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# Syntheses, Characterization and Study of Use of Manganese (III) Schiff-Base Complex as Thermal Initiation in Radical Polymerization of Styrene

**Ahlam Said Maroof***

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## Abstract

The new schiff base complex: Chloro- (bis (salicylaldehyde) ethylene diiminato) aqua manganese (III) is synthesized and characterized. It is used as thermal initiation in radical polymerization of styrene at 80 c° in dark without inhibition and retardation complication, and the rate of polymerization is directly proportional to the squre root of initiator concentration $[I]^{1/2}$ . gravimetry technique is used for deteremination of the rate polymerization, and viscometery is used for determination of average of polymerization. The uv- visble spectrophotometry is used to determine the rate constant of initiator decomposition ($k_a$). The value of the kinetic parameter ratio $k_p / k_t^{1/2}$ (Where $k_p$ & $k_t$ are the rate constants, propagation and termination respectively).

**Key words:** Thermal Initiation, polystyrene

# تحضير وتشخيص معقد قاعدة شف للمنغنيز الثلاثي ودراسة استخدامه كبادئ حراري في البلمرة الجذرية للستايرين

## الخلاصة

تم تحضير وتشخيص معقد قاعدة شف جديدة كلوروبس ( سالسالديهايد ) اثلين ثنائي امين- مائي منغنيز (III) .تم استخدامه كبادئ حراري في عملية البلمرة الجذرية للستايرين عند درجة حرارة ( 80) م° وفي الظلام بدون حدوث تعقيدات الاعاقة والمنع. ووجد ان معدل سرعة البلمرة يتناسب طرديا" مع الجذر التربيعي لتركيز البادئ $[I]^{1/2}$.تم استخدام الطريقة الوزنية لتعيين معدل سرعة البلمرة ,واستخدمت طريقة مقياس اللزوجة لتعيين معدل درجة البلمرة , في حين استخدمت مطيافية الاشعة فوق البنفسجية – المرئية لتعيين ثابت سرعة تجزئة البادئ ($k_a$) ومن ثم ايجاد قيمة الثابت الحركي $k_p$ / $k_t^{1/2}$ ( حيث ان $k_p$ و $k_t$ هما ثابتا سرعة التكاثر والانتهاء على التوالي) .

## Introduction:-

### Chain reaction:-

Free radical polymerizations are chain reactions. The addition of a monomer molecule to an active chain end regenerates the active site at the chain end. Hence, alarge number of monomer molecules are "consumed" for each active site introduced into the system. In chain reaction polymerization we many recognize four distinet types of processes.

They are (1) :

1- chain initiation---- a process in which highly reactive transient molecules or active centers are formed .

$$Initiator \xrightarrow{kd} 2R^{\cdot}$$

$$R^{\cdot} + M \xrightarrow{ki} R_1^{\cdot}$$

Where $R^{\cdot}$ is an initiator free radical.

M is a molecule of monomer.

Kd & ki is the rate constant of Initiator

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* **Chemical Engineering Department, University of Technology/Baghdad**

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2- chain propagation – the addition of monomer molecules to the active chain end, accompanied by regeneration of the terminal active site.

$$R_1^{\cdot} + M \longrightarrow R_2^{\cdot}$$

$$R_n^{\cdot} + M \xrightarrow{kp} R_{n+1}^{\cdot}$$

Where R·n is the propagation free radical with a degree of polymerization n

Kp is the rate constant for propagation.

3- Chain transfer ---- involving the transfer of the active site to another molecule (e.g., monomer) the molecule that has lost the active site is now “dead” from a chain- propagation point of view. The molecule that has accepted the active site can start a new chain.

$$R_n^{\cdot} + YZ \longrightarrow R_n Y + Z^{\cdot}$$

Where YZ is a chain transfer agent that may be solvent, monomer, initiator or polymer molecules.

4- Chain termination ---- a reaction in wich the active chain centers are destroyed.

$$R_n^{\cdot} + R_m^{\cdot} \xrightarrow{kt} P_{n+m}$$

$$R{\cdot}n + R{\cdot}m \xrightarrow{kt} Pn + Pm$$

Where Pn is the final inactive polymer.

$K_t$ is the rate constant for termination.

