

# The Study of The Effect of Adding Polyhydroxyphenylene on Lubricating Oils

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**ABSTRACT** - Nano scale PHQ was prepared via modified El-Garf polymerization method which proved to possess substantial characteristics, if compared with PHQ prepared by other polymerization techniques. The prepared polymer was collected in the form of dark-brown very fine powder. The structure and characteristics of the purified produced polymer were investigated using FTIR-ATR spectroscopy, X-ray diffraction, Thermal analysis (TGA, DTA and DSC) and Gel permeation chromatography.

PHQ was proved to be a potential antioxidant for lubricating oil by measuring the rheological properties (change of viscosity with time at constant temperature). This suitability arises from the high thermal stability of PHQ and its capability to reduce the lubricating oil oxidation. It was revealed that as PHQ concentration increase, the ability of the lubricating oil to absorb the thermal energy resulting from friction of the engine parts increase until reaching the optimum PHQ concentration by measuring the change of the loss modulus with angular frequency.

Another interpretation of the oxidation stability was also explained by the activation energy required for the oxidation reaction, therefore from the kinetic data of oxidizing the oil via TGA technique, the activation energy of decomposition of free base lubricating oil and lubricating oil containing 0.06 wt% of PHQ were calculated and showed that the oil containing PHQ have activation energy of oxidation higher than that of free base lubricating oil by 1.5 times, i.e. the lifetime of the lubricating oil is increased.

**Index Terms** – Polymer , Polymer characterization , Antioxidants , Lubricating oil , Thermal stabilization , Rheology , Activation energy ,

## 1 INTRODUCTION

Synthesis of thermally stable polymers at present is one of the main trends in the field of polymers. Up to now, there are several methods for poly(hydroquinone) (PHQ) synthesis in the literature including: Chemical polymerization, Electro-chemical polymerization, Enzymatic polymerization, and dehalogenative organometallic polycondensation.

Generally, there is no record in the literature for the polymerization of hydroquinone by  $\text{FeCl}_3$  using  $\text{AlCl}_3$  as a catalyst, And its utilization as an antioxidant for the thermal stabilization of lubricating oil [1].

## 2 POLYMERIZATION OF HYDROQUINONE

Polyhydroquinone (PHQ) is a main-chain type redox polymer. Its redox active units, quinone and hydroquinone (HQ), are among the simplest ones. Its redox potential is low, and it can undergo direct two-electron oxidation and reduction. However, this polymer received much less attention than other redox polymers, such as polyaniline and polythiophene. The main reason may be the difficulty in its preparation.

Up to now, there are several methods for PHQ synthesis in the literature including: chemical polymerization, electrochemical polymerization, enzymatic polymerization, and dehalogenative organometallic polycondensation.

Among them, chemical polymerization is the simplest. PHQ can be obtained by one-pot oxidative polymerization of HQ or p-benzoquinone in alkali solutions. Unfortunately, this method lacks control over the structure of the products. In contrast, PHQ with a well-defined structure can be synthesized by enzymatic polymerization or organometallic polycondensation, however, both methods involve several

steps of reaction and also expensive reagents [1].

## 3 THERMAL STABILIZATION OF LUBRICATING OIL

The rate of these oxidative processes varies greatly with the nature of oils, the extent of processing in refining, the temperature, and the presence of a metallic catalyst.

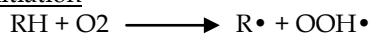
Such oxidations have a drawback on the oil, thus leading to failures in lubrication that accompanied by damage of machines. Large degree of damage is due to the formation of viscous, solid bodies, or jelly-like emulsions which interfere with the regular distribution of the lubricant. Consequently, antioxidant additives became highly required to decrease oil oxidation, with a secondary effect of reducing corrosion of certain types of sensitive bearing materials [2].

### 3.1 Oxidation Mechanisms of Lubricating Oils

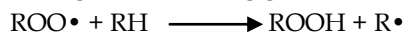
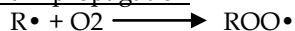
The oxidation of hydrocarbons consists of a multitude of different reactions that can be categorized under a few simple headings. The general reaction scheme in the liquid phase is primarily considered to be a free radical process. The separate steps that, as a whole make up hydrocarbon oxidation reactions are initiation, propagation, branching and termination. The oxidation processes in the liquid phase can be catalysed by metals or inhibited by several different mechanisms.

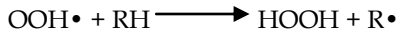
Oil oxidation mechanism can be expressed as following:

#### Initiation

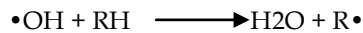
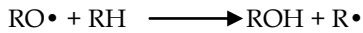
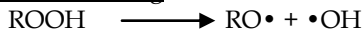


#### Chain propagation

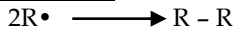




#### Chain branching



#### Termination



It was also noted that the rate of oil oxidation is affected by:

- Oxygen availability,
- Temperature,
- The presence of catalysts
- The composition of the basestock [3].

### 3.2 Inhibition Effects of Antioxidants on Lubricating Oils

Antioxidants are essential additives incorporated into lubricant formulations to minimize and delay the onset of lubricant oxidative degradation.

The proceeding lubricant degradation mechanism makes clear several possible counter measures to control lubricant degradation. Blocking the energy source is one path but is effective only for lubricants used in low-shear and temperature situations. However, more practical for most lubricant applications are the trapping of catalytic impurities and the destruction of hydrocarbon radicals, alkyl peroxy radicals, and hydroperoxides. This can be achieved through the use of radical scavengers, peroxide decomposers, and metal deactivators [4].

The literature contains nothing about the study of oxidation stability of lubricating base oil in the presence of PHQ as an antioxidant. Therefore this study is initiated.

## 4 EXPERIMENTAL PROCEDURE

### 4.1 Methods

#### 4.1.1 Polymerization

Polymerization is carried out by modified El-Garf polymerization method according to the Egyptian patent no. 0024/2013.

#### 4.1.2. Oil Samples Preparation

Oil samples were prepared: Blank, 0.03 wt%, 0.06 wt% and 0.1 wt% (g PHQ / g base oil). The materials are weighed on a 4-decimal place sensitive balance and mixed together by shaking to ensure homogenous distribution of the polymer in oil.

### 4.2. Polymer Characterization

#### 4.2.1. Scanning Electron Microscopy and Particle Size determination

Determination of particle size distribution was carried out using Beckman Coulter N5 Submicron Particle Size Analyzer.

The particle size was investigated by the use of scanning electron microscopy via JEOL JSM-5300 scanning microscopy. The polymer was dispersed in absolute ethyl alcohol by means of an ultra sonicator for a period of 15 minutes.

#### 4.2.2. Gel Permeation Chromatography

GPC was carried out to investigate the Molecular weight of the prepared polymer. The test was carried out using Agilent GPC-Addon Rev. B.01.01. GPC was carried out on waters with RID A, Refractive Index Signal detector using DMF eluent at a flow rate of 1.0 ml/min.

#### 4.2.3. FTIR-ATR

Infrared absorption spectrum was carried out at room temperature using a Bruker Vertex 70 spectrophotometer on both the raw material (Hydroquinone) and the purified prepared PHQ. Infrared absorption band positions are expressed in wave number from 400 to 4000 cm<sup>-1</sup>. The samples were analyzed via ATR procedure.

