Synthesis and Cyclopolymerzation of N-Aryl Di AllylAmins As Antioxidants for Lubricant's Oil

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Abstract

In this research many new N-aryl substituted di allylAmins were synthesized [A1-A2] which were Polymerized by free radically mechanism by using Ammonium per sulfate as an initiator at 70^0C .The new hindered amines as cyclo polymers were characterized by FTIR and H-NMR Spectroscopies ,Physical and chemical properties were measured using TGA and DSC to study the thermal stability of prepared cyclopolymers . These prepared N-aromatic substituted di allylamins cyclopolymers [A3 - A4] were used as antioxidants for lubricant oil . which give high stability when comparing with standard antioxidant . The oxidation stability of base oil with (1%) additive were examined according to Institute of Petroleum testing method IP280 .

Key words: cyclopolymers , di allylAmins anti-oxidant, hindered amines

الخلاصة

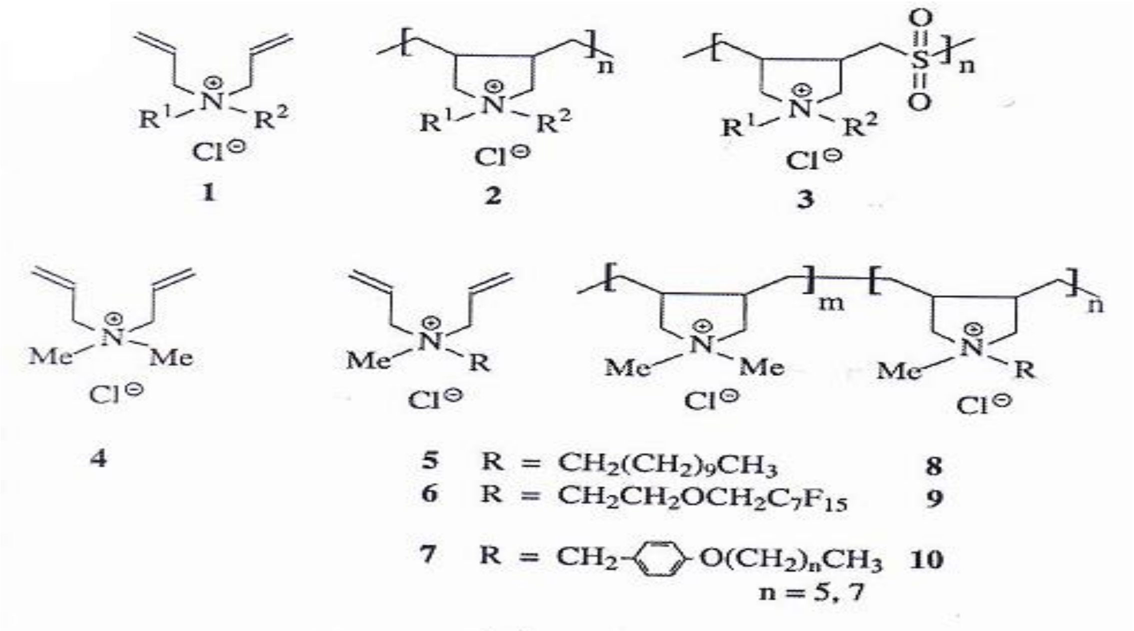
في هذا البحث حضرت العديد من مونومرات N-أريل ثنائي أليل امين المعوضة [A1–A2] والتي تم بلمرتها بالجذور الحرة باستخدام الأمونيوم بير سلفات كباديء في 70درجة مئوية، شخصت البوليمرات الحلقية الأمينية المعوضة و المعوقة الجديدة بواسطة طيف الاشعة تحت الحمراء وطيف الرنين النووي المغناطيسي ، تم قياس الخواص الفيزيائية والكيميائية. وقد درست TGA. و DSC حيث درس الاستقرار الحراري للبوليمرات المحضرة. تم استخدام هذه البوليمرات[A3 – A4] كمضادات أكسدة لزيوت التشحيم. والتي أعطت الاستقرار الحراري العالي بالمقارنة مع مضادات الأكسدة القياسية. تم فحص ثبات الأكسدة للزيت الاساس المضاف ب (1٪) وفقا لطريقة الاختبار للمنشآت النفطية IP280.