Numerous substance decompose to free radicals when heated. If the decomposition temperature corresponds to a convenient temperature range for polymerization. The substance may be useful as an initiator In fact, it is dependence of the initiator decomposion rate on the temperature which determines the usfulness of the compound as an initiator. Such thermal decompositions usually yield two free radicals from on initiator molecule by first –order reaction process (2).

The ability of certain metal chlates to produce free – radicals when heated was first pointed out by Arnet and Mendelsohn (3) in the course of investigations on the oxidation of these compounds thus, in the case of ferric acetyl acetonate they postulated the following reaction :-

$$Fe^{+3}\ (acac)_3 \xrightarrow{\Delta} Fe^{+2}(\ acac)_2 + acac\cdot$$

Several trasition metal acetylacetonate complexes were tested as thermal initiators of the polymerization of styrene at 110 c◦ (4) , the following order of reactivity emerged:-

MnIII > CeIV > CoIII>FeIII> AlIII = crIII = sty. > VIII

$Mn^{III}$ ( acac)$^3$ was the most effective initiator while VIII $(acac)_3$ acted as inhibitor of styrene polymerization.

Bamford and Lind (5) have studied in detail the mechanism of thermal initiation of styrene, MMA and acrylonitrile (AN) by $Mn^{III}$ $(acac)_3$ and Mn III ( $facac)_3$ complexes. It was found that initiation by $Mn^{III}$ $(facac)_3$ is monomer selective. This chelate is much more effective than Mn III $(acac)_3$ in initiating polymerization of MMA an AN in temperature range 60-80 c◦ .but is relatively inactive towards vinyl acetate and quite inactive towards styrene, and the following reaction was proposed :-

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$$M_n^{III}(\text{facac})_3 \xrightarrow[CH_2=CHX]{M} M_n^{II}(\text{facac})_2$$

$$+\text{facac}-CH_2=C^{\cdot}HX$$

Saleh and Aliwi(6) studied the thermal polymerization of styrene by anoval type of metal chelate complex: chloro-oxo-bis[N-(4-bromophenyl) saliylide-neiminate ] vanadium(v)=
VD( $BrC_6H_4NCHOC_6H_4Cl)_2$ Cl
AliWi and Al-Hayali (7) studied the thermal polymerization of MMA by Manganese III dithio carbomate complex also the thermal polymerization of the same initiator in presence of electron doner was studied (8) Siemeling and co-workers investigated two different types of imido and phosphonate ligand used for copolymerization of MMA , and vinyl actates AV (9) on other hand Manmeekcawr and sirvastava studied the thermal polymerization of MMA by certain trastion metal chelates (10) Recently Saleh studied the thermal polymerization of MMA at 80 c◦ by methoxy oxo-bis [N-(4-( bromo phenyl)salicylideneiminato] vanadium(v).
vo($Brc_6H_4N$:$CHOC_6H_4)_2OCH_3$ (11) .
In this work the complex chloro-(bis(salicyladehyde)ethylene diiminato) aqua manganese (III).
Was prepared and used for the first time as athermal initiator for the polymerization of styrene at 80 c◦.

**Experimental :**

1-Materials :
Styeren monomer ( Fluka.A.G.).
Ethylene diamine ( Riedel dehaen).
Salieyladehyde ( Fluka.A.G.).
Analar ethanol (B.D.H.LTd).
Manganese chloride (Fluka.A.C.)
Hydrogen peroxide (B.D.H.LTd).

2- Synthesis of the materials:

1. Schifft base:- N,N bis (Salcyliden) ethylene diamine prepared as described by marzilli and co-workers (12) method, 0.05 mole of salicylaldehyde was mixed with 0.025 mole of ethylene diamine [ using ethanol as a solvent]. The mixture was reflexed with stirring for one houre .yellow precipitate was formed.it was filtered and recrystallized from ethanol. The product was dried at room temperature under reduced pressure stored in a desicator.
M.P. = 126-128 C◦

2. Schifft Complex:
Chloro-c bis (Salicylaldehyde) ethylene diiminato aqua manganese (III) was prepared as described by Fabratti and Co-workers (13) methode, 5 ml of
30% hydrogen peroxide was added to ( 0.01 mole of Mncl2 .6H2o . The solution mixture is added drowis with continuous stirring to ethanoic solution containing 0.01 mol of N,N bis ( Salcyliden ) ethylene diamine ligand at room temperature.
Brown precipitate was formed. It was filtered and dried at room temperature under reduced pressure stored in adesicator.
M.P. = 270-272 c◦ .

