

# Synthesis of New Poly (Subs- Vinyl Malonate Imide) from Malonyl ester

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**Abstract:** *New polymers were prepared by malonyl ester. Malonyl ester was prepared from reacted malonic acid and PVA, these polymers were prepared by several steps. The first step was reacted malonyl ester with different alkyl halide (1-6). Bromine was added to produce polymers (7-10) in Second step. The last step was added phthalimide and succinimide to prepared poly [(2-alkyl imido-2-alkyl) vinyl oxy malonate] (11-18). All the prepared polymers were characterized by FT-IR, and some of them 1H-NMR, and DSC, and measured some of different physical properties as, solubility and softening point.*

**Keywords:** malonyl ester, polyimide, DSC

## 1. Introduction

Malonyl ester prepared from converted malonyl chloride to 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<sup>(1)</sup>. Polyimides are a class of thermally stable polymers that are often based on stiff aromatic backbones. Polyimides are a class of polymers containing a heterocyclic imide unit in the polymer backbone and are derived from the reaction of anhydrides and amines. Historically, the first report concerning polyimides was made by Bogert and Renshaw in 1908<sup>(2)</sup>. However, only in the early 1960s were polyimides successfully introduced as commercial polymeric materials (Kapton) by DuPont<sup>(3)</sup>. Since that time, an impressive variety of polyimides have been synthesized and reported in the literature<sup>(4-7)</sup>. Polyimides are important, both scientifically and commercially, because of their combination of outstanding key properties, including thermal, thermo-oxidative stability, high mechanical strength, high modulus, excellent electrical properties<sup>(8-9)</sup>, and superior chemical resistance. Therefore, in spite of their general difficulty in processing and high cost, polyimides are widely used as matrix resins, adhesives, coatings, printed circuit board and insulators for high performance applications in the aerospace, automotive, electrical, electronics and packaging industries. Polyimide are mainly used in the aerospace and electronics industries in the form of film and moldings, but high melting points and insolubility in organic solvents limited their applications<sup>(10-11)</sup>. The polyimide contain either a heterocyclic imide or open linkage the repeating unit<sup>(12)</sup>. Polyimides has been investigated for various applications. For example Polyimide is often used in the electronics industry for flexible cables, as an insulating film on magnet wire and for medical tubing. For example, in a laptop computer<sup>(13)</sup>.

## 2. Experimental

### 1) General procedure for preparation of poly [(2-alkyl) vinyl oxy malonate]<sup>14</sup>.

In a 250 ml round bottom flask was dissolved (0.5 g) sodium metal in (20 ml) methanol. Sodium methoxide was product and added to poly (vinyl oxy malonate) to prepared poly (sodium vinyl oxy malonate), then added (1 mol) of different alkyl halide to (1 mol) of poly (sodium vinyl oxy malonate) with (1 ml) Et<sub>3</sub>N to remove the salts, the product was refluxed for (8-10) hrs. The mixture was filtered, washed with water and dried, then purified by dissolved in DMSO and reprecipitating from another solvent such as (water, ethanol, and acetone)

