Synthesis of New Poly (Subs- Vinyl Malonate Amine) from Malonyl Chloride

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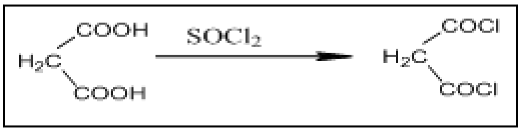
Abstract: ***New polymers were prepared by malonyl chloride. malonyl choride was prepared from malonic acid, these polymers were prepared by several steps. The first step was included reaction of poly vinyl alcohol with malonyl chloride to produce poly vinyl malonate (1). Second step was reacted of poly sodium vinyl malonate with different alkyl halide (3-6). Bromine was added to produce polymers in third step (7-10).The last step was added different amines (primary and secondary amines) to prepared poly [(2-alkyl amino-2-alkyl) vinyl malonate] [(11-18), (19-30)]. All the prepared polymers were characterized by FT-IR, and some of them ^{1}H-NMR, and measured some of different physical properties as, solubility and softening point.***

Keywords: malonic acid, polyvinyl alcohol, polyester, polyamine

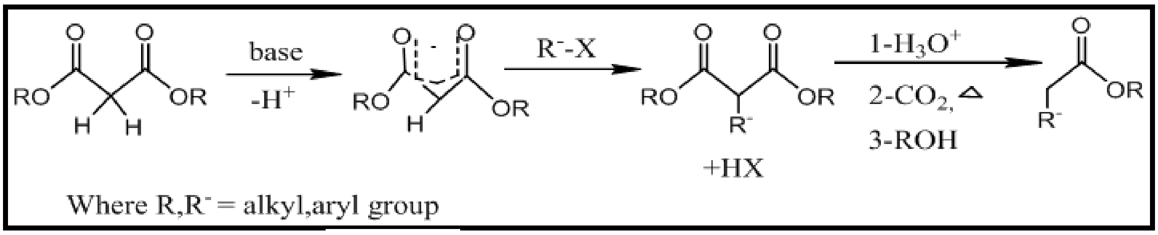
1. Introduction

Malonyl chloride which is a derivative of malonic acid which can prepared from reaction of malonic acid with thionyl chloride equation (1). Malonyl chloride may be used as other acyl halides in Friedal-Crafts and related reactions; it has two nucleophilic centers so that it can yield heterocycles. Thereaction proceeds via initial HCl elimination from malonyl chloride to give ketene intermediate which may then react with the nucleophile or it dimerizes[1].



Equation 1: Preparation of malonyl chloride

Malonyl chloride converted into diethyl malonate which is more important commercially. It is colorless, fragrant liquid boiling at 199 C. Malonic acid and its esters contain active methylene groups which have relatively acidic alpha-proton due to H atoms adjacent to two carbonyl groups. The reactivity of its methylene group provides the sequence of reactions of alkylation, hydrolysis of the esters[2], as shown below:



Equation 2: alkylation, hydrolysis of the esters

Malonic acid and its esters [3] are characterized by the large number of condensation products; they are important intermediates in synthesis, anti-inflammatory agents, other numerous pharmaceuticals, flavors and fragrances compounds. 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[4-6].Polyvinyl alcohol (PVA), which is essentially made from polyvinyl acetate through hydrolysis, is easily degradable by biological organisms and in water is a solubilized crystalline structure polymer. PVA is a biodegradable imitation of natural polymers[7]. This polymer is widely used by blending with other polymer Compounds, such as biopolymers and other polymers with hydrophilic properties; it is utilized for various industrial applications to enhance the mechanical properties of films because of its compatible structure and hydrophilic properties[8].Polyamine is an organic compound consists of amino groups (-NH2). Polyamines are synthesized in cells and play essential role in the proliferation and development of mammalian cells. In addition, polyamines have been shown to exert antioxidant activity[9] anti-allergenic effect[10], and suppression on glycation process[11, 12]. Polyamines are abundantly available in the liver of poultry, fermented soybeans, mushrooms and soybeans. The content of polyamines in the body declines with age regardless of the consumption of food rich in polyamines. Lately, Polyamines has been reported to prevent arteriosclerosis [13] and promotion of hair growth [14, 15] due to its anti-inflammatory properties and cell proliferative effect respectively.