3. Purification of styrene:
Styrene was washed three times with soduim hydroxide (10% w/v) to remove p-t-Butyl-cate-chol inhibitor. Traces of NaoH was removed

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by repeated washing with distilled, then the monomer was dried over calcium hydride for 24 hours. The styrene was filtered and fractionlly distilled under reduced pressure (60 mm/Hg at 50 c◦). Styrene was stored under argon in the refrigerator at -188 c◦ .

**Techniques:**

1- Determination of the rate of polymerization:

A polymerization process was carried out in apyrex tube 15 cm in length, 1.5 cm in diameter, and 10 cm3 capacity connected to an argon gas puring system. Dissolved air was removed by bubbling (32). Styrene saturated argon gas (Puring 99.96%) for 10 minutes. The reaction tube was protected from light using aluminum foil and placed in a bath at 80 c◦ ± 1 c◦ [ General purpose stirred thermostatic baths/ circulators-Grant-GA 100,GD 100, GD120).

Average rate of polymerization were measured gravimetrically by precipitation of the polymer in pure ethanol and the rate of polymerization was calculated as follow (14).

$$R = \frac{d[m]}{dt} = \frac{[m]}{100} * \frac{\%conv.}{t} --1$$

where [m]= is the initial monomer concentration.

% conv.= is the percentage of conversion of monomer to polymer.

t= time of reaction in second.

2- viscometery:

The namber average molecular weight of polymer (poly styrene) was generally determined viscometrically in benzene at 30 c◦ with aid of Mar-Houwink equation(15).

$$|h| = k * \bar{M}_n^{\,a} ---2$$

$|h|$ is the intrinsic viscosity and α and k are constant for a given polymer–solvent system at particular temperature. For poly Styrene $^{(16)}$.

$$|h| = 2.0 * 10^{-5} * \bar{M}_n^{\,0.74} ---3$$

The intrinsic viscosity of polymer solution was measured with an ostwald-u-tube viscometer.

Solution were made by dissolving the polymer in a solvent (penzene) in (gm/100ml) and the flow times of polymer solution and pure solvent are t and t0 respectively.

$$h_{sp} = \frac{t - t_0}{t_0} ---4$$

$h_{sp}$ = specific viscosity

Plotting of $h_{sp}$/c versus concentration the intercept of line gives the intrinsic viscosity at finite dilution (16) (i.e $c \longrightarrow 0$ ).

$$\frac{h_{sp}}{c} = |h| + k\,|h|^2 c\,\mathbf{L}\,\mathbf{L}\,5$$

c= concentration of polymer solution in g.dl$^{-1}$.

3- Changes in the Absorption spectra during photochemical reaction:-

The photo composition of the initiator at 355 nn ( at 25 c◦ ) was followed with the aid of Hitachi-u-2000 double beam spectro-photometer using the quartz uv-cell of 10 mm path length the shown in Fig.(9).

The change in absorbance was measured for different irradiation times at a different wave lengths. In order to study the kinetics of photodecay of the initiator in certain monomer for measurements of the absorbance at infinite irradiation time ($A\infty$ ), the solution was given prolonged irradiation for at least 10 half lives of the rate of inihiator (about 6 hours).

In order to calculate the specific rate constant of the decomposition of the initiator (ka) the following equation was used (31) .

$Ln\ (a-x) = Ln\ a-kat$ ---6

Where:

a= concentration of initiator before irradiation.

x= the concentration of inititor after irradiation.

t= time of irradiation of initiator solution.

$A_{\circ}$= Absorbance of initiator before irradiation.

$a-x= At-A\infty$ ---7

$Ln(At-A\infty) = Ln(A_{\circ}-A\infty)-kat$---8

Thus aplot of Ln IAt-A∞I with versus variety irradiation time (t) gives astriaight line with slope equal to ka($s^{-1}$).