### 2) General preparation of poly [(2-bromo- 2-alkyl) vinyl oxy malonate]<sup>15</sup>.

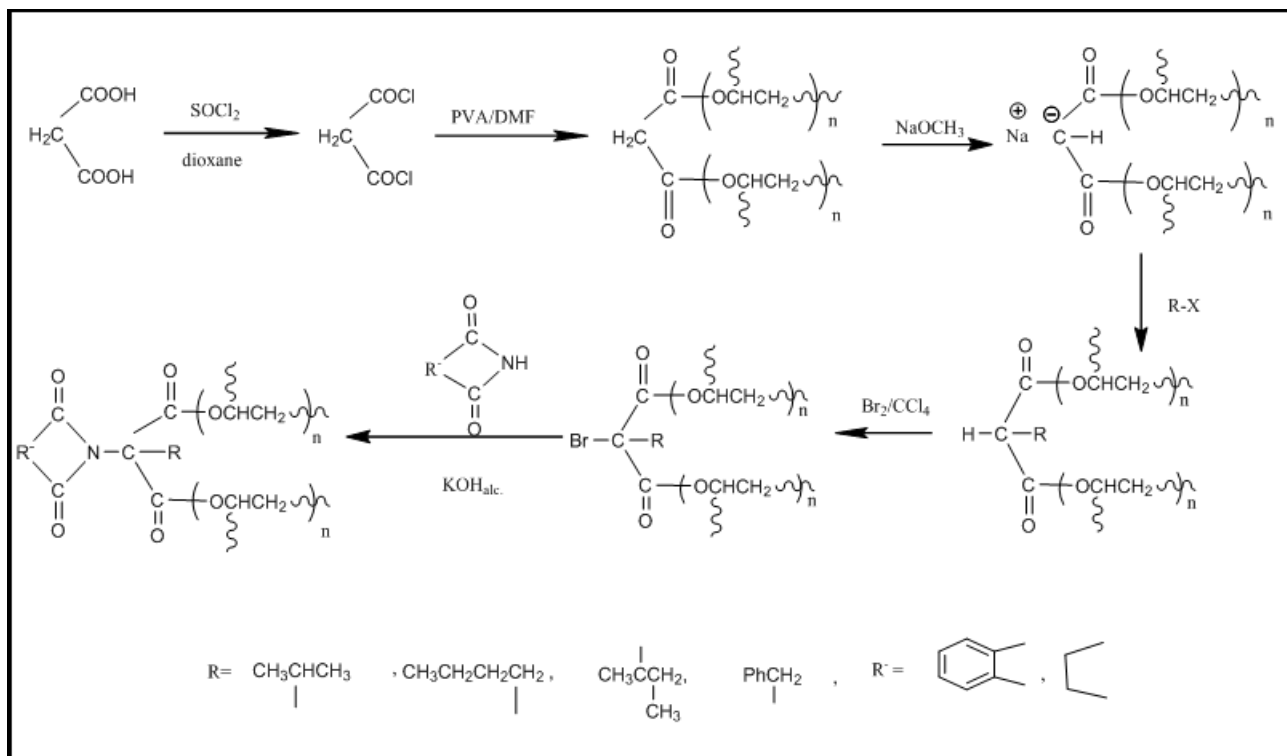
In a 250 ml round bottom flask was dissolved (4 ml) of bromine in (15 ml) CCl<sub>4</sub> then added (1 mol) of poly [(2-alkyl) vinyl oxy malonate] with (1ml) of Et<sub>3</sub>N, The mixture was refluxed for 4 hrs. Filtered and purified by dissolved in DMSO and reprecipitating from another solvent such as (water, ethanol, acetone, and THF)

### 3) General procedure for preparation of Poly [(2-alkyl-2-subs. imido-)vinyl oxy malonate]<sup>16</sup>

In a 250 ml round bottom flask was dissolved (1 mol) of poly [(2-bromo-2-alkyl) vinyl oxy malonate] in (20 ml) DMF then added (1 mol) of (potassium succinimide and potassium phthalimide) which prepared by dissolving potassium hydroxide in alcohol and adding the solution to the (1mol) (succinimide and phthalimide). The mixture was refluxed for 2-3 hrs. Filtered, washed with water to remove salt, dried and purified by dissolving with DMF and reprecipitating from another solvent such as (ethanol, acetone, and dioxan).

## 3. Result and Discussion

In the current study of synthesis of the targeted compounds Synthesis of new Poly (Subs- vinyl oxy malonate imide) were obtained by series reactions. All products have conversion ratio ranges {54-91} %. The syntheses of compounds (1-18) are outlined in scheme (1).