الكلمات المفتاحية: سايكلو بوليمر، داي ألبولي امين, مضادات الأكسدة، الأمينات المعاقة

Introduction

Butler reported that diallyl quaternary ammonium salts polymerized in the presence of catalytic qunatities of tert-butylhydroperoxide to form water-soluble, noncrosslinked polymers (Butler and Ingelo,1951) . A characteristic feature of the free-radical polymerization of allyl monomer is a cyclic intra and intermolecular polymerization mechanism (Butler and Ingelo,1957)

Many polymers derived from Radical cyclopolymerizations of 1, 6-dienes to yield two possible repeating cyclic structures , five and six-membered rings (Hawthome *et al.,* 1976) . A six-membered rings and its radical formed during the propagation could be more stable than a six - membered rings and its radical formed, respectively. However, a six - membered ring is found quite often as a repeating unit in the polymers derived from 1,6-dienes (Hawthome *et al.* 1976, Wandrey *et al.,* 1981)as shown in scheme (1).



Scheme 1.

Di allyl p-toluene sulfonamide (Crawshaw *et al.*, 1972) . gives cyclopolymers consisting of five- membered repeating units in the main chain . In these monomers, two allyl groups are attached to the same atoms and the close proximity of the two allyl groups induces cyclization. It is interesting to note that hydrochloride salts of N -alkyl, N, N-di allyl amines have been reported to form water-soluble polydiallylamine hydrochlorides by gamma ir-radiation or persulfate initiation . On the other hand , these monomers in their free base tend to form gel during polymerization under the same conditions (Jackson, 1976) .

N , N–diallyl morpholinium bromide has been synthesized in high yields (96%)by stepwise condensation of morpholine with allyl chloride and allyl bromide.

Polymerizability of the quaternary ammonium salt has been studied using various radical initiators such as (K2S2O8) and t-butyl hydroperoxide. High yields of polymers have been obtained by precipitation polymerization in n-butanol with t-butyl hydroperoxide as radical initiator. This method gives low molecular weight polymers, whereas polymers with moderate molecular weights have been obtained in concentrated aqueous solutions (Yunusa *et al.*, 2010) .

Many other monomer such as sulfur di oxide , N,N-diallyl-N-carboethoxymethylammonium chloride and the hydrophobic monomers N,N-diallyl-N-dodecylammonium chloride or N,N-diallyl-N-octadecylammonium chloride were cyclo copolymerized in dimethyl sulfoxide using azobisisobutyronitrile (AIBN) as the initiator to afford water-soluble cationic polyelectrolyte (CPE) having five-membered cyclic structure on the polymeric backbone. The (CPE) on acidic (HCl) hydrolysis of the pendent ester groups gave the corresponding cationic acid salt (CAS) which was converted to the anionic polyelectrolyte (APE) by treatment with sodium hydroxide (Bufler *et al.*, 1991).

The solution properties of the (CPE) and (APE) containing varying amount of the hydrophobic monomers . The polymers showed that concentration of hydrophobic association less than (1 wt%) was required for the manifestation , and displayed significant hydrophobic association in salt (NaCl) free as well as salt-added solutions(Milligan *et al.*, 1993).

Cyclopolymerization of hydrophilic and hydrophobic diallyl monomers in such high concentrations has been reported to yield random rather than micro blocky coplymers even though the hydrophobic monomer possesses surfactant properties (Han and Chang 2000). Novel methods for the preparation of modified oligodeoxynucleotides (ODNs) have been actively pursued in the last two decades (Agrawa 1999). due to their potential use in therapeutic and diagnostic applications (Milligan 1993). An important prerequisite of synthetic (ODNs) and their stability against biological nucleases that result in the cleavage of the phosphodiester backbone in RNA and DNA (Miller and Hamma 1999)

Experimental Part

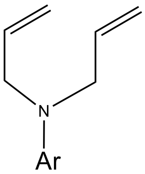
All chemicals used were analytical grade and they were purchased from (Fluka), , allyl bromide, ($K_2S_2O_8$) (E. Merck), DMSO (E. Merck); other chemicals such as 2,4-diaminophenol and 2,5-dimethylaniline were used without further purification. Tetrahydrofuran(THF) were Di ethyl ether were Acetone and Absolut alcohol were purchased from BDH.

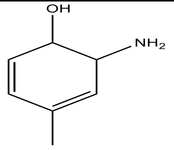
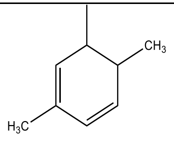
Preparation and methods

Synthesis of N-substituted phenyl diallyl ammonium bromide [A1 - A2]

In a 250 ml round-bottom flask equipped with a condenser (0.1 mole) of aromatic amines such as 2,4-diaminophenol or 2,5-dimethyl aniline and (2.4 g , 0.2mole) of allyl bromide were dissolved dissolve in 20 ml of THF and (10ml) of triethylamin. The mixture was refluxed for 1hr at 70℃ and stirred with magnetic stirrer the cyclo polymer was obtained recrystillized and dried .Table (1) lists the physical properties of prepared N-substituted diallylamine .