#### 4.2.4. Thermal Analysis

TGA (Thermogravimetric analysis) and DTA (Differential Thermal Analysis) was carried out in SDT Q600 V20.9 Build 20 in nitrogen atmosphere. The sample was placed in an Aluminum sample holder, and the thermal degradation measurements were carried out between 25°C and 1000°C at a speed rate of 10 K/min. DSC (Differential Scanning calorimetry) was carried out in LENSEIS STA PY-1000 in air atmosphere. The sample was placed in an Aluminum sample holder, and the thermal degradation measurements were carried out between 25°C and 550°C at a speed rate of 10 K/min.

#### 4.2.5. X-Ray Diffraction (XRD)

XRD was performed on SHIMADZU XRD-7000 X-RAY DIFFRACTOMETER.

### 4.3. Study of rheological and oxidation properties of lubricating oil via Rheometer and TGA

Lubricating base oil and Lubricating oil containing 0.03, 0.06 and 0.1 wt% of PHQ, were oxidized via Rheometer using a plate-and-plate geometry (35-mm diameter, 0.25-mm gap). Rotational shear tests were carried out at a constant temperature of 260°C and constant shear rate of 70 S-1 in a sealed chamber designed especially for the purpose of studying the oxidation stability of oil in terms of viscosity change with time.

Rheological measurements were carried out on samples of lubricating base oil and lubricating oil containing 0.03, 0.06 and 0.1 wt% of PHQ in rheometer using a plate-and-plate geometry (35-mm diameter, 0.25-mm gap). Oscillatory shear tests were carried out in a frequency range between 0.1 and 500 rad/s under isothermal conditions (90°C).

Rheological properties study was carried out using MCR 102 Rheometer Rheoplus Antonpaar.

Lubricating base oil and Lubricating oil containing 0.06 wt% of PHQ was oxidized via TGA to determine the onset oxidation temperature of both to confirm the results obtained from the rheology study.

TGA study was also used to calculate the activation energy of decomposition according to Ozawa's [5] method by performing TGA study of lubricating base oil and lubricating

oil containing 0.06 wt% PHQ from ambient to 500°C with heating rates 10, 20 and 30°C/min, assuming that the oxidation follows first order kinetics [6].

TGA study was carried out using SHIMADZU DSC-60A.

## 5 RESULTS AND DISCUSSION

### 5.1. Polymerization

El-Garf et. al. have developed a new method for the preparation of poly(hydroxyl phenylenes) by reacting substituted and unsubstituted phenols using anhydrous aluminum chloride as a catalyst and under pressure [7],[8],[9].

Old El-Garf polymerization method needed higher amounts of catalyst to increase the reaction yield also the reaction environment was difficult to control. Thus modified El-Garf polymerization method was developed to overcome these limitations and to provide a more secure environment of reaction and more controllable one.

Modified El-Garf polymerization method is for the first time utilized to synthesis PHQ in the solid state from HQ as a monomer. There is no record in literature so far for utilizing such technique in PHQ production. The produced polymer is collected in the form of a dark-brown very fine powder with substantial characteristics and high yield if compared with PHQ produced by other polymerization techniques mentioned in literature.

$$\begin{aligned} \text{The actual yield of the purified PHQ} &= (63.5/80) \times 100 \\ &= 79.37\% \end{aligned}$$

The present work utilizing modified El-Garf polymerization method produced PHQ at a yield of approximately 79.4 % which is six times higher than that produced by the old El-Garf polymerization method performed under pressure with the same molar ratio of HQ : AlCl<sub>3</sub> (1:1) and polymerization time of 6 hours.

### 5.2. Polymer Characterization

#### 5.2.1. Scanning Electron Microscopy and Particle Size Distribution

Figures (5.1) and (5.2) show the SEM study of the produced polymer.

SEM study showed that the particles of the polymers are agglomerated, the phenomenon that can be overcome by further grinding and sieving of the polymer and prolonged sonication time.

At magnification of 5000, it can be seen that the agglomerates sizes ranged from 0.2 to 0.73 μm. while at magnification of 20000, the agglomerates sizes ranged between 52.08 and 93.75 nm.

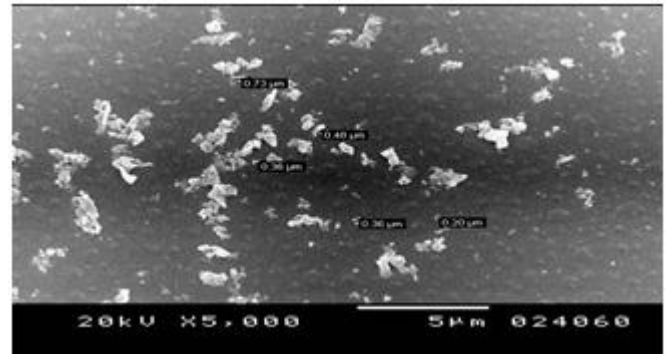


Fig. (5.1): SEM study of the produced polymer at magnification of 5000

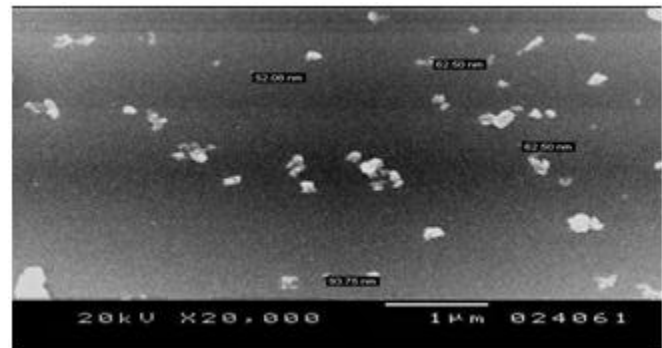


Fig. (5.2): SEM study of the produced polymer at magnification of 20000

For further understanding of the particle size, particle size distribution analysis was carried out.

Figure (5.3) shows the particle size distribution of the purified polymer. It can be noticed from the curve that there are two distribution curves one at the angle of 11.10 which indicates that the mean of the particle size is 14.9 nm and the other is at the angle of 90.00 indicating a mean of the particle size of 192.5 nm. This means that the range of the particle size lies within the nano scale with lower limit of 14.9 nm and upper limit of 192.5 nm.

Up till now this is the smallest particle size to be recorded for PHQ prepared by chemical polymerization.

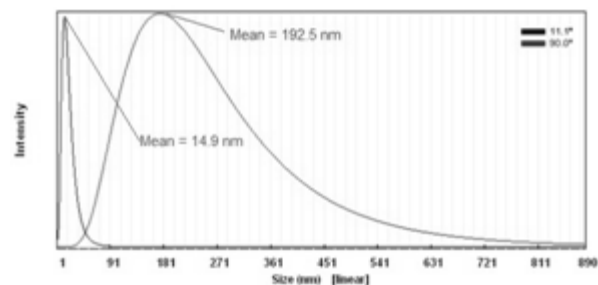


Fig. (5.3): Unimodal particle size distribution of the produced purified polymer

### 5.2.2. Gel Permeation Chromatography

Figure (5.4) demonstrates the GPC study of the prepared purified polymer. From the figure it can be concluded that the prepared purified polymer has an average molecular weight of 18500 g/g.mol. This by far is the highest average molecular weight of PHQ recorded up till now. The highest average molecular weight of PHQ mentioned in literature prepared by Jian He et. al. is 8800 g/g.mol [10]. The average molecular weight of our new PHQ prepared via modified El-Garf method is double that of the later.