Scheme (1)

Compounds {1, 2, 3, 4, 5, and 6} were prepared by reaction of malonyl chloride with PVA then with 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<sup>-1</sup>. (νC-H) aliphatic at (2817-2990) cm<sup>-1</sup>. and the other absorption band is listed in Table (2). <sup>1</sup>H-NMR spectrum of polymer 1 showed signals at δ 0.55 ppm of (s, 2H, CH<sub>2</sub>-CO), δ 3.4 ppm of (t, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>), δ 3.8 ppm of [m, 2H, (O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>n</sub>]. <sup>1</sup>H-NMR spectrum of polymer 3 showed signals at δ 0.47 ppm of (m, 2H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), δ 2.3 ppm of (q, 2H, =CH-CH<sub>2</sub>-CH<sub>2</sub>), δ 1.8 ppm of (t, 2H, CH<sub>3</sub>-CH<sub>2</sub>), δ 3.8 ppm of [t, 2H, (O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>n</sub>].

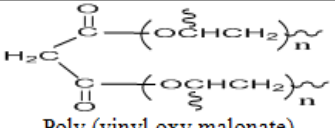
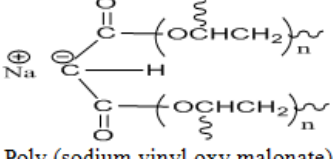
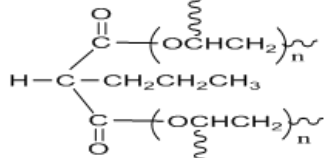
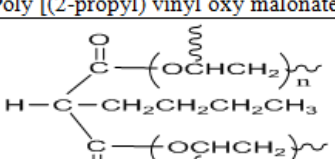
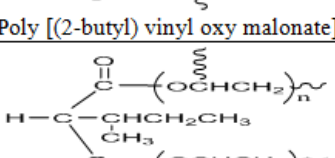
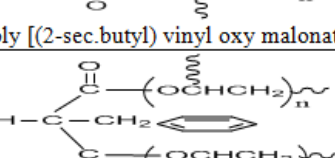
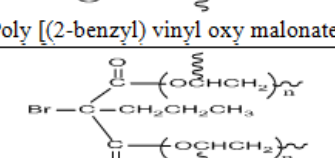
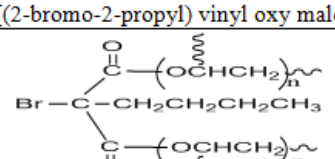
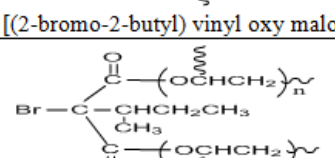
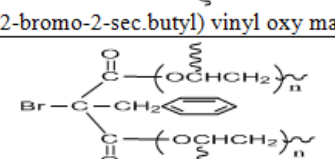
Compounds {7, 8, 9, and 10} were prepared by reaction of poly [(2-alkyl) vinyl oxy malonate] with bromine. The softening point's ranges were {203-242} °C and conversion ratio were {54-80} %, and all the physical properties of the prepared compounds are listed in the Table (1). FTIR spectra of Compounds {7, 8, 9, and 10} showed appearance of the absorption bands of (νC=O) ester at (1733-1749) cm<sup>-1</sup>, (νC-H) aliphatic at (2780-2981) cm<sup>-1</sup>. And appearance new absorption region at (622-773) cm<sup>-1</sup> due to (νC-Br). The other absorption band are listed in Table (2). <sup>1</sup>H-NMR spectrum of polymer 10 showed signals at δ 0.7 ppm of [m, 2H, (O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>n</sub>], δ 1.8 ppm of (t, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>), δ 3.3 ppm of (s, 2H, CH<sub>2</sub>-Ph), and δ 7.4 ppm of (m, 5H, Ph-