Table (1) Physical properties of prepared cyclo monomers (A1-A2)

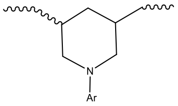


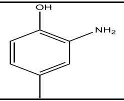
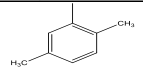
Compound No.	Ar	Color	Softens Point ℃	Yield%	Purification Solvent
A1		Deep Black	Oily	95%	THF
A2		Dark Black	Oily	92%	THF

Cyclopolymerization of monomers A1 and A2 to A3 and A4

3g of prepared diallyl amine monomer [A1] or[A2] were dissolved in 10ml of (0.1N HCl). 0.1g of Potassium per sulfate was dissolved in 5ml of water . The mixture was heated at 70℃ for 2 hr . The crude cyclopolymerization was washed with acetone and absolute alcohol, filtered and dried in a vacuum oven at 70℃. until it reached a constant weight.

Table (2) list the physical properties of (A3-A4) Cyclo polymer



Compound	No.Ar	Color	Softens Point ℃	Yield%	Solvent
A3		Black	302℃-330℃	80%	Acetone ,ethanol, DMF,THF
A4		Dark Brown	305℃-326℃	64%	Acetone, ethanol, DMF,THF

Oxidation Stability

Oxidation is initiated by the reaction of oxygen with the hydrocarbon materials to form precursors to harmful products. Wilson noted that the rate of oil oxidation is affected by oxygen availability, temperature , the presence of catalysts and the composition of the base stock. (Zainab, 2013).

Oxidation stability of the synthesized additives was determined according to Institute of Petroleum testing method IP 280. 25 g of inhibited oil were blended with 0.25 g of soluble metal catalyst (iron and copper). An oxygen flow (1L/h) was passed through the oil for 164 hours at 120°C. After the test the volatile acids, the total acidity (T.A) of the oil and the total precipitated sludge (T.S) were measured and their values were used to calculate the total oxidation products (TOP).

$$\mathrm{TOP\%} = \mathrm{T.S} + 180\,\frac{\mathrm{T.A}}{561}$$

Where, T.A = total acidity, mg KOH/g

T.S = total sludge, % weight

180 = the average molecular weight of oil oxidation acids.

The efficiency of oil blends [A1] was calculate by the following equation :-

$$\text{Efficiency } \% = \frac{\text{TBN of sample} - \text{TBN of blend}}{\text{TBN of blend}}$$

Table(3) Oxidation stability of antioxidant [A3] and [A4]

Lub. Insp.Data	Blank	A3	A4	Standard
Vol. Acidity mg KOH/gm oil	0.334	0.0139	0.0025	0.0060
Sol. Acidity mg KOH/gm oil	1.419	0.258	Nil	0.1230
Total Acidity mg KOH/gm oil	1.753	0.2719	0.0025	0.1290
Total sludge % wt	0.6184	1.002	0.6332	0.088
TOP	1.180	1.09	0.634	0.1298

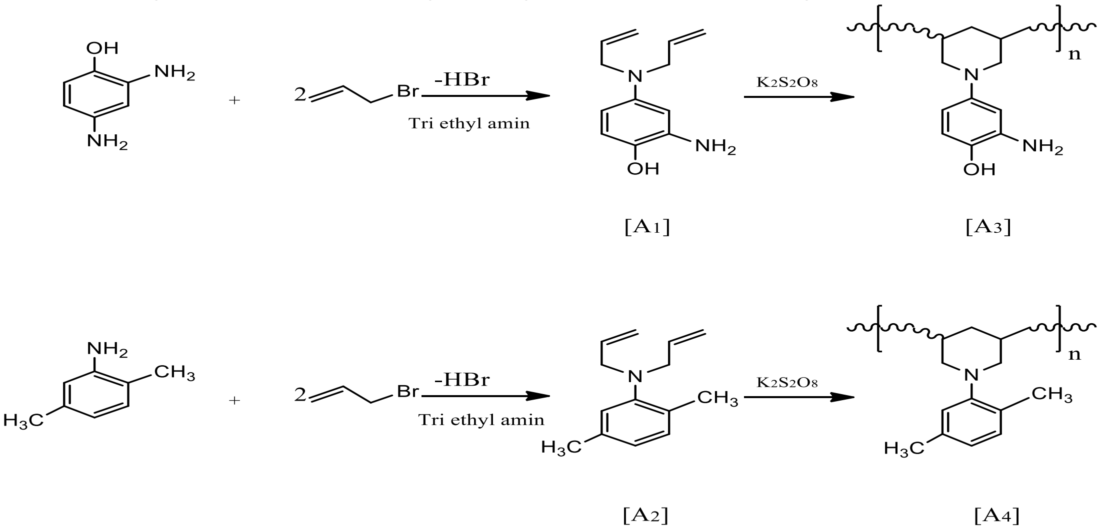
Table(4)Base oil Properties

Base oil	60 stock
Vis.cst-100	8.5
V.I	95
Flash points	238
Pour points	-6
Color	1.0 – 2.0
Acidity	0.01
S% wt	1.2

Result and Discussion

To increase time of usage for Lubricant oil and to obtain desired propertied and to reduce the a major problem of oxidation as a result of over –reduction , and to replace many additives of base oil in one additive, we design. The new cyclopolymers as hindered amino cyclopolymers which act as antioxidant and modified the viscosities of oil instead of another additives .