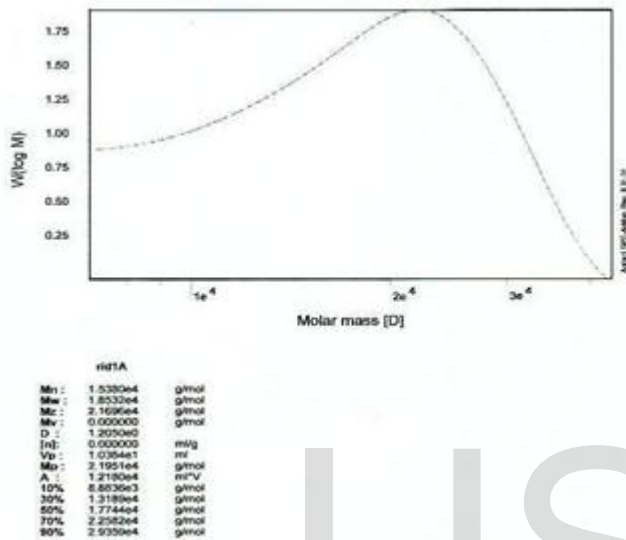


Fig. (5.4): GPC chart of the purified prepared polymer

### 5.2.3. FTIR Study

Figure (5.5) and figure (5.6) shows the FTIR-ATR spectra for the purified polymer and the monomer (Hydroquinone) respectively.

As shown in figure (6.5) The hydroxyl groups of the PHQ are united by strong intermolecular and intramolecular hydrogen bonds, as shown by the presence of a broad strong band at 3389.61 cm<sup>-1</sup> within the 3400 - 3200 cm<sup>-1</sup> region [11],[12],[13],[14],[15],[16].

The strong band at 1621.83 cm<sup>-1</sup> is attributed to the aromatic benzene ring since it lies in the range (1650-1500 cm<sup>-1</sup>) which indicates that there is no ring break down [84]. This band can also be attributed also to the presence of (C=O) stretching vibrations indicating the presence of quinones [12]. The presence of a peak at 1737.80 cm<sup>-1</sup> within the range of (1692 - 1882 cm<sup>-1</sup>) denotes the presence of 1,2,3,4 substitutions on the benzene ring [11],[12].

Absorption band at 1441.97 cm<sup>-1</sup> within the range of (1400 - 1500 cm<sup>-1</sup>) indicates aromatic C-C stretching. This absorption band also lies in the range of (1440 - 1465 cm<sup>-1</sup>) which corresponds to aromatic (-C=C-) skeletal in plane vibrations [11],[14],[16],[17].

Phenols in the solid state absorb infrared at 1390 - 1330 cm<sup>-1</sup> (medium) and 1260 - 1180 cm<sup>-1</sup> (strong) which represent -OH deformation and C-O stretch which interact somewhat [18].

The presence of a peak at 1340.21 cm<sup>-1</sup> is due to the

presence of phenolic C-O and -OH deformation[12],[14]. At 1186.20 and 1053.63 cm<sup>-1</sup> the absorption bands indicates the presence of aromatic C-H in plane bends.

The absorption bands at 1621.83 and 1441.97 cm<sup>-1</sup> is attributed to C=C stretching.

The out of plane vibration of the (C-H) bonds of the aromatic ring is represented by the absorption band at 805.99 cm<sup>-1</sup>[17] or wagging of the phenyl ring indicating that the phenyl rings are linked at the same position [12].

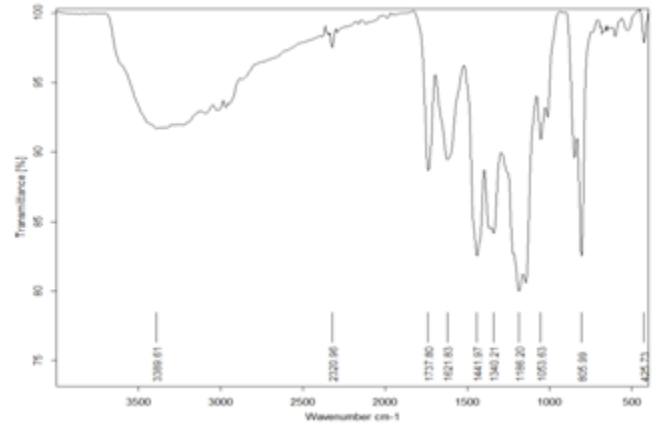


Fig. (5.5): FTIR-ATR spectra of the prepared purified polymer

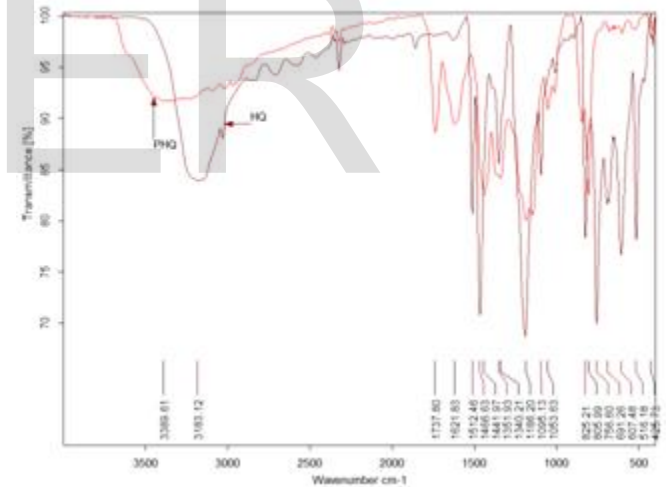


Fig.(5.6): FTIR-ATR spectra of the monomer (Hydroquinone) and the prepared purified polymer

Figure (5.6) shows the FTIR-ATR spectra of the monomer (Hydroquinone) and the prepared purified polymer.

In the region of 3100 - 3400 cm<sup>-1</sup> it can be noticed that the intensity of the hydroxyl group between the monomer and the polymer decreased this may be attributed to the amorphous nature of the produced polymer which decreases the H-bonding between the chains of the produced polymer.

Two new peaks appeared in the FTIR spectra of the produced polymer, The strong band at 1621.83 cm<sup>-1</sup> which is attributed to the presence of (C=O) stretching vibrations and the peak at 1737.80 cm<sup>-1</sup> which denotes the presence of 1,2,3,4 substitutions on the benzene ring. These two peaks confirms



that the reaction proceeded towards the formation of PHQ with the suggested structure and mechanism, they also confirm the position of the repeating unit.

The intensity of the peak at 1186.20 which is attributed to the presence of aromatic C-H in plane bends decreased, this is due to the substitution of the H atom on the benzene ring by another repeating unit.

Also there is an increase in the intensity of the peak at 1441.97  $\text{cm}^{-1}$  which is attributed to C-C stretching vibrations which confirms the bonding between successive aromatic rings.