2. Experimental

1) Preparation of malonyl chloride [16]

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 dioxane then 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 of poly (vinyl malonate) [17].

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

3) General preparation of poly [(2-alkyl) vinyl malonate] [18].

In 250 round bottom flask was dissolved (0.1 mol) sodium metal in absolute methanol (30 ml) the product was sodium methoxide then added to poly(vinyl malonate) to prepared poly (sodium vinyl malonate). Then added different alkyl halide (1 mol) to poly (sodium vinyl malonate) (1 mol) with (1 mol) tri ethyl amine and refluxed for (8-10) hrs. The mixture was wash with 15 ml of water to remove the salts from product. Finally the product was purified by dissolved in DMSO and reprecipitating from another solvent such as (water, ethanol, acetone, THF.

4) General preparation of poly [(2-bromo- 2-alkyl) vinyl malonate] [19].

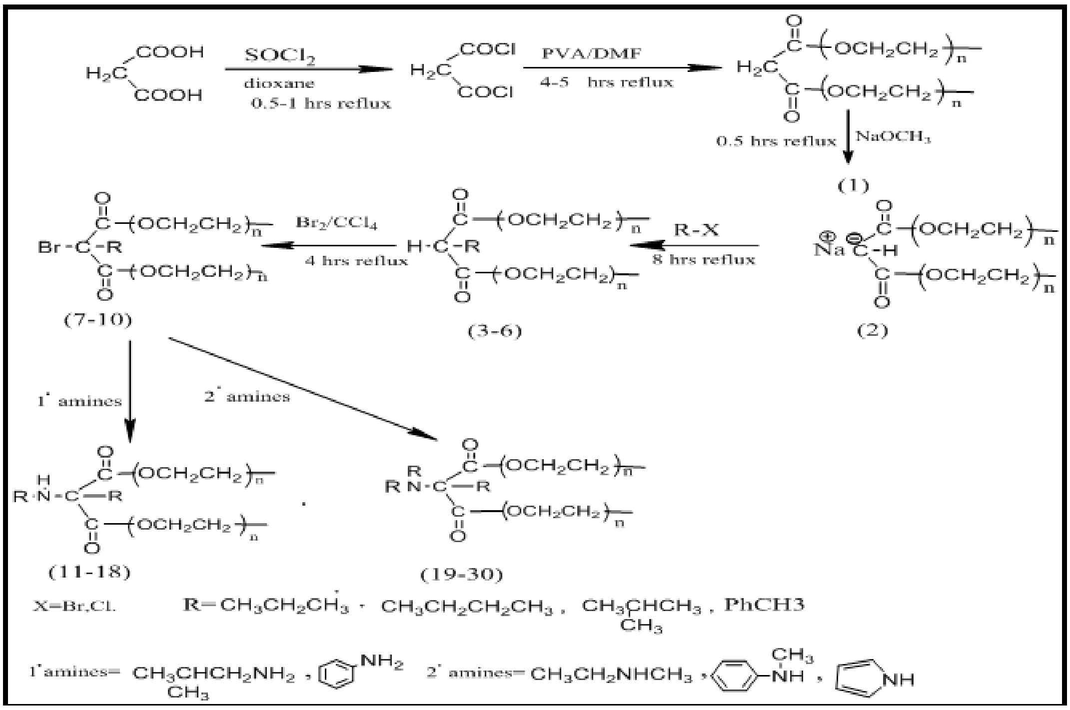
In 250 round bottom flask was dissolved (4 ml) of Bromine in (20 ml) CCl_4, then added (1 mol) of prepared different poly [(2-alkyl) vinyl malonate]. The mixture was refluxed for 4 hrs. Then washed the product with water to remove salt, the product was purified by dissolved in DMSO and reprecipitating from another solvent such as (water, ethanol, acetone, THF.