In this research a novel cyclo monomer [A1-A2] were synthesized via reaction of two moles, allyl bromide with substituted aniline such as 2,4-diamino phenol (A1) and 2,5- di methyl aniline (A2) then cyclopolymerized free radically as shown below:-



Scheme (2)

In this work hindered amine polymers were prepared which act as electron- transfer complex (Firyal, 2000) . The electronic effects of substituent in aromatic hindered amines lead to increased activity ,this attributed to move conjugation to aromatic hindered amines polymers and their stability . The oxidation process can illustrated as following (Nehal et al. , Ludema et al.1996) :-

Initiation: $R\text{-}H \longrightarrow R^{\cdot} + H^{\cdot}$

Propagation : $R^{\cdot} + O2 \longrightarrow ROO^{\cdot}$

$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$

Branching : $ROOH \longrightarrow RO^{\cdot} + {}^{\cdot}OH$

$RO^{\cdot} + RH \longrightarrow ROH + R^{\cdot}$

${}^{\cdot}OH + RH \longrightarrow R^{\cdot} + H_2O$

Termination : $ROO^{\cdot} + ROO^{\cdot} \longrightarrow RR + 2O_2$

$ROO^{\cdot} + InH \longrightarrow ROOH + In^{-}$

$RO^{\cdot} + InH \longrightarrow ROH + In^{-}$

Inhibition $R^{\cdot} + InH \longrightarrow RH + In^{-}$

The prepared polymer [A3] and [A4] were characterized by FTIR spectroscopy ,

Fig.(1) FTIR spectrum of [A3] showed main band at 3450cm^{-1} ,3388cm^{-1},3352 cm^{-1},which attributed to NH_2,OH,and OH respectively as stretching vibration absorption at 3100 cm $^{-1}$and 2976 cm^{-1}assigned CH aromatic and alphatic respectively at 1979 cm^{-1} indicated N-H ,ammonium ion .Which formed through polymerization and 1398 cm^{-1} due to(C-N) ,at 1597 cm^{-1} attributed to(C=C) aromatic ring .

Fig. (2), FTIR spectrum of cyclopolymer [A4] showed the main bands at 3414 cm^{-1}and 1900 cm^{-1}due to NH ammonium salt which formed through liberated HBr, 3076 cm^{-1}and 2920 cm^{-1}due to CH aromatic and aliphatic respectively and at 1633 cm^{-1},1396 cm^{-1}and 1166 cm^{-1}were appeared due to C-O and C-N.

Fig.(3) TGA and DSC of cyclopolymer [A3] showed the function of temperature with weight loss indicated the thermal stability ranged between (330.6℃ – 519℃).

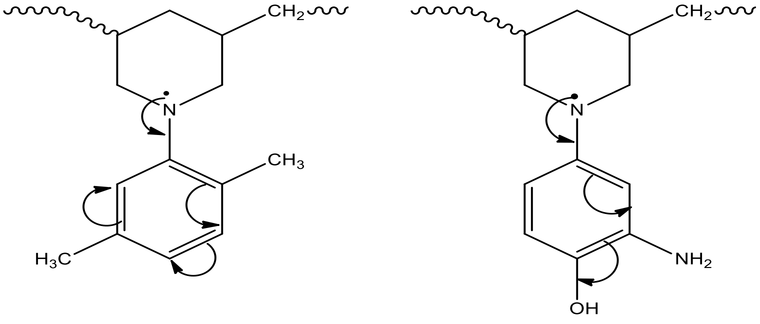
Fig.(4)showed thermal stability of cyclopolymer [A4] ranged between (285.5 ℃ – 319℃) indicated the high stabilities of prepared cyclopolymer due to the presence of aromatic rings which substituted though beakbone of cyclo di allyl amin and their substituted with another groups such as (OH phenolic) in [A3] and 2,5-dimethylaniline in [A4].