4- InFra- Red Spectroscopy:-

Aye unicam SP3-100 infra-red spectrophotometer was used to record IR spectra between 4000-200 $cm^{-1}$ using cesium iodide disc technique.

5-Molar conductivity measure-ement Copenhagen-CDM83 was used.

6- Flam atomic absorption appar-atus shimadzu-760G was used.

7- Ion selective electrode orian/ metohm-686-Titroprocessor was used.

**Results and Discussion:-**

1- Characterization:

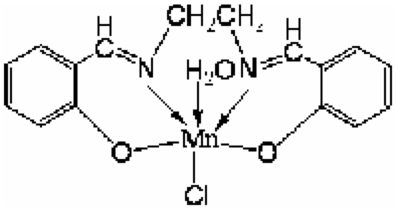
The ligand and its complex ws characterized by IR spectroscopy, molar conductivity measurement, flame atomic absorption apparatus and Ion selective electrode all characterization data in Table(1),(2),(3) and figure (1).

In the IR spectra of the free ligand and it’s complex rc=N shifted to a lower wave number by ca.15 cm-1 upon coordination. In addition, the disappearance of the OH band of the free ligand in the Maganese (III) complex indicates that the OH group has become deprotonated and bonded to the metal ion as-0(17-18),Anew bands appear at 462.9, 441.7, 351 and 505.3 wich cold be attributed to the M-O19, M-N20 , M-Cl21,M-H2O.

Fig.(1) shows the relation between the molar conductivity (AM) ($cm^2.ohm^{-1}.mol^{-1}$) and the square root of the Schiff base complex concentration not line.it indicates that the chelate complex weak electrolet in solution so the chlor atom inner sphere coordinate (33).

On the basis of these result it can concluded that in the complex the Schiff base is coordinated to manganese atom as hexadente.

Therefore we suggest that the structure of complex.



2- kinetics of Thermal initi-ation:

the complex chloro[bis(salic-yaldehyde) ethylene-diiminato] aqua manganese (III) was used as initiator it was readily initiate the polymerization of styrene at 80c°.

The rate of polymerization of about $0.7*10^{-6}$ $mol.\ l^{-1}\cdot s^{-1}$ for styrene in the absence of the chelate complex. Figure(2) shows that the average rate polymerization was estimate from eq.(1), proportional to the square root of the chelate concentration at constant monomer conc. (8.7 $mol.l^{-1}$) and temperature, the straight line in fig(2) corresponds to the relation(9)(31).

$$w = \frac{k_p}{k_t^{1/2}}[m][I]^{1/2} - - - 9$$

it was found

$$w = 0.3\times10^{-2}[I]^{1/2} - - - 10$$

from fig.(2), relation (10) and fig.(3) the striate lines pass through the origin which indicate the polymerization process in this system is simple and does not involve inhibition or retardation or any other comp-lected side reactions(22)(23).

The slope of the logarithmic plot of the relation between rate of polymerization and initiator conc.(fig.4) is found *0.5* this confirms the free radical nature of the present initiating system (23).

The kinetic parameter ratio $kp/kt^{1/2}$ was determined using the relation (9).the result in the table (2).the mean value of $kp/kt^{1/2}$ in table (2) equals to $3.9*10^{-4}$ $mol^{-1/2}.\ l^{3/2}.s^{-1/2}$ and is good agreement with the literature value of unretarded free radical polymerization styrene (24,25, 26).

The value of $kp/kt^{1/2}$ is characteristic for a given monomer at certain temp. and it does not depend on the type of initiator or mechanism of initiation. From the value of $kp/kt^{1/2}$ one can know whether the polymerization. Involves some complications, such as inhabitation, retardation….etc (32).

(fig.5) is the relation between the specific viscosity to the conc. Of polymer solution in gm/.dl plotting of ήsp/c and conc. By applying equations(5), (3) was used to determine the molecular weight of polymer(27).

It was found $3*10^{6}\ mol.gm^{-1}$.

Measurement of the number average degree of poly. $\bar{Dp}$ of polystyrene was found $\bar{Dp}$ =3*10 from the relation(11) (27) .

$$\bar{Dp} = \frac{\bar{m}_n\ of\ \ polymer}{m.wt\ \ of\ \ monomer} - - - 11$$

3- UV-Visble absorption:

The uv-visble absorption spectrum of manganese chelate in ethanol sol-ution and the manganese chelate in styrene-ethanol solution and styrene spectrum are shown in (fig6,.7,8)respetively.