5) General preparation of poly [(2-alkyl amino-2-alkyl) vinyl malonate] [20].

In 250 round bottom flask was dissolved (1 ml) of poly [(2-alkyl) vinyl malonate]in (20 ml) DMF then added (1 mol) of different (primary and secondary) amines with (1 ml) of tri ethyl amine to mixture. The mixture was refluxed for 4-6 hrs. The product was washed with water to remove salt, the product was purified by dissolved in DMSO and reprecipitating from another solvent such as (water, ethanol, acetone, THF.

3. Result and Discussion

In the current study of synthesis of the targeted compounds Synthesis of new Poly (Subs- vinyl malonate amine) were obtained by series reactions. All products have conversion ratio ranges {49-90} %. The syntheses of compounds (1-30) 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} c° and conversion ratios were {57-89} %. All the physical properties of the prepared compounds are listed in the Table (1).

FTIR spectra of Compounds {1, 2, 3, 4, 5, and 6} showed appearance of the absorption band of (νC=O) ester at (1724-1740) cm^{-1}. (νC-H) aliphatic at (2817-2990) cm^{-1} and the other absorption band is listed in Table (3).

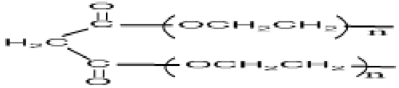
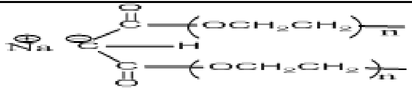
Compounds {7, 8, 9, and 10} were prepared by reaction of poly [(2-alkyl) vinyl malonate] with bromine. The softening point's ranges were {203-242} c° and conversion ratio were {54-80} %, and all the physical properties of the prepared compounds are listed in the Table (1).

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

Compounds {11-30} were prepared by reaction of poly [(2-alkyl) vinyl malonate] with bromine. The softening point's ranges were {263-294} c° and conversion ratio were {49-90} %, and all the physical properties of the prepared compounds are listed in the Table (1).

FTIR spectra of Compounds {11-30} showed appearance of the absorption band of (νC=O) ester at (1727-1782) cm^{-1}, (νC-H) aliphatic at (2740-2999) cm^{-1}, and the other absorption band are listed in Table (3).

Table 1: Physical Properties of the compounds

No.	Structure	Colour	S.Pc°	Conversion %
1		yellow	141-156	57
2		yellow	146-160	78
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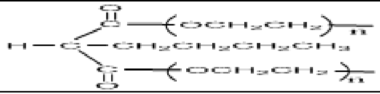
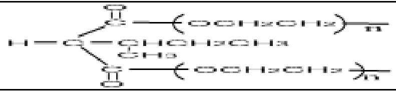
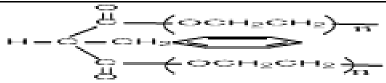
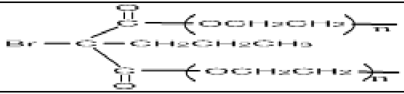
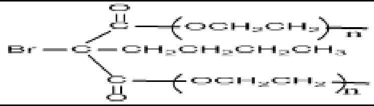
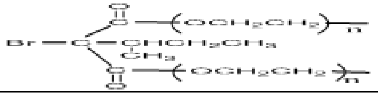
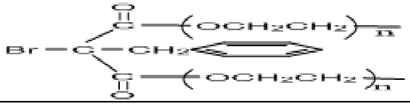
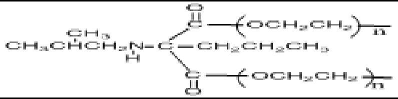
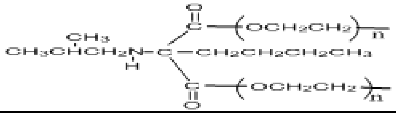
4		brown	181-196	79
5		Deep orange	187-203	68
6		Black	198-213	79
7		Light yellow	203-211	78
8		yellow	209-223	75
9		orange	217-230	80
10		Deep orange	229-242	54
11		Brown	263-275	90
12		Deep yellow	267-281	81