### 5.2.4. XRD Study

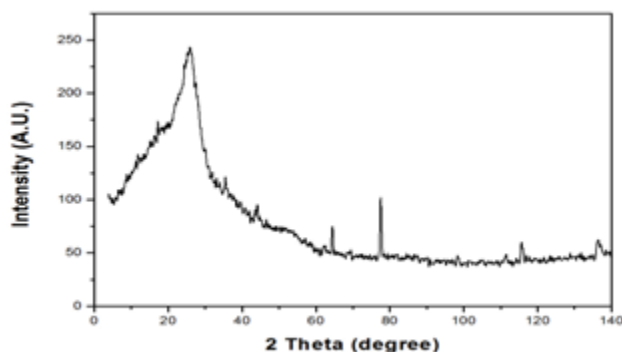


Fig. (5.7): X-rays diffraction pattern for the pristine purified PHQ polymer

Table (5.1): XRD data list for 2theta and corresponding d-spacings

2Theta (deg)	d (Å)	2Theta (deg)	d (Å)	2Theta (deg)	d (Å)	2Theta (deg)	d (Å)	2Theta (deg)	d (Å)
5.7800	15.7390	28.8900	3.0803	59.8100	1.5764	85.2900	1.1370	115.7000	0.9691
4.4300	20.3112	29.9950	2.9767	62.2800	1.4894	84.8300	1.1209	117.0350	0.9634
8.4550	10.2084	30.8200	2.8912	64.4600	1.4435	90.0000	1.0861	117.9900	0.8973
11.0200	8.0223	31.7800	2.8136	65.3800	1.4263	91.1100	1.0787	119.3000	0.8924
12.0700	7.3267	33.1200	2.7024	65.9700	1.4189	92.6000	1.0657	120.9500	0.8854
14.0900	5.9485	34.0300	2.6324	68.5600	1.3674	94.6600	1.0493	121.7400	0.8817
16.4900	5.1746	35.4500	2.5208	69.2850	1.3508	95.7300	1.0387	122.3000	0.8752
17.2900	5.1268	36.8900	2.4362	70.7400	1.3241	97.0400	1.0292	124.8200	0.8491
18.0100	4.8210	37.7000	2.3815	72.0400	1.3098	98.3300	1.0181	125.8000	0.8450
19.9750	4.4418	39.6400	2.2573	73.3800	1.2894	100.5300	1.0148	127.3400	0.8347
20.1000	4.4141	40.8800	2.2053	74.6500	1.2794	101.8200	0.9952	128.7800	0.8342
21.1900	4.1914	41.8500	2.1548	74.9400	1.2584	102.1200	0.9903	130.0100	0.8499
21.8200	4.0492	46.1400	2.0509	77.5550	1.2293	104.8400	0.9718	130.9400	0.8467
23.1400	3.8378	48.9400	2.0149	78.4750	1.2178	106.5700	0.9609	131.4700	0.8428
24.8900	3.5755	49.5800	1.9423	79.2300	1.2025	107.8900	0.9524	134.0500	0.8347
25.1400	3.5344	50.1700	1.9149	80.2900	1.1940	108.8400	0.9471	134.9700	0.8304
25.8400	3.4514	50.8800	1.8992	81.8700	1.1757	111.4300	0.9329	136.3400	0.8290
27.5000	3.2493	51.7900	1.7432	83.0400	1.1429	112.2400	0.9273	137.7200	0.8258
28.0900	3.1752	57.1500	1.6104	84.8700	1.1459	114.4950	0.9143	138.7000	0.8219

Figure (5.7) and table (5.1) show the X-ray diffraction patterns of the produced purified polymer.

The presence of a broad intense peak at 3.6 $\text{\AA}$  and the absence of d-spacings at 3.306 $\text{\AA}$ , 4.318 $\text{\AA}$ , 4.908 $\text{\AA}$ , 6.048 $\text{\AA}$ , 7.232 $\text{\AA}$ , 4.259 $\text{\AA}$ , 10.152 $\text{\AA}$ , 12.885 $\text{\AA}$  and 13.625 $\text{\AA}$  indicate that our purified polymer exhibits an amorphous nature [11],[12]. This may be attributed to the high molecular weight and the long chains of the polymer.

In the produced polymer a d-spacing of 4.4 $\text{\AA}$  was found which is in the same range of that of kovacic which denotes the presence of the phenyl ring [19],[20].

The absence of 4.26 $\text{\AA}$  d-spacing implies that there is no

lateral packing, probably due to the presence of 2 hydroxyl groups in the repeated unit of the produced polymer which is indicated by the previous FTIR study [11].

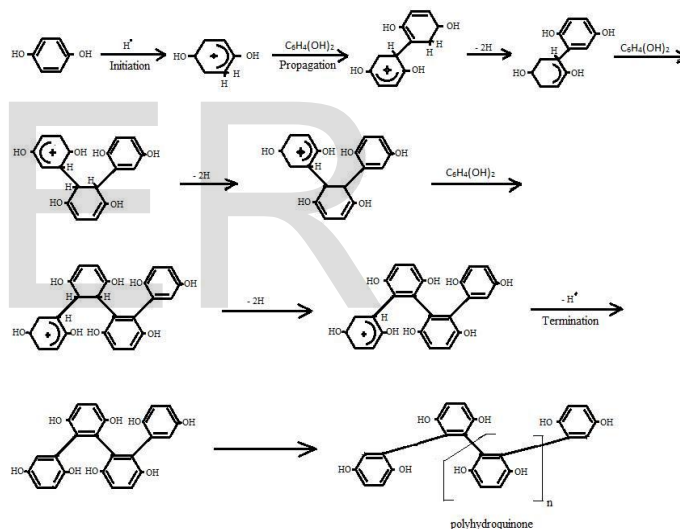
The study also shows the absence of d-spacing of 12 $\text{\AA}$  and 9.07 $\text{\AA}$  implies the absence of low molecular weight oligomers and that the repeated unit is only one phenyl ring respectively [12],[21].

A d-spacing of 8.518 $\text{\AA}$  and 10.152 $\text{\AA}$  is absent, which excludes the possibility of presence of two benzene rings in the repeated unit.

Also the absence of d-spacing of 12.885 $\text{\AA}$  excludes the possibility of presence of crystalline region in the produced purified polymer respectively [12].

### 5.2.5. Suggested Mechanism of Polymerization of Hydroquinone (cationic radical)

From the FT-IR and X-ray diffraction studies, we suggest the following scheme for the polymerization of hydroquinone which is similar to that suggested by Kovacic and El-Garf and Nour El-Din for polymerization of benzene with anhydrous  $\text{AlCl}_3\text{-CuCl}_3$



### 5.2.6. Study of Thermal Properties

#### 5.2.6.1. TGA Study

Figure (5.8) summarizes the thermal decomposition of the monomer (Hydroquinone) under air atmosphere.

From the figure it can be concluded that the monomer starts its decomposition at 165 $^{\circ}\text{C}$  -which is the melting point of the monomer- while the outmost decomposition temperature for the monomer is recorded to be 246.3 $^{\circ}\text{C}$ , during this phase the monomer experiences a weight loss of 91.65% of its initial weight.

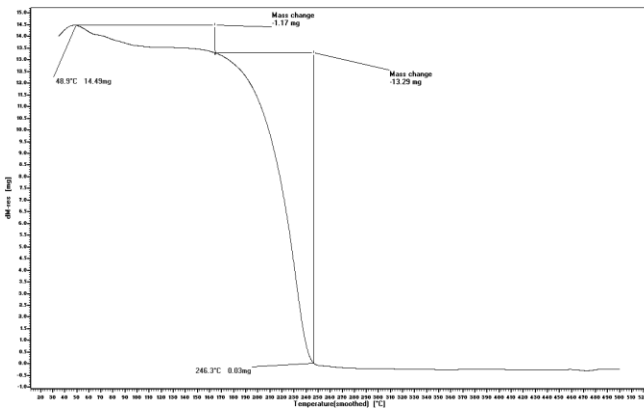


Fig. (5.8): TGA study under air atmosphere for the monomer (Hydroquinone)

The thermal decomposition of the purified polymer under nitrogen atmosphere is represented in figure (5.9), Hence giving an idea about its thermal stability.

According to figure (5.9) the purified polymer was observed to decompose on three stages. The first one presents the thermal stability of the polymer which is up to 358.34°C where it starts to experience a small weight loss which reaches 1.625% of its initial weight. A significant weight loss occurs at 387.40°C with total weight loss of 20.78%. Then its weight is fixed over a temperature interval from 387.40°C to 611.34°C where another significant weight loss is observed which indicates the final decomposition of the produced polymer.

