	2846 2775	3062	1563 1534	3430 3421	–	–
15.	1737	2968 2937	–	–	–	3386	ν(C=O) amide=1631
16.	1739	2972 2943	–	–	–	3290	ν(C=O) amide=1629
17.	1737	2975 2935	–	–	–	3238	ν(C=O) amide=1635
18.	1745	2998 2890	3087	1568 1534	–	3367	ν(C=O) amide=1665
19.	1750	2960 2779	3028	1590 1550	–	3149	ν(C=O) amide=1695
20.	1735	2997 2979	3074	1577 1514	–	3250	ν(C=O) amide=1657
21.	1737	2979 2840	3020	1518 1514	–	3190	ν(C=O) amide=1665
22.	1726	29232854	3116	15841572	–	3211	ν(C=O) amide=1626

H-NMR of prepared compounds

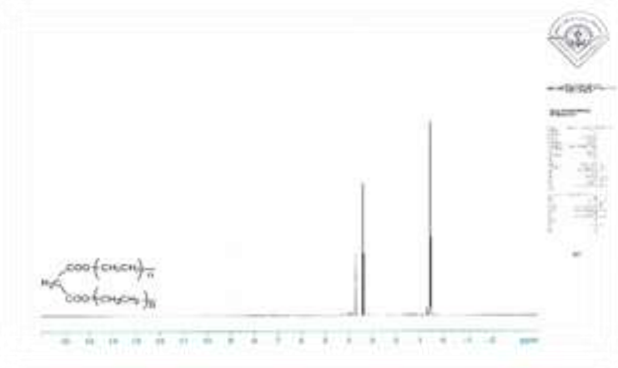


Figure 1

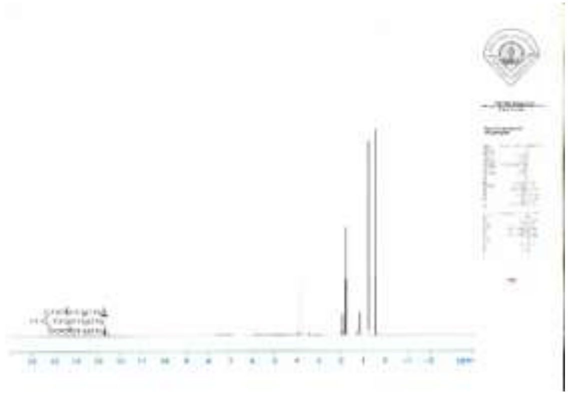


Figure 2

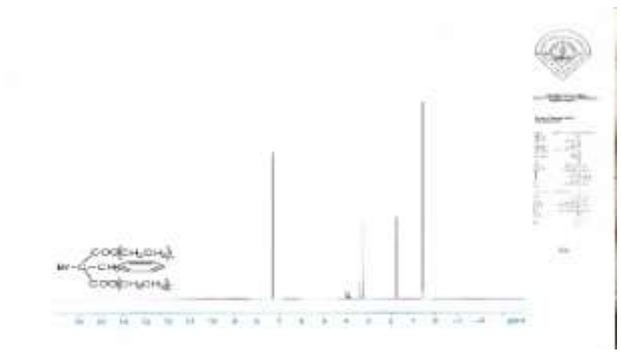


Figure 3

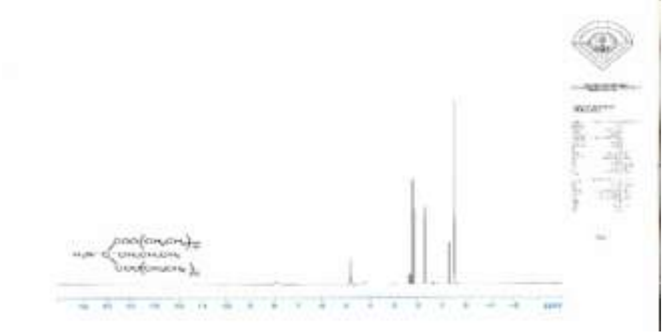


Figure 4

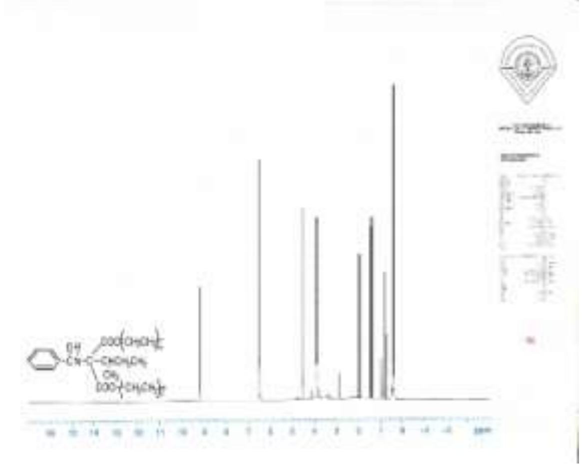


Figure 5

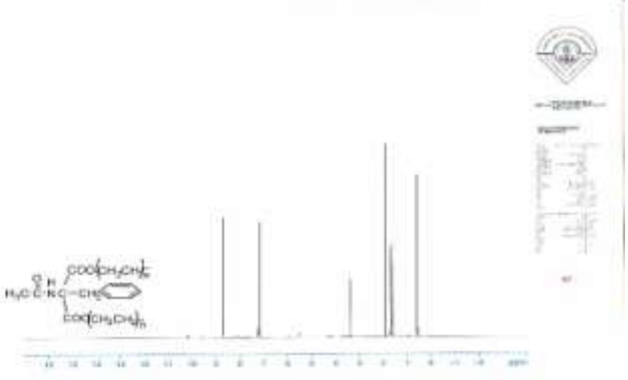


Figure 6

References

[1] F. A. Carey, "Organic Chemistry", McGraw-Hill, Inc. America, 3,453 (1880).

[2] H.Staudinger,Liebigs." HeterocyclicComp". Ann. Chem.356, 51 (1907).

[3] I. Goodman," Encyclopedia of Polymer Science and Engineering"; 2nd ed.; Wiley, New York, Vol. 12, 1988, pp.239-251.

[4] I. Goodman; J. A. Rhys, "Polyesters: Saturated Polymers;" I liffe Books: London, Vol. 1. 1965, pp.311-329.

[5] P. W. Morgan, "Condensation Polymers: By Interfacial and Solution *Methods*", Inerscience Publishers, New York, 1965, pp.230-251.

[6] F. Yasumasa "Preparation and characterizeation of new polyamide containing ethidium bromide", Polymer Bulletin, 45, 2001, 65-470.

[7] A.I. Chernukhina, and G.A. Gabrielyan, "Thermal Stabilization of Alphatic Polyamides and Fibres Based on Them."Fiber chemistry, vol. 25, No. 6, 1993, pp.468.

[8] Nnnnn

[9] A.I. Vogel, "A text book of practical organic chemistry "3td Ed. Iongman group limited, London, 1974, pp.389.

[10] Ali,A.A. Movahedi,F.and Esmaill,A..(2006)."A new method for the synthesis of functionalized melaimides" Tetrahedron Lett.47: 4469.

[11] Julio, A.Juan, j.and Jose,B."The Modren Hetrocyclic Chemistry. Chemistry of 2-Azetidinones(B-Lactams)",Wiley-VCH Verlag GmbH and Co. KGaA.Ch24(2011).

[12] Bhusare, S.Pawar,V.Shinde,S.Pawar, R.and Vibhute,YT.(2003)"Synthesis of some new heyrocyclic",Int.J.Chem.Sci.,1(1):31-36.