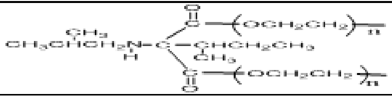
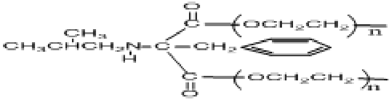
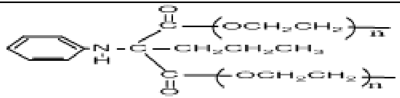
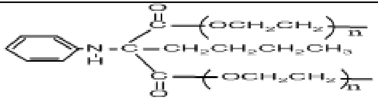
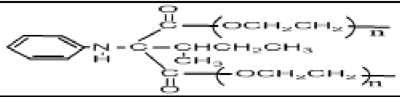
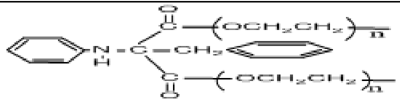
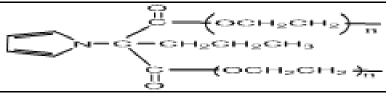
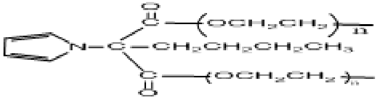
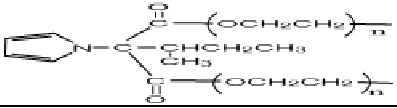
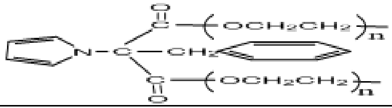
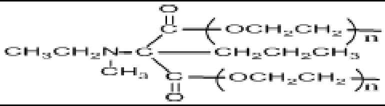
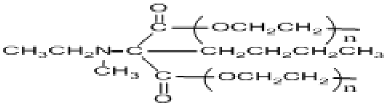
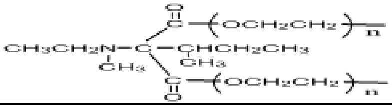
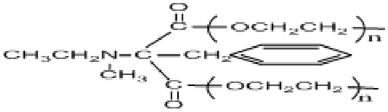
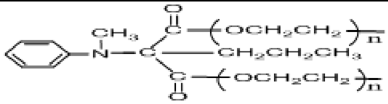
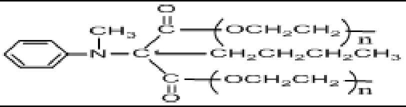
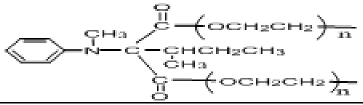
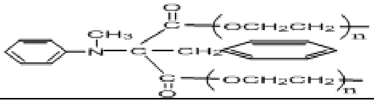
13		Brown	271-284	87
14		Black	285-301	79
15		Deep red	283-297	86
16		Deep yellow	286-299	71
17		brown	293-305	64
18		Black	303-316	61
19		Deep orange	254-267	77
20		Deep red	258-271	87
21		Deep yellow	263-279	85
22		Black	269-281	49
23		Deep orange	246-259	59
24		Brown	248-263	87
25		Brown	251-266	75
26		Black	267-278	75
27		Deep red	271-284	79
28		Black	274-290	83
29		brown	279-293	68
30		Black	281-294	89

Table 3: 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.
23.	Ins.	Ins.	Ins.		S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.
24.	Ins.	Ins.	Ins.		S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.
25.	Ins.	Ins.	Ins.		S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.
26.	Ins.	Ins.	Ins.		S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.
27.	Ins.	Ins.	Ins.		S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.
28.	Ins.	Ins.	Ins.		S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.
29.	Ins.	Ins.	Ins.		S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.
30.	Ins.	Ins.	Ins.		S.	Ins.	S.	Ins.	Ins.	Ins.	Ins.