The DTG curve, plotted in the same figure, supports the above observations by the presence of two pronounced peaks indicating the first and final polymer decomposition temperatures of the produced polymer. It can also be noted from the same curve, the narrow distribution of the pronounced peaks which indicates the purity of the prepared polymer.

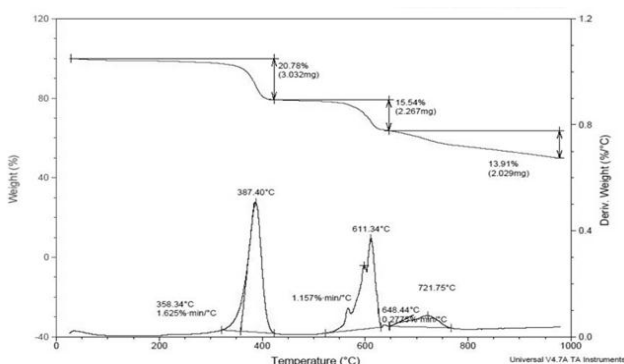


Fig. (5.9): TGA and DTG study of the prepared purified polymer under nitrogen atmosphere

### 5.2.6.1. DTA Study

Figure (5.10) and (5.11) shows the DTA study of the monomer (Hydroquinone) and the prepared purified polymer respectively under air atmosphere.

From figure (5.10) it can be noticed that there is a first endothermic peak which indicates the evaporation of trapped

water in the sample (humidity). A second endothermic peak is observed to begin at 170°C with maximum at 184°C which is attributed to the melting point of hydroquinone. An exothermic peak is shown which begins at 232.6°C and ends at 477.3°C with an average peak of 351.8°C, which indicates the decomposition of Hydroquinone

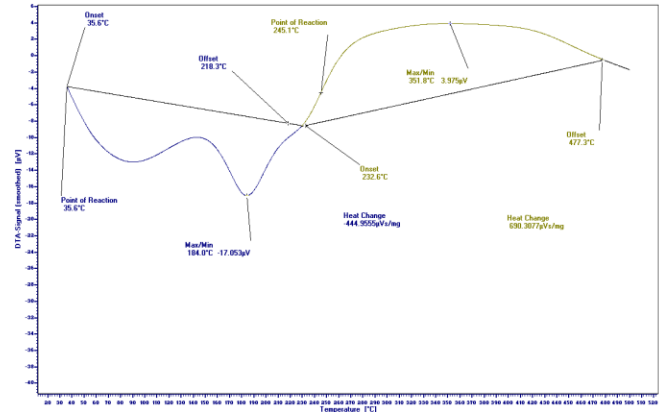


Fig. (5.10): DTA analysis of the monomer (Hydroquinone) under air atmosphere

From figure (5.11) it can be noticed that there is an endothermic peak which indicates the evaporation of trapped water in the sample (humidity). An exothermic peak is shown which begins at 358.5°C and ends at 463.6°C with an average peak of 391.1°C, which indicates the first decomposition temperature of the prepared polymer.

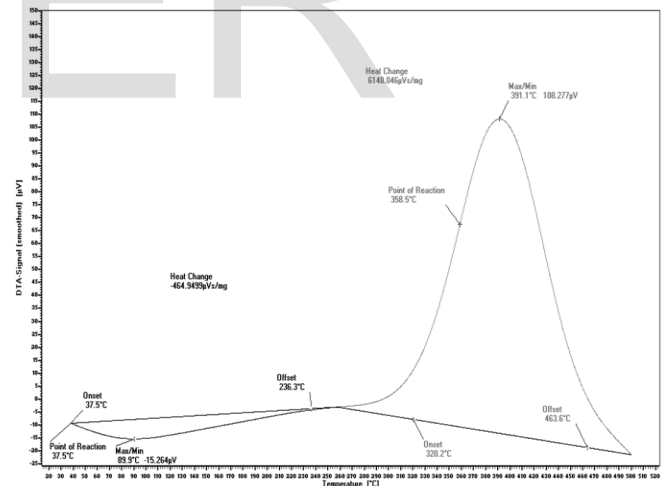


Fig. (5.11): DTA analysis of the prepared purified polymer under air atmosphere

By comparing the average peak of decomposition the monomer and the prepared purified polymer it can be noticed that there is an increase of 39.3°C. This increase in oxidation temperature (i.e. increase in thermal stability) between the monomer and the prepared polymer is another proof that the polymerization reaction took place.

Figure (5.12) shows the DTA study of the prepared purified polymer under nitrogen atmosphere.

As shown in figure (5.12), decomposition of PHQ takes place with stages depending on the energy required to cause

the rupture of bonds. It can be seen from the figure that exothermic peaks appear on the DTA curve in the range 209.43–223.27°C, which probably result from the partial oxidation of hydroquinone groups. The most relevant peak, located at 392.27°C, corresponds to dehydroxylation process and to oxidative scission of quinone rings. These data supports the above conclusions from the TGA study of the polymer. These observations are also in close resemblance to those investigated in literature [13].

Generally the DTA of the produced polymer does not show any endothermic melting peaks which means that the polymer does not melt up to 1000°C. The exothermic peaks do not show any crystallization because there are no phase transitions.

Therefore these exothermic peaks are due to decomposition as they correspond to DTG curves.

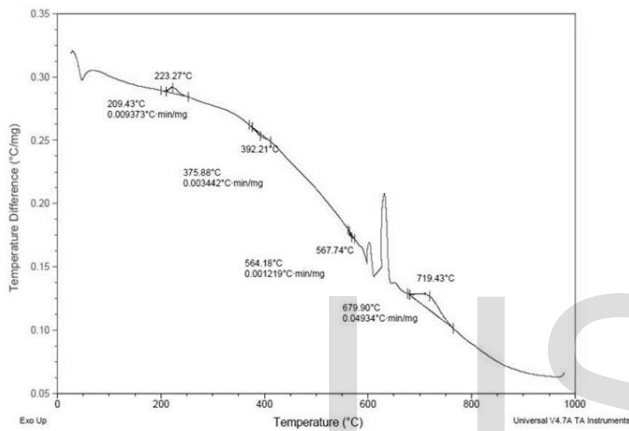


Fig. (5.12): DTA analysis under nitrogen atmosphere for the prepared purified polymer

### 5.2.6.3. DSC Study

DSC measures heat flow associated with structure (amorphous and crystalline) and changes in structure (transitions) of materials as a function of time and temperature in a controlled atmosphere. The utility of DSC comes from the fact that all changes in structure involve the absorption or release of heat.

Figures (5.13) show the DSC study of the produced purified polymer.

From figure (5.13) it can be noticed that there is an endothermic peak at 80.4°C with enthalpy of -2537.109 J/g, which is the enthalpy of evaporation of water. An exothermic peak is noticed at 392.7°C with enthalpy of oxidation of 13724.89 J/g which indicates the first oxidation temperature of the prepared purified polymer.

These values agree with the results obtained from the DTA and TGA studies which confirm the high thermal stability of the prepared PHQ.