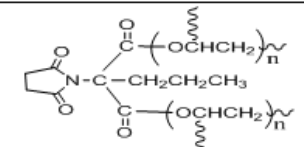
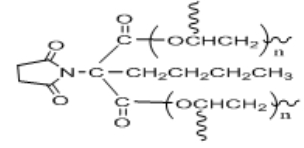
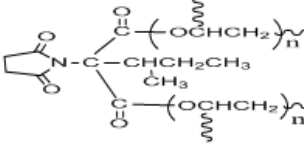
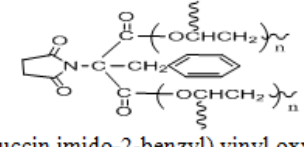
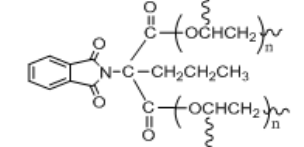
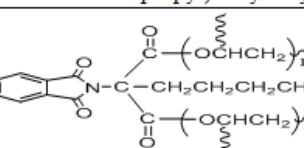
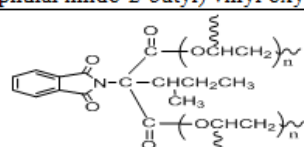
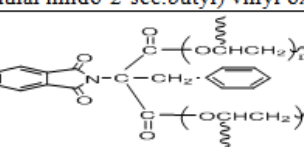
H). <sup>1</sup>H-NMR spectrum of compound 11 showed signals at δ 0.51 ppm of (t, 2H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), δ 0.69 ppm of (t, 2H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), δ 1.8 ppm of (t, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>), δ 2.2 ppm of (m, 2H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), δ 2.4 ppm of [m, 2H, (O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>n</sub>], and δ 4.9 (s, 2H, NH<sub>2</sub>).

Compounds {11-18} were prepared by reaction of poly [(2-bromo 2-alkyl) vinyl malonate] with succinimide, phthalimide. The softening point's ranges were {249-291} °C and conversion ratio were {68-91} %, and all the physical properties of the prepared Compounds are listed in the Table (1).

FTIR spectra of Compounds {11-18} showed appearance of the absorption band of (νC=O) ester at (1722-1774) cm<sup>-1</sup>, (νC-H) aliphatic at (2817-2998) cm<sup>-1</sup>, and the other absorption band are listed in Table (2). <sup>1</sup>H-NMR spectrum of polymer 13 showed signals at δ 0.75 ppm of (d, 2H, CH<sub>3</sub>-CH), δ 0.6 ppm of (t, 2H, CH<sub>3</sub>-CH<sub>2</sub>), δ 0.95 ppm of (d, 2H, CH<sub>3</sub>-CH-CH<sub>2</sub>), δ 1.4 ppm of (qt, 2H, CH<sub>3</sub>-CH<sub>2</sub>-CH), δ 1.1 ppm of (t, 2H, CH<sub>2</sub>-CH<sub>2</sub>), δ 3.4 ppm of (t, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>), <sup>1</sup>H-NMR spectrum of polymer 14 showed signals at δ 1.1 ppm of (t, 2H, CH<sub>2</sub>-CH<sub>2</sub>), δ 1.9 ppm of (m, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>), δ 2.4 ppm of (s, 2H, CH<sub>2</sub>-Ph), δ 3.3 ppm of (t, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>), δ 7.6 ppm of (s, 5H, Ph-H). <sup>1</sup>H-NMR spectrum of polymer 15 showed signals at δ 0.95 ppm of (t, 3H, CH<sub>3</sub>-CH<sub>2</sub>), δ 1.4 ppm of (m, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>), δ 2.2 ppm of (s, 2H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), δ 5.1 ppm of (t, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>), δ 7.6 ppm of (s, 2H, Ph-a), δ 7.9 ppm of (s, 2H, Ph-b).