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

Table 4: 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(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)=746
8.	1741	2921 2845	–	–	–	ν(C-Br)=744
9.	1739	2981 2830	–	–	–	ν(C-Br)=773
10	1749	2960 2780	3028	1590 1550	–	ν(C-Br)=782
11	1735	2987 2906	–	–	3259	ν(C=O) amide=1659
12	1730	2981 2777	–	–	3268	ν(C=O) amide=1669
13	1736	2974 2880	–	–	3142	ν(C=O) amide=1681

14	1730	2997 2910	3092	1590 1585	3262	ν(C=O) amide=1657
15	1739	2970 2740	3074	1622 1583	3147	ν(C=O) amide=1653
16	1746	2958 2923	–	1620 1586	3190	ν(C=O) amide=1652
17	1733	2925 2854	3083	1627 1569	3232	ν(C=O) amide=1667
18	1736	2925 2850	3080	1618 1595	3226	ν(C=O) amide=1660
19	1752	2918 2854	3070	1591 1550	–	–
20	1772	2981 2779	3032	1587 1567	–	–
21	1736	2921 2854	3063	1583 1573	–	–
22	1728	2923 2856	3085	1552 1544	–	–
23	1733	2972 2781	–	–	–	–
24	1737	2972 2744	–	–	–	–
25	1764	2972 2758	–	–	–	–
26	1734	2925 2856	3080	1598 1542	–	–
27	1727	2981 2839	3023	1587 1567	–	–
28	1743	2974 2844	3020	1589 1560	–	–
29	1782	2999 2939	3076	1587 1542	–	–
30	1737	2991 2823	3018	1590 1550	–	–

H-NMR of prepared compounds

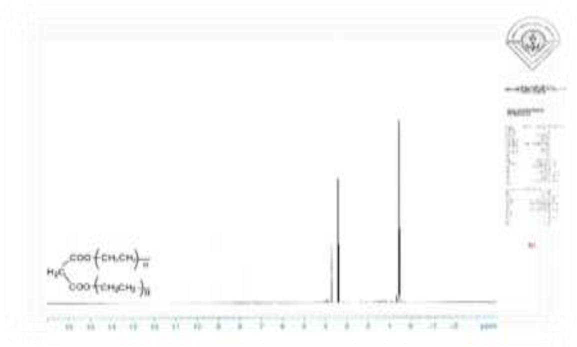


Figure 1:

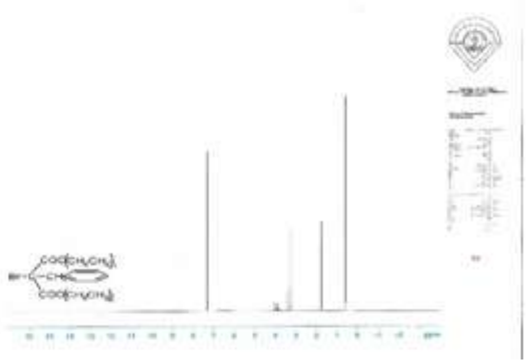


Figure 3:

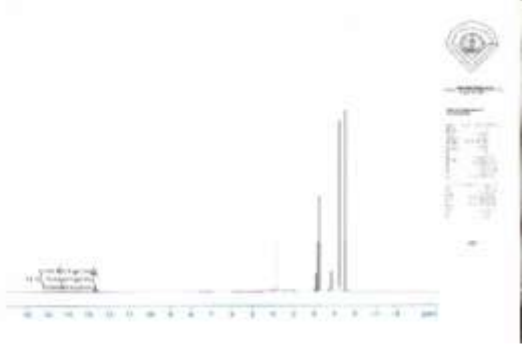


Figure 2:

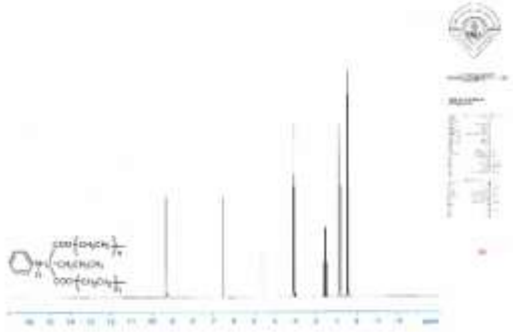


Figure 4:

References

[1] H.Staudinger, Liebigs." Heterocyclic Comp". Ann. Chem.356, 51 (1907).
[2] Deg, Innocenti, A.; Dembech, P.; Mordini, A.; Ricci, A.; Seconi, "Synthesis and hydrolysis of ester", Organic chemistry 1991, second Ed.pp267.
[3] Smith, Janice Gorzynski.2008. "Ester synthesis" Organic Chemistry Second Ed. pp 905-906.
[4] I. Goodman," Encyclopedia of Polymer Science and Engineering"; 2nd ed.; Wiley, New York, Vol. 12, 1988, pp.239-251.
[5] I. Goodman; J. A. Rhys, "Polyesters: Saturated Polymers;" I liffe Books: London, Vol. 1. 1965, pp.311-329.
[6] P. W. Morgan, "Condensation Polymers: By Interfacial and Solution *Methods*", Inerscience Publishers.
[7] Liu, M.; Guo, B.; Du, M.; Jia, D. Drying induced aggregation of halloysite nanotubes in polyvinyl alcohol/halloysite nanotubes solution and its effect on properties of composite film. Appl. Phys. A Mater.Sci. Process. **2007**, 88, 391–395.
[8] N.; Prodpran, T.; Benjakul, S.; Prasarpran, S. Influences of degree of hydrolysis and molecular weight of poly (vinyl alcohol)(PVA) on properties of fish myofibrillar protein/PVA blend films. Food Hydrocoll. **2012**, 29, 226–233.
[9] Fujisawa S. *et al.*, Kinetic evaluation of polyamines as radical scavengers. *Anticancer Res.* 25, 965-70 (2005).
[10] Soda K. *et al.*, Spermine, a natural polyamine, suppresses LFA-1 expression on human lymphocyte. *J. Immunol.* 175, 237-45 (2005).
[11] Gugliucci A. *et al.*, The polyamines spermine and spermidine protect proteins from structural and functional damage by AGE precursors: a new role for old molecules?*Life Sci.* 72, 2603-16 (2003).
[12] Gugliucci A., Alternative antiglycation mechanisms: are spermine and fructosamine-3-ki nase part of a carbonyl damage control pathway?. *Med. Hypotheses.* 64. 2603-16 (2005).
[13] Soda K., Polyamine intake, dietary pattern, and cardiovascular disease. *Med. Hypotheses.* 75. 299-301 (2010).
[14] RamotY.*et al.*, Polyamines and hair: a couple in search of perfection.*Exp. Dermatol.* 19, 784-90 (2010).
[15] Ramot Y., Spermidine promotes human hair growth and is a novel modulator of human epithelial stem cell functions. *Plos One*, 6,1-11(2011).
[16] Morrison R. T., Boyd R. N., *Organic Chemistry*, Pearson Education, Inc. 6th edition 1992.
[17] A.I. Vogel, "A text book of practical organic chemistry "3td Ed. Iongman group limited, London, 1974, pp.389.
[18] Ali,A.A. Movahedi,F.and Esmaill,A..(2006)."A new method for the synthesis of functionalized melaimides" Tetrahedron Lett.47: 4469.
[19] 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).
[20] 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.