Fig.(5) 1H-NMR spectrum of [A3] cyclopolymer appeared the signals at 0.98 ppm assigned for CH-$\underline{CH2}$ as doubletf,1.5-1.4 ppm assigned to $-CH/\overset{CH2}{\overline{\qquad}}\backslash CH-$ as triplet, 3 ppm and 2.8 ppm assigned to 2N- $\underline{CH2}$-CH as doublet all these signals were repeated on the other meta di allylamine cyclopolymer the aromatic ring was appeared the signals at 5.4 ppm due to (OH-phenolic) , at5.7 pmm indicated the ortho proton between 2N and at 6.56 ppm due to ortho aromatic proton as a singlet . 7.3 ppm assigned to meta behind (OH) group appeared as doublet.

Fig.(6) 1H-NMR spectrum of [A4] cyclopolymer gave a singals at0.92 ppm assingned to $\underline{CH}$-CH2-CH as Triblet , 1.67 ppm assigned to $\underline{CH}$-CH2 as a Triblet , 1.6ppm and 1.4 ppm due to CH2-CH2-CH appeared as multiplet , The aromatic ring which substituted by ortho CH3 gave a signal at 2.1 ppm and other para CH_3 appeared at 2.35 ppm as a singlet . At 6.9 ppm assigned to proton in meta position as a singlet , and 6.9 ppm assigned to other in meta position as a singlet .

The resistance oxidation under specific conditions within habited by N-substituted di allyl amine cyclopolymers [A3] and [A4] have been used , the Top indicated the better oxidation stability , another test such as Total sludge (wt%) , volatile acidy and soluble acidity mg (KOH/g oil) were measured which gave a good results as shown in Table (3) .

The oxidation stabitiy was observed due to the extended of conjugated system in addition the presence of (OH phenolic) in cyclopolymer [A3] .



[A4] [A3]

Scheme (3).

[A3] could acted as a good antioxidant because it has two functional groups in creased the efficiency of antioxidant hindered amines and phenolic groups which the resonance stabilizer . The advantage of these cyclopolymers hindered amines have a high softening points which could resisted the high temperature although it could enhanced the modified properties of base oil.

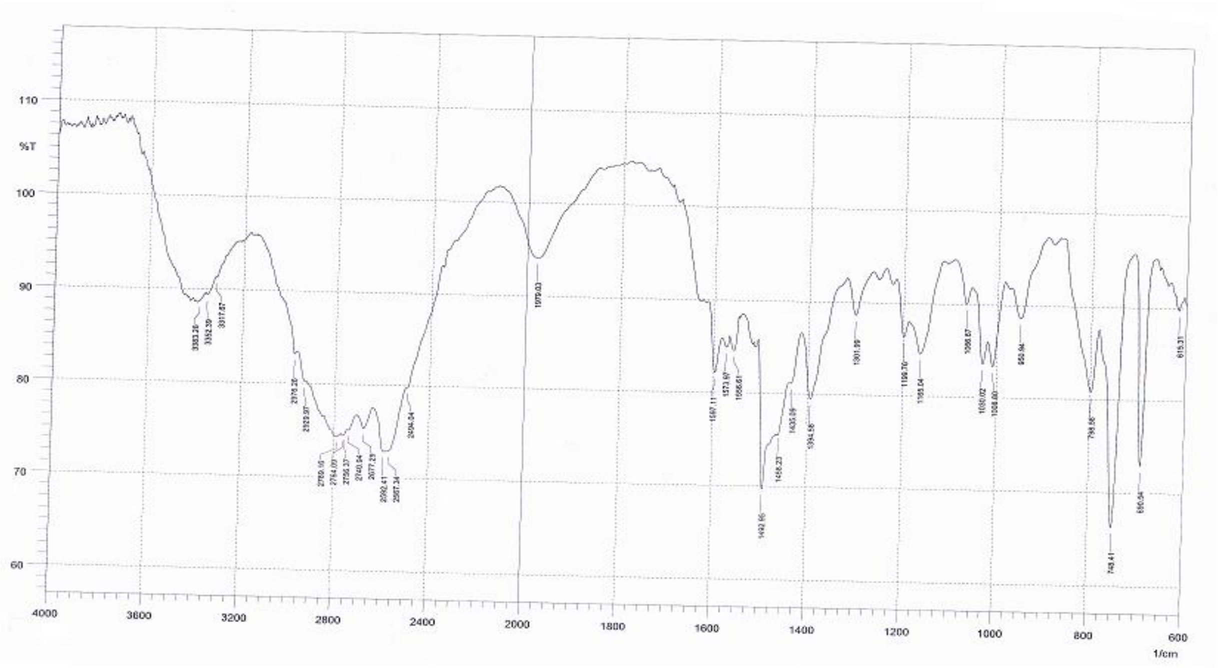


Fig.(1) FTIR spectrum of [A_3]