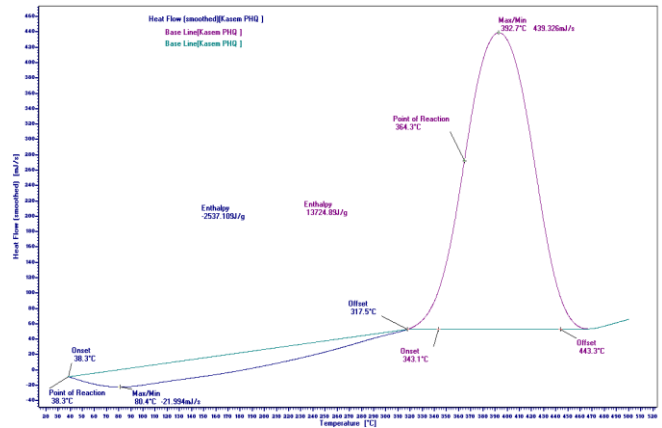


Fig. (5.13): DSC analysis in Air atmosphere for the purified polymer

## 5.3 The Use of PHQ as Antioxidant for Lubricating Base Oil

### 5.3.1. Rheology

Figures (5.14), (5.15), (5.16) and (5.17) show the change of the viscosity with time under a constant temperature of 260°C and shear rate of 70 S-1 of a sample of blank lubricating oil, free lubricating oil containing 0.03 wt% of PHQ, free lubricating oil containing 0.06 wt% of PHQ and free lubricating oil containing 0.1 wt% of PHQ respectively.

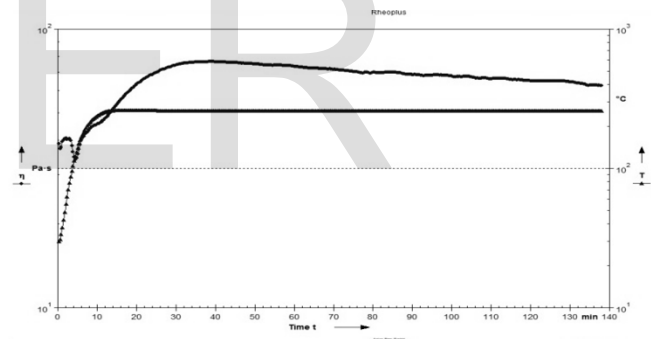


Fig. (5.14): Change of Viscosity with time of a blank lubricating oil at shear rate of 70 S-1 and Temperature of 260°C

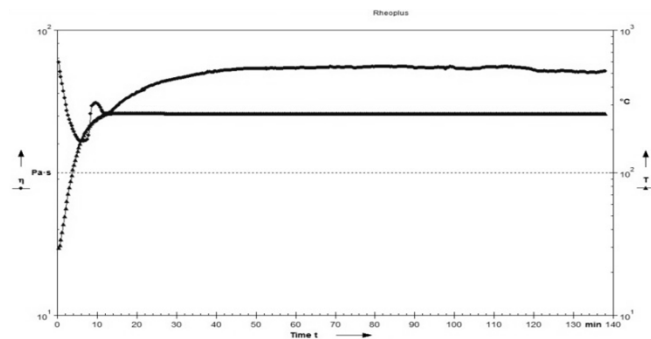


Fig. (5.15): Change of Viscosity with time of free lubricating oil containing 0.03 wt% of PHQ at shear rate of 70 S-1 and Temperature of 260°C

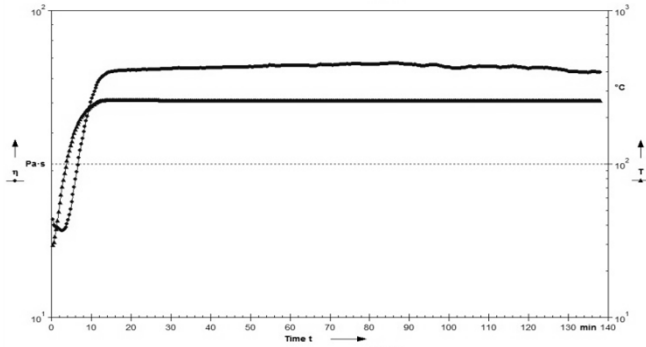


Fig. (5.16): Change of Viscosity with time of free lubricating oil containing 0.06 wt% of PHQ at shear rate of 70 S-1 and Temperature of 260°C

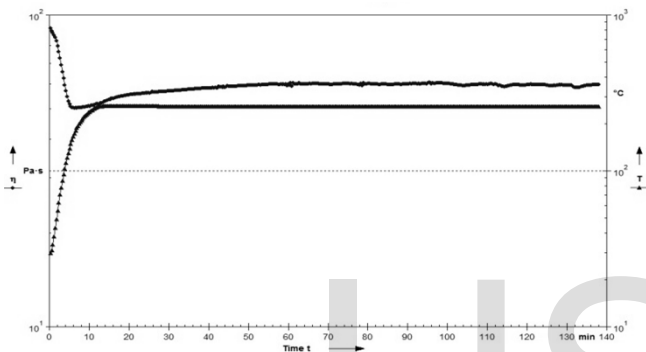


Fig. (5.17): Change of Viscosity with time of free lubricating oil containing 0.1 wt% of PHQ at shear rate of 70 S-1 and Temperature of 260°C

It can be noted from the previous figures that the time range of constant viscosity of blank lubricating oil is 15 minutes and that of free lubricating oil containing 0.03 wt% is 75 minutes. While adding 0.06 wt% of PHQ to the free lubricating oil increased the time range of constant viscosity to 111 minutes, the addition 0.1 wt% of PHQ gave a time range of only 57.6 minutes, i.e. using 0.06 wt% of PHQ as an additive increased the time range of constant viscosity by 7.4 times.

The reason behind the decrease of the time range of constant viscosity from 111 minute for lubricating oil containing 0.06 wt% PHQ and lubricating oil containing PHQ concentration of 0.1 wt% may be attributed to the increase in concentration of the free radicals produced by the antioxidant (PHQ). Thus the free radicals produced by the antioxidant combine with each other and separate from the system so the inhibition effect of the antioxidant decreases substantially.

From the above observations it can be concluded that the optimum concentration of PHQ to be added to free lubricating oil is 0.06 wt%. Table (6.1) and figure (6.18) summarizes the effect of adding the prepared PHQ with different concentrations on the stability of viscosity.

Table (5.2): The effect of adding the prepared PHQ with different concentrations on the stability of viscosity

PHQ concentration in blank oil	Time range of constant viscosity (minutes)
Blank oil	15
0.03 wt%	75
0.06 wt%	111
0.1 wt%	57.6

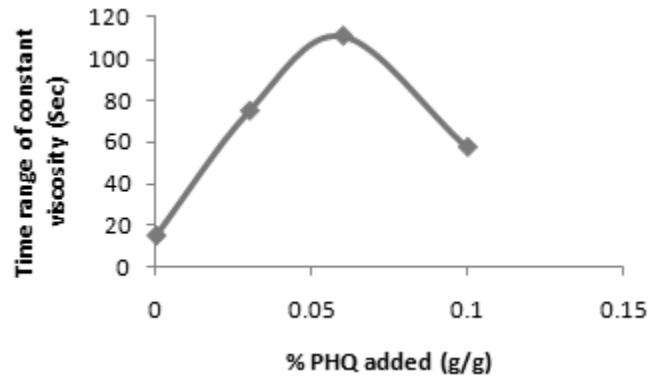


Fig. (5.18): The effect of adding the prepared PHQ with different concentrations on the time range of viscosity

Figure (5.19) shows the change of the loss modulus as a function of angular frequency. It can be concluded from the figure that as the polymer concentration increase the loss modulus increase, i.e. as PHQ concentration increase the ability of the lubricating oil to absorb the thermal energy resulting from friction of the engine parts increase. Therefore as PHQ concentration increase, the thermal stabilization of lubricating oil increase. Until reaching the optimum concentration which is 0.06 wt% then the effect is decreased for the 0.1 wt%. Thus by adding a very small concentration PHQ (0.06 wt %) the oxidation tendency of the lubricating oil is decreased.