The absorption between (400-600)nm is broad and low intensity may be attributed to d-d electron transition [ligand field transition],the absorption range between (*300-400)nm* which present charge transfer transition were due to electron transition between molecular orbitals located near the metal and the molecular orbital located near the ligand inrespect to that the oxidation state of Mn(III) (28)(29).

The absorption range between (280-350)nm represent ligand spectra which occur as a result of electron transition between the ligand molecular orbital ($\Pi \rightarrow \Pi^*$) & ($n \rightarrow \Pi^*$) (30).

On heating of the initiator solution in styrene at 80 c◦ the absorption spectrum changes as shown in (fig.9) and ultimately becomes indisting-uishable from that of manganese chelate in styrene (fig.7).

The isosebestic points appeared at 355nm indicate that the overall chemical changes are relatively simple it is also noticed that ther is alittle increase in the absorption intensity in the range between (300-600) nm during the heating process. This very broad low intensity peaks may be attributed to d-d electronic transitions for Mn(III) complex.

The decomposition of Mn(III) complex in styrene and ethanol mixture during heating at 80 c◦ has been monitored spectrophotometrically, aseries of wavelength 355 nm has been selected for this purpose.the value of (At-A∞) decreases exponentially with the reaction time corresponding to the first order (31) chelate decomposition and consisten values for the first order rate constant (ka) were obtained.(fig.10) shows the variation of ln(At-A∞) of manganese chelate in styrene solution with time of heating at 80 c◦ and ka found $4.5\times10^{-2}$ $s^{-1}$ when the concentration of initiator was $2.6\times10^{-4}$ $mol.l^{-1}$ .the rate of thermal decomposition of chelate manganese was found $1.2\times10^{-5} mol.l^{-1}.s^{-1}$ according to the equation(12):

$$\frac{dc}{dt} = n \times k_a [I] ---12$$

When: n=1 [first order]

fig.(11) reaction scheme might be suggested for the generation of the initiating chelate manganese (III) in styrene solution during heating at *80c◦*.

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**Table (1) characterization data for free Schiff base and it's complex Mn(III).**
**IR data ( cm-1)**

| *Group* | *Free ligand* | *Complex* |
|---|---|---|
| rc=N | 1635 | 1620.1 |
| BOH | 1207 | - |
| rc-o | 1245 | 1296 |
| rc=c | 1610.5 | 1542.9 |
| rc=c | 1498 | 14504 |
| rc=c | 1577 | 1404.1 |
| BCH | 1417 | 1444.6 |
| BCH2 | 1286 | 1155.3 |
| M-O | - | 462.9 |
| M-N | - | 441.7 |
| M-Cl | - | 451.0 |
| M-H2O | - | 505.3 |

**Table (2) Analyses of complex Mn(III)**

| *Matel* | *%* |
|---|---|
| Mn (III) | % 11.9 |
| Cl | % 7.3 |

**Table(3): date of rates polymerization, concentration initiator co% and rate contants at 80 c◦ & [8.7] mol.l-1 monomer.**

| *Co%* | $R \times 10^{-5}$ $mol.l^{-1}.s^{-1}$ | $[I] \times 10^{-5}$ $mol.l^{-1}$ | $kp/kt^{1/2} \times 10^{-4}$ $(mol^{-1/2}.\ l^{3/2}\ .\ s^{-1/2}$ |
|---|---|---|---|
| 0.39 | 0.95 | 1 | 3.41 |
| 0.57 | 1.38 | 2.1 | 3.44 |
| 0.60 | 1.65 | 3.2 | 3.38 |
| 0.80 | 1.95 | 4.2 | 3.34 |
| 0.89 | 2.15 | 5.3 | 3.38 |