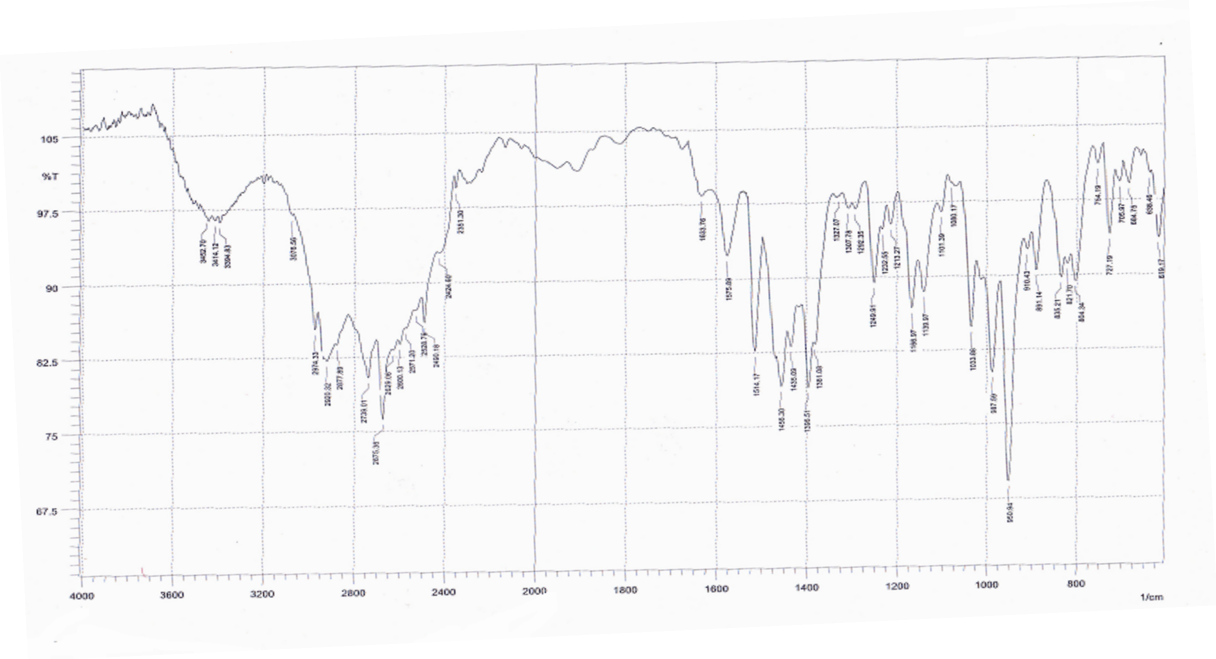


Fig.(2) FTIR spectrum of [A_4]

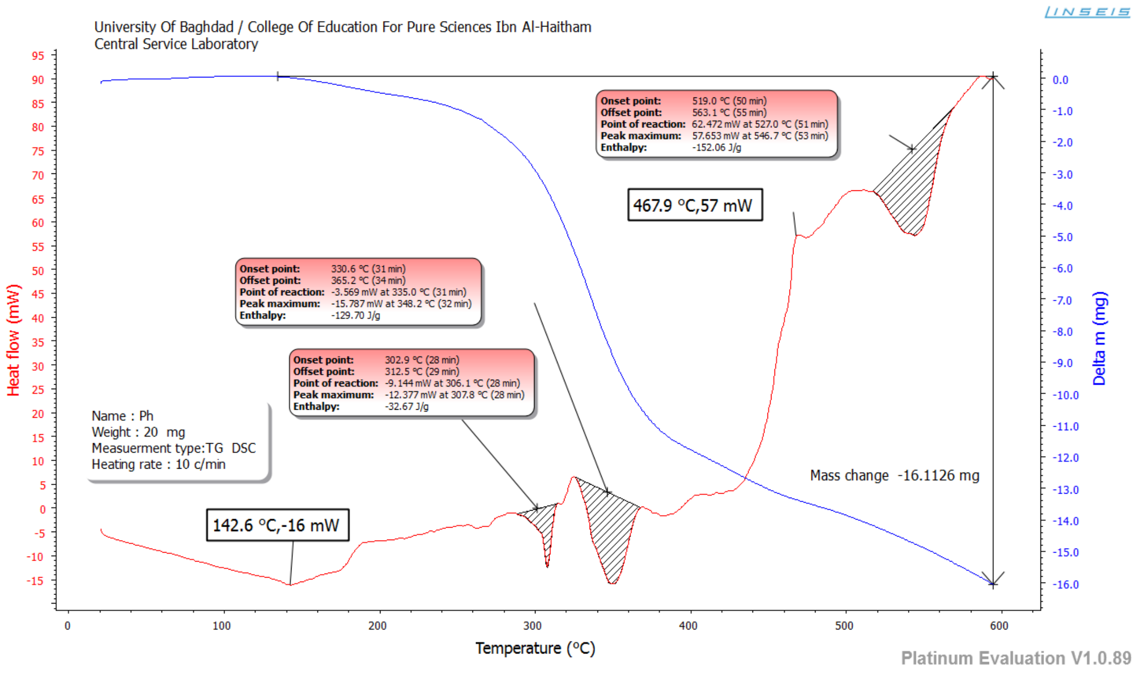


Fig. (3)TG , DSC of [A3]

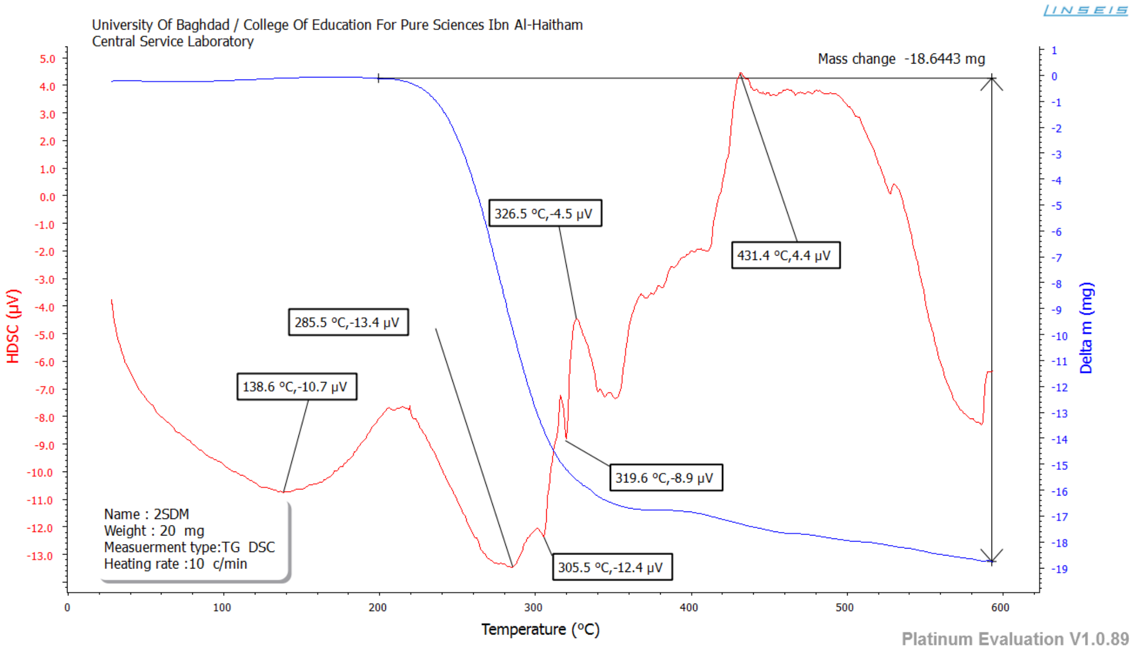


Figure 4- TG , DSC of [A4]