**Table 1: Physical Properties of prepared compounds [1-18]**

NO.	Structure and name	Color	Softening point c <sup>o</sup>	Conversion %
1	 <p>Poly (vinyl oxy malonate)</p>	Yellow	141-156	57
2	 <p>Poly (sodium vinyl oxy malonate)</p>	Yellow	146-160	78
3	 <p>Poly [(2-propyl) vinyl oxy malonate]</p>	Deep yellow	176-186	89
4	 <p>Poly [(2-butyl) vinyl oxy malonate]</p>	Brown	181-196	79
5	 <p>Poly [(2-sec.butyl) vinyl oxy malonate]</p>	Deep orange	187-203	68
6	 <p>Poly [(2-benzyl) vinyl oxy malonate]</p>	Black	198-213	79
7	 <p>Poly [(2-bromo-2-propyl) vinyl oxy malonate]</p>	Light yellow	203-211	78
8	 <p>Poly [(2-bromo-2-butyl) vinyl oxy malonate]</p>	Yellow	209-223	75
9	 <p>Poly [(2-bromo-2-sec.butyl) vinyl oxy malonate]</p>	Orange	217-230	80
10	 <p>Poly [(2-bromo-2-benzyl) vinyl oxy malonate]</p>	Deep orange	229-242	54

11		yellow	249-256	91
12		Deep brown	253-259	89
13		Pale orange	258-267	79
14		Pale brown	262-273	88
15		Brown	259-271	79
16		Orange	265-277	86
17		yellow	272-283	68
18		Pale yellow	281-291	73

**Table 2:** FTIR absorption ( $\text{cm}^{-1}$ ) of the prepared compound

No.	$\nu(\text{C}=\text{O})$ Ester	$\nu(\text{C}-\text{H})$ Aliphatic.	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{O}-\text{C})$	Other bands
1	1739	2985-2941	1269	1155	—
2	1740	2987-2939	1225	1145	—
3	1724	2950-2990	1240	1132	—
4	1731	2943-2817	1236	1190	—
5	1724	2987-2910	1263	1159	—
6	1739	2977-2945	1239	1190	$\nu(\text{C}-\text{H})$ Aromatic 3024 $\nu(\text{C}=\text{C})$ Aromatic 1580-1545
7	1733	2972-2844	1217	1133	$\nu(\text{C}-\text{Br})=746$
8	1741	2921-2845	1228	1128	$\nu(\text{C}-\text{Br})=744$
9	1739	2981-2830	1249	1105	$\nu(\text{C}-\text{Br})=773$
10	1749	2960-2850	1215	1108	$\nu(\text{C}-\text{Br})=782$ , $\nu(\text{C}-\text{H})$ arom. 3028, $\nu(\text{C}=\text{C})$ arom.1590-1550
No.	$\nu(\text{C}=\text{O})$ Ester	$\nu(\text{C}-\text{H})$ Aliphatic.	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{N})$	Other bands

1	1732	2943-2817	1248	1390	
2	1722	2975-2850	1276	1380	
3	1743	2916-2850	1229	1355	
4	1754	2934-2914	1213	1363	v(C-H), arom. 3035, v(C=C) arom1602-1520
5	1764	2995-2943	1243	1377	v(C-H), arom. 3017, v(C=C) arom1585-1569
6	1774	2998-2923	1267	1367	v(C-H), arom. 3093, v(C=C) arom1630-1598
7	1734	2985-2858	1224	1294	v(C-H), arom. 3016, v(C=C) arom1580-1550
8	1724	2992-2912	1252	1366	v(C-H), arom. 3064, v(C=C) arom1608-1564