The ability of the polymer to absorb the thermal energy arises from the ability of polymers to absorb any kind of energy and utilizing it for the conformation of the chains shapes, which is a well known phenomenon in polymer science [22].

Figure (5.20) illustrates the change of the loss modulus as a function of complex viscosity. It can be observed that for complex viscosities less than 1 Pa.S the loss modulus is approximately constant until reaching complex viscosity of 1 Pa.S the trend is changed to be as complex viscosity increase the loss modulus increase. This can be explained from the definition of the complex viscosity, where at the low values of the complex viscosity the storage phenomenon is dominating but as the values increase the phase of energy storage stops and the loss modulus increase, i.e. the oil tendency to dissipate the thermal energy rather than storing it increase (the excess amount of energy is released in the loss modulus).



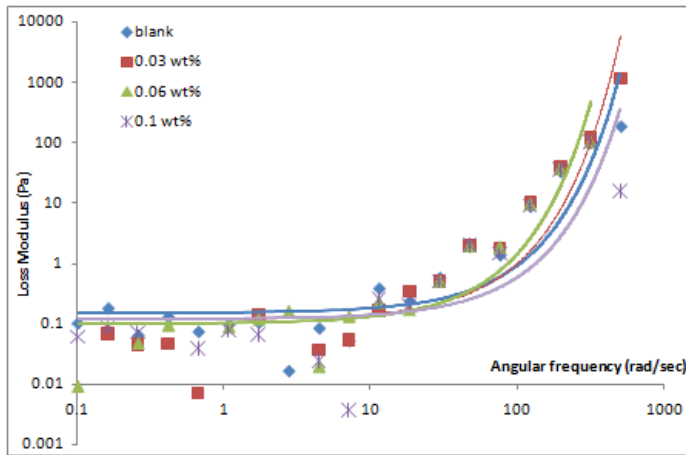


Fig. (5.19): The change of the loss modulus as a function of angular frequency Angular frequency range (0.1 - 500 rad/sec) and constant temperature of 90°C

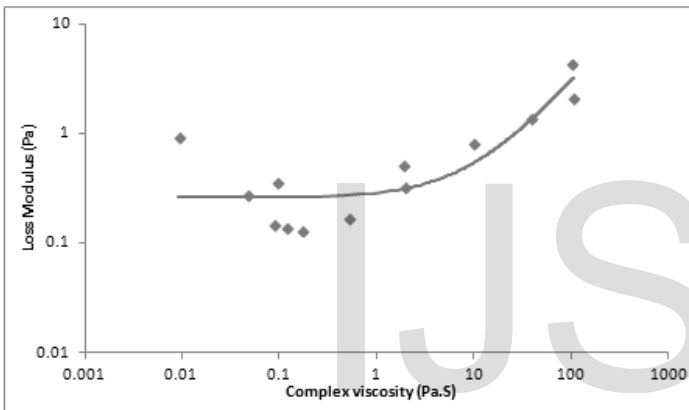


Fig. (5.20): The change of the loss modulus as a function of complex viscosity at Angular frequency range (0.1 - 500 rad/sec) and constant temperature of 90°C

**5.3.2. TGA study**

Evaluation of oxidation stability of base oil may be expressed by means of activation energy according to Ozawa’s method [5].

Ozawa’s method explained that by plotting the logarithm of the heating rates on the ordinate against the reciprocal of the absolute temperature on the abscissa at the same weight loss, the slope was found to be directly proportional to ΔE (i.e. A linear correlation can be obtained by plotting the logarithm of heating rate or the scan speed against the reciprocal of the absolute temperature at the same conversion or weight loss percentage).

It was assumed that TG curve obeyed first order kinetics and ΔE is calculated from the following equation

$$\text{Slope} = (0.4567/R)\Delta E$$

Where R is the universal constant of gases.

From these data the rate constant and the half life time can be also calculated.

Figures (5.21) and (5.22) show typical TGA curves for free base lubricating oil and lubricating oil containing 0.06 wt%

PHQ respectively. From these figures, at different percentage decomposition, Arrhenius data were obtained as indicated in tables (5.3) and (5.4) for free base lubricating oil and lubricating oil with 0.06 wt% PHQ respectively.

Table (5.5) was obtained from the TGA curves of free base lubricating oil and lubricating oil containing 0.06 wt% PHQ. Once more to minimize errors the thermogravimetric decomposition curves was assumed to obey first order kinetics. The rate constant at different temperatures is then obtained by determining the slope of the figures (5.23) and (5.24) which were drawn from table (5.5).

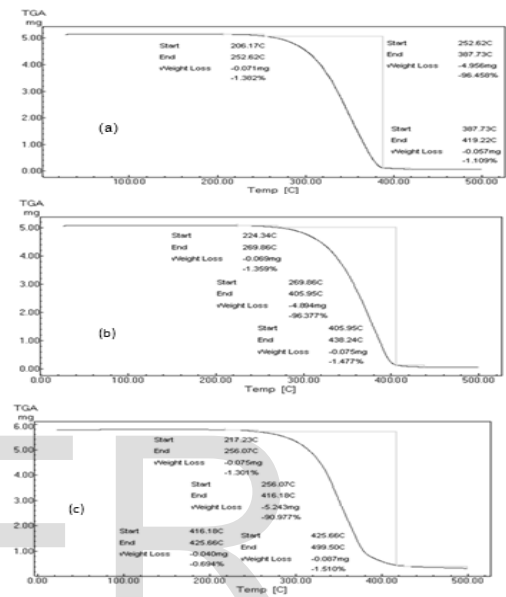


Fig. (5.21): TGA curve for base lubricating oil under nitrogen atmosphere at a rate of (a)10<sup>0</sup> C/min, (b)20°C/min and (c)30°C/min

Table (5.3): Arrhenius data obtained from TGA curves for free base lubricating oil

% Decomposition		Log Heating Rate		
		1.0000	1.3010	1.4771
10%	°C	296.15	315.61	306.82
	°K	569.15	588.61	579.82
	1000/K	1.7570	1.6989	1.7247
25%	°C	320.21	341.06	331.35
	°K	593.21	614.06	604.35
	1000/K	1.6857	1.6285	1.6547
35%	°C	330.71	352.03	340.88
	°K	603.70	625.03	613.88
	1000/K	1.6564	1.5999	1.6290
50%	°C	342.84	364.88	351.45
	°K	615.84	637.88	624.45
	1000/K	1.6238	1.5677	1.6014
65%	°C	354.20	375.36	363.47
	°K	627.20	648.36	636.47
	1000/K	1.5944	1.5424	1.5712
75%	°C	362.25	382.52	371.17
	°K	635.25	655.52	644.17
	1000/K	1.5742	1.5255	1.5524

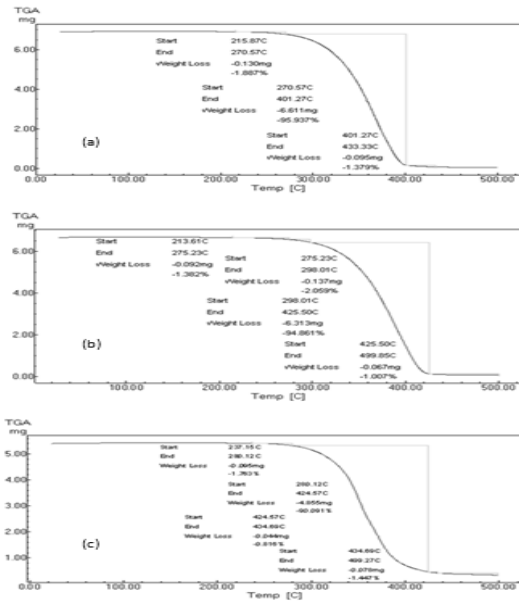


Fig. (5.22): TGA curve for lubricating oil containing 0.06 wt% of PHQ under nitrogen atmosphere at a rate of (a)10<sup>o</sup> C/min, (b)20<sup>o</sup>C/min and (c)30<sup>o</sup>C/min