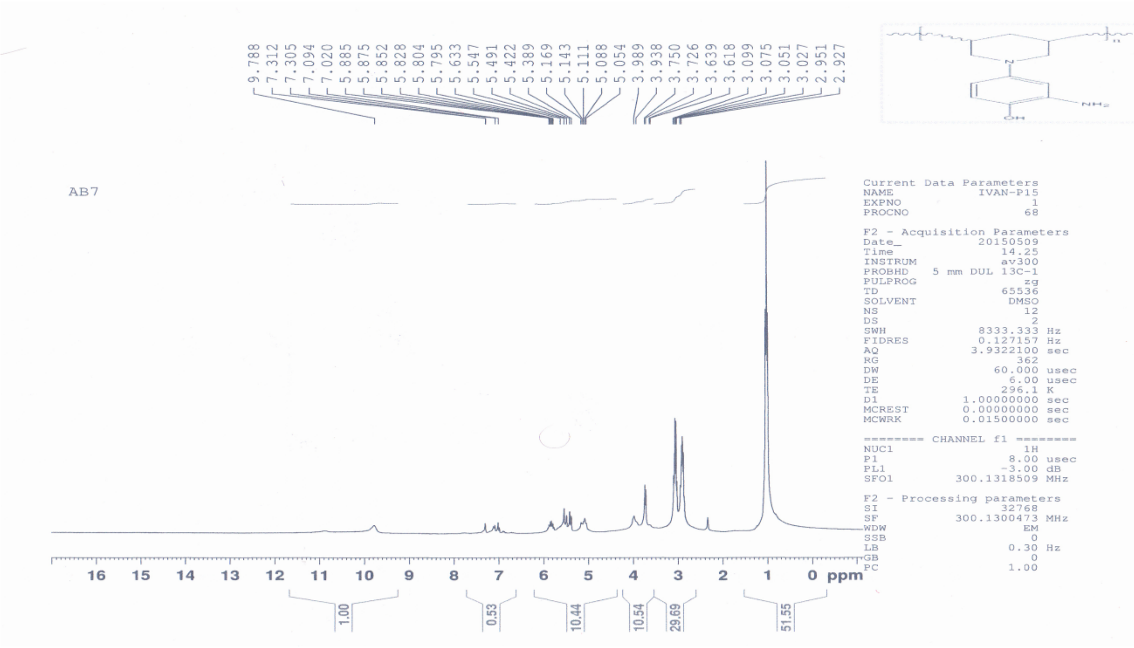


Fig. (5) HNMR spectrum of [A3]

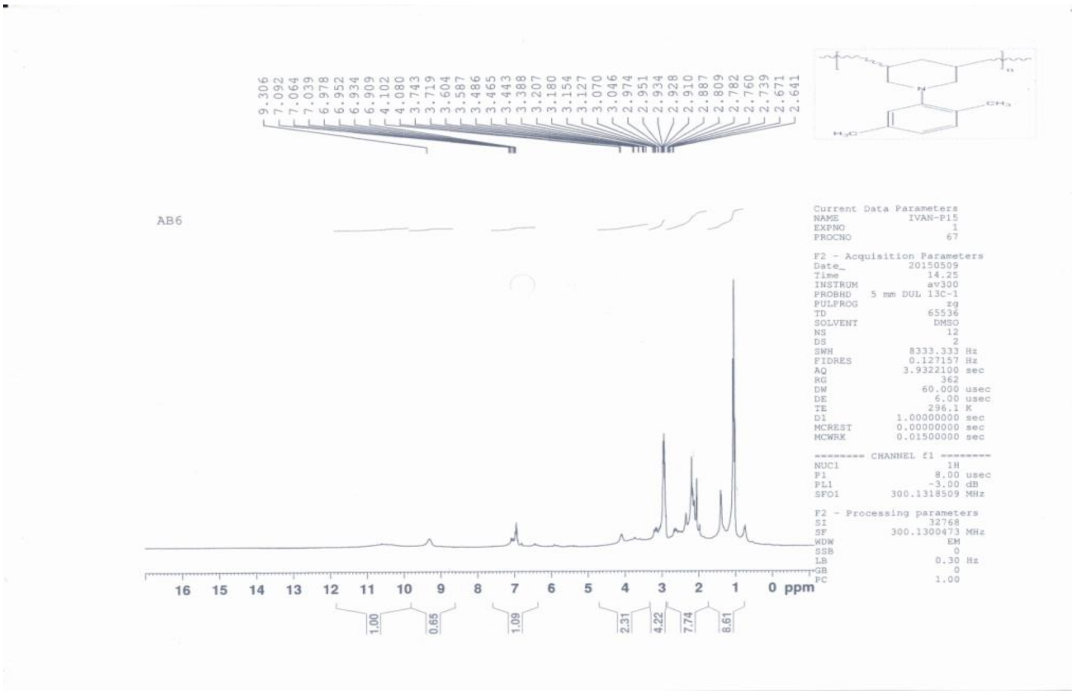


Fig.(6) HNMR spectrum of [A4]

Conclusions

Cyclopolymerization were carried by free radical which exhibited giving six-membered rings and five membered rings through back bone of polymers.

In this research novel N-substituted aryl diallyl amine cyclopolymer [A3] and [A4] were gave a good antioxidant compared with standard sample and blank sample the high effeciency wa s obtained .[A3] cyclo polymer gave higher stability than [A4] , this attributed to the presence of phenolic and hindered amino groups.

These cyclopolymers were acted as hindered amines which have high conjugated systems [A3] and [A4] with other modified properties.

Technical and economic feasibility

Synthesis material (Antioxidants for Lubricant's Oil) alternative for imported and feasible economic.

List of Symbols

Symbols No.	Symbol	The meaning of the symbol
1	[A1]	2-amino-4-(diallylamino)phenol
2	[A2]	N,N-diallyl-2,5-dimethylaniline
3	[A3]	Poly 2-amino-4-(3-methylpiperidin-1-yl)phenol
4	[A4]	N,N-diallyl-2,5-dimethylaniline
5	THF	Tetrahydrofuran
6	TOP	Total oxidant products
7	DSC	Differential scanning calorimetry
8	T G	Thermogravimetric analysis

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