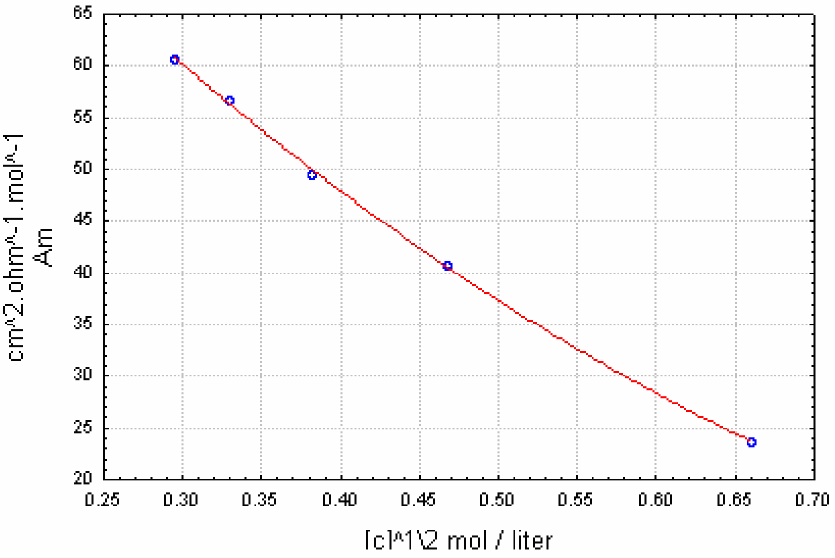

Figure (1) Relation between molar conductivity and sequare molar conductivity (A) a
square root of concetration [c]^1\2

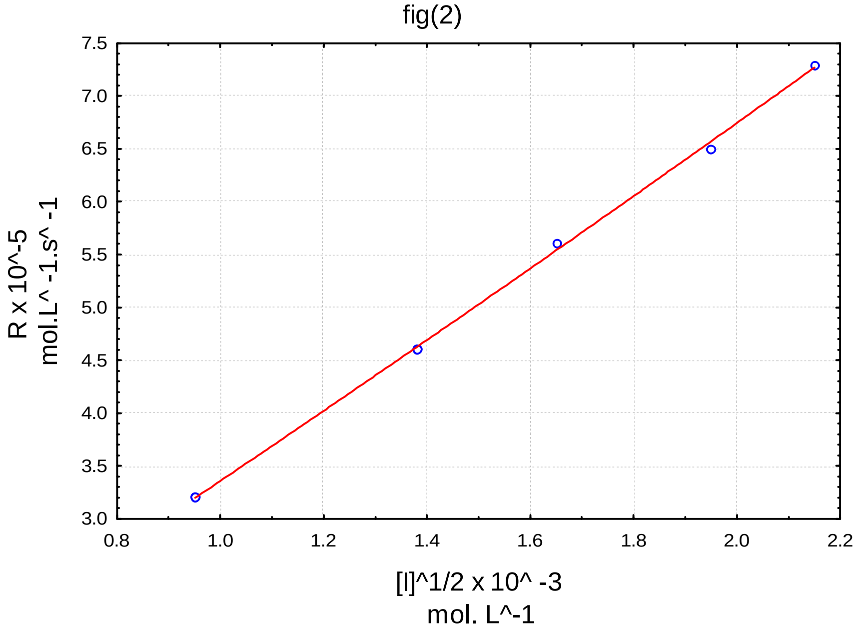

Figure (2) Relation between rate Polymerization and square root of the chelate con. at constant monomer con.

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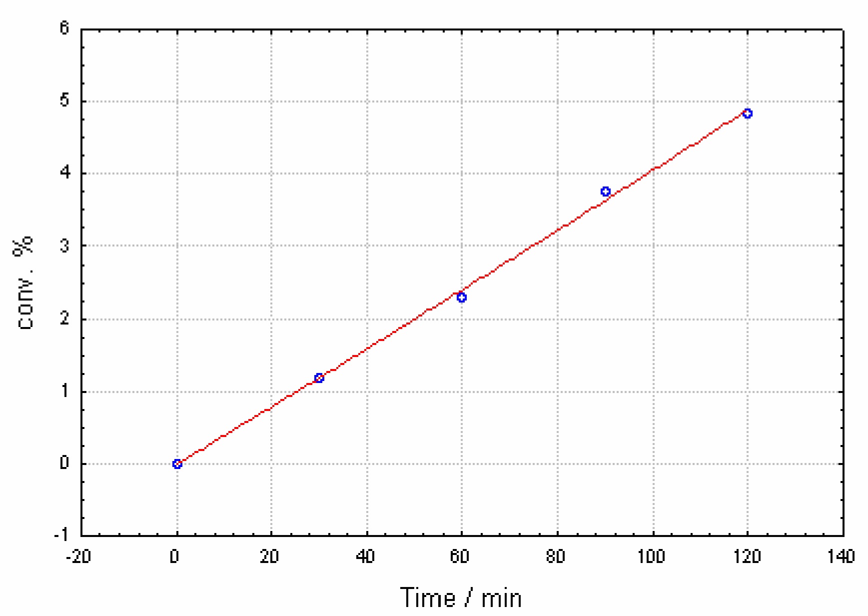

fig.(3) Relation between conversion percentage. And Time

fig(4)

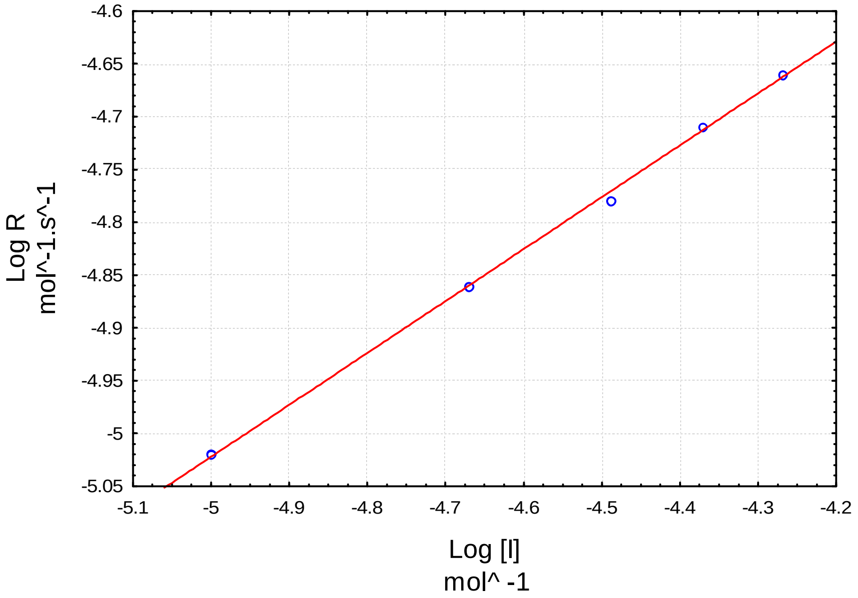

Figure (4) Relation between logarithmic rate of polymerization at 80C$^{o}$ logarithmic initiator con.

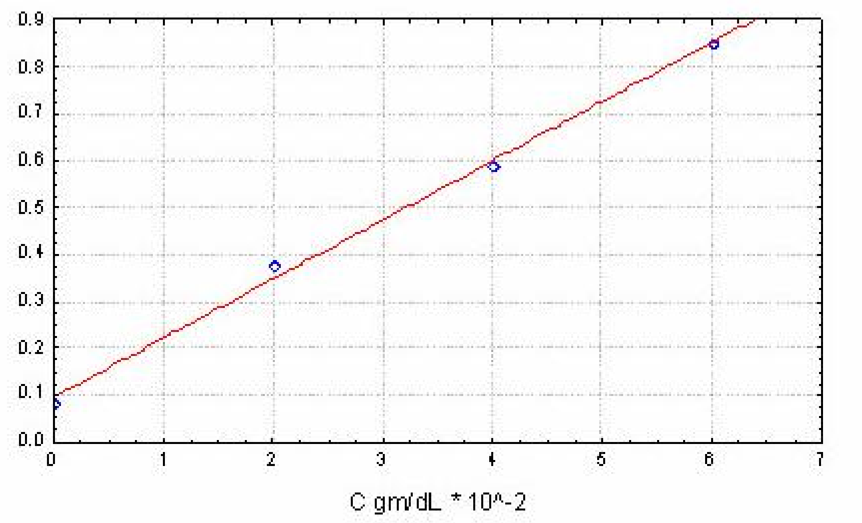

FIG (5) Relation between the intrinsic Viscosity to the Conc. of poymer Sol. And Conc. of polymer in gm.dL^-1