Table (5.4): Arrhenius data obtained from TGA curves for lubricating oil containing 0.06 wt% PHQ

Log Heating Rate		1.0000	1.3010	1.4771
10%	<sup>o</sup> C	310.27	326.73	317.94
	<sup>o</sup> K	583.27	599.73	590.94
	1000/K	1.7145	1.6674	1.6922
25%	<sup>o</sup> C	335.48	353.76	340.29
	<sup>o</sup> K	608.48	626.76	613.29
	1000/K	1.6434	1.5955	1.6306
35%	<sup>o</sup> C	345.91	365.59	348.07
	<sup>o</sup> K	618.91	638.59	621.07
	1000/K	1.6157	1.5650	1.6101
50%	<sup>o</sup> C	358.64	378.71	357.39
	<sup>o</sup> K	631.64	651.71	630.39
	1000/K	1.5832	1.5344	1.5863
65%	<sup>o</sup> C	369.07	390.00	370.29
	<sup>o</sup> K	642.07	663.00	643.29
	1000/K	1.5575	1.5083	1.5545
75%	<sup>o</sup> C	375.93	397.67	379.07
	<sup>o</sup> K	648.93	670.67	652.07
	1000/K	1.5410	1.4910	1.5336

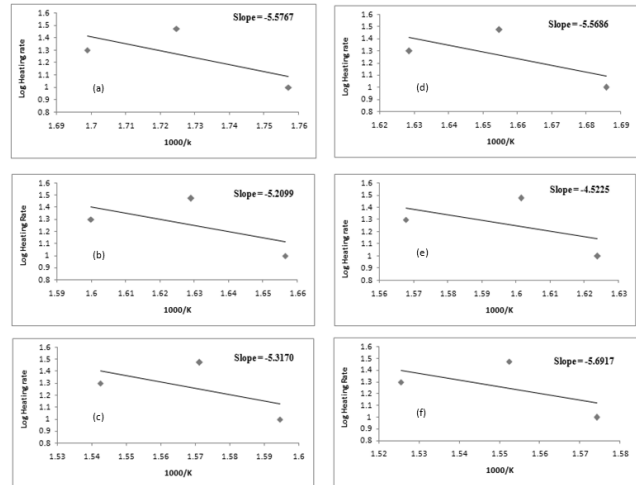


Fig. (5.23): Arrhenius plots for TGA of base lubricating oil at (a)10%, (b)25%, (c)35%, (d)50%, (e)65% and (f)75% decomposition

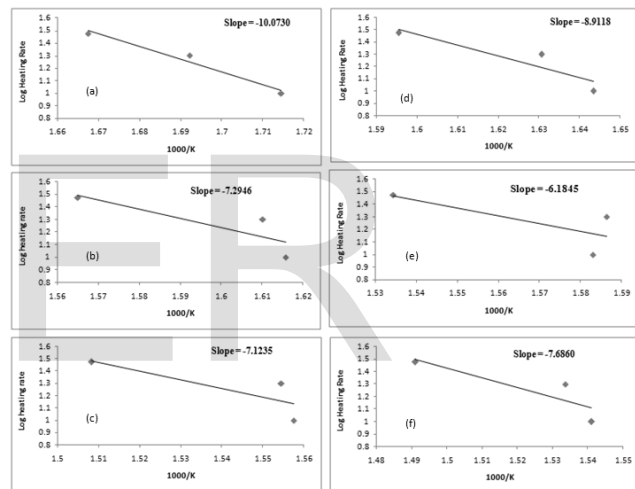


Fig. (5.24): Arrhenius plots for TGA of lubricating oil containing 0.06 wt% of PHQ at (a)10%, (b)25%, (c)35%, (d)50%, (e)65% and (f)75% decomposition

Table (5.5): Activation energies of decomposition of base lubricating oil compared with that of lubricating oil containing 0.06 wt% PHQ

% Decomposition	$\Delta E$ for free lubricating base oil (KJ/mole)	$\Delta E$ for lubricating oil containing 0.06 wt% PHQ (KJ/mole)
10	101.5211	183.3740
25	101.3736	162.2350
35	94.8437	132.7946
50	82.3299	112.5858
65	96.7388	129.6798
75	103.6146	139.9199
<b>Average <math>\Delta E</math>, (KJ/mole)</b>	<b>96.7369</b>	<b>143.4315</b>

From table (5.5), it is evident that the addition of 0.06 wt% PHQ as an oxidation inhibitor additive to lubricating base oil increases its activation energy of oxidation by 1.5 times. This increase in  $\Delta E$  means that the oil requires more energy to oxidize, accordingly the life time of the lubricating oil is increased also it is another support for the stabilization of lubricating oil by our prepared purified PHQ.

These observations lead us to the suggestion that PHQ may inhibit the formation of free radicals and peroxides during lubricating oil oxidation.

The use of PHQ as an antioxidant for lubricating oils part is protected by the Egyptian patent No. 1292/2015.

## 6 CONCLUSION

PHQ was prepared via modified El-Garf polymerization method which proved to possess substantial characteristics, if compared with PHQ prepared by other polymerization techniques. The prepared polymer was collected in the form of dark-brown very fine powder.

The pristine method yielded PHQ with particle size within the range of nano scale, the property that opens a door for further research and promising applications.

The FT-IR and XRD study of the monomer and the purified prepared PHQ indicated that the polymerization reaction proceeded towards the formation of PHQ with the suggested mechanism of reaction and structure.

The prepared PHQ was thermally stable up to 387.40°C. TGA analysis showed that the polymer possesses 2 peak upon oxidation, the first at 387.4°C and the final one at 611.34°C. Between these two peaks the polymer experiences a phase of thermal stability without any weight loss.

The narrow peaks observed in the DTG is an evidence of the purity of our purified prepared PHQ and confirms our conclusion from the XRD study that there is no low molecular weight oligomers.

PHQ was proved to be a potential antioxidant for lubricating oil if added with the optimum concentration of 0.06 wt%. This suitability arises from the high thermal stability of PHQ and its capability to reduce the lubricating oil oxidation.

The rheology study revealed that the optimum concentration of PHQ to be added is 0.06 wt% as this concentration gave the highest time range of constant viscosity. It also revealed that PHQ increases the ability of the lubricating oil to absorb the thermal energy resulting from friction of the engine parts, by measuring the change of the loss modulus with angular frequency. Again the optimum concentration (0.06 wt %) gave the best results for dissipating the thermal energy. It also revealed that as the complex viscosity increases the loss modulus increases, this is due to the increase of oil tendency to dissipate the thermal energy rather than storing it.

Another interpretation of the oxidation stability was also explained by the activation energy required for the oxidation reaction, therefore from the kinetic data of oxidizing the oil via TGA technique, the activation energy of oxidation of free base lubricating oil and lubricating oil containing 0.06 wt% of PHQ

were calculated and showed that the oil containing PHQ has activation energy of oxidation higher than that of free base lubricating oil by 1.5 times, i.e. the lifetime of the lubricating oil is increased.

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