$^1\text{H-NMR}$  of some prepared compounds

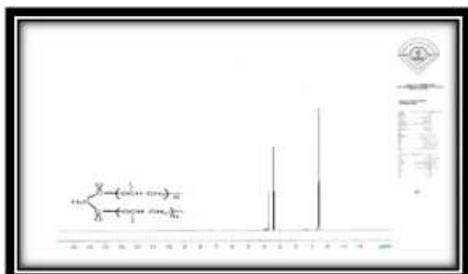


Figure 1:  $^1\text{H-NMR}$  Spectrum of polymer 1

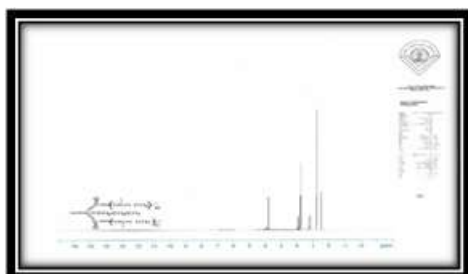


Figure 2:  $^1\text{H-NMR}$  Spectrum of polymer 3

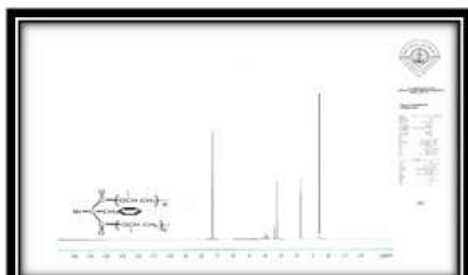


Figure 3:  $^1\text{H-NMR}$  Spectrum of polymer 10

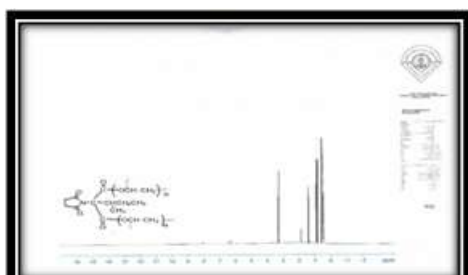


Figure 4:  $^1\text{H-NMR}$  Spectrum of polymer 13

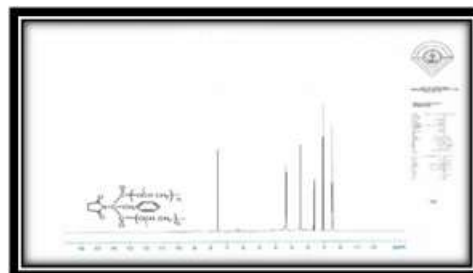


Figure 5:  $^1\text{H-NMR}$  Spectrum of polymer 14

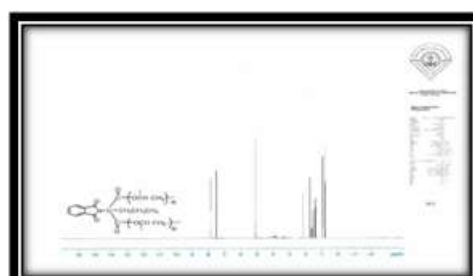


Figure 6:  $^1\text{H-NMR}$  Spectrum of polymer 15

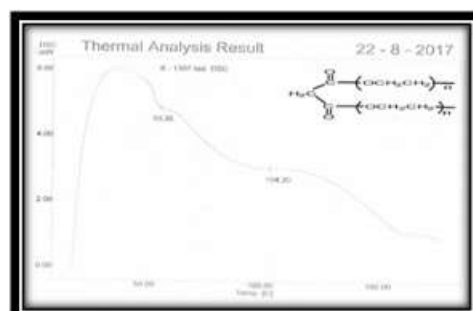


Figure 7: Thermal analysis (DSC) of polymer 1

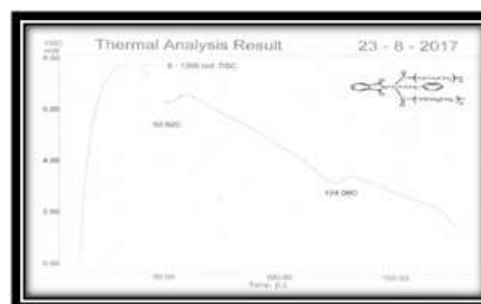


Figure 8: Thermal analysis (DSC) of polymer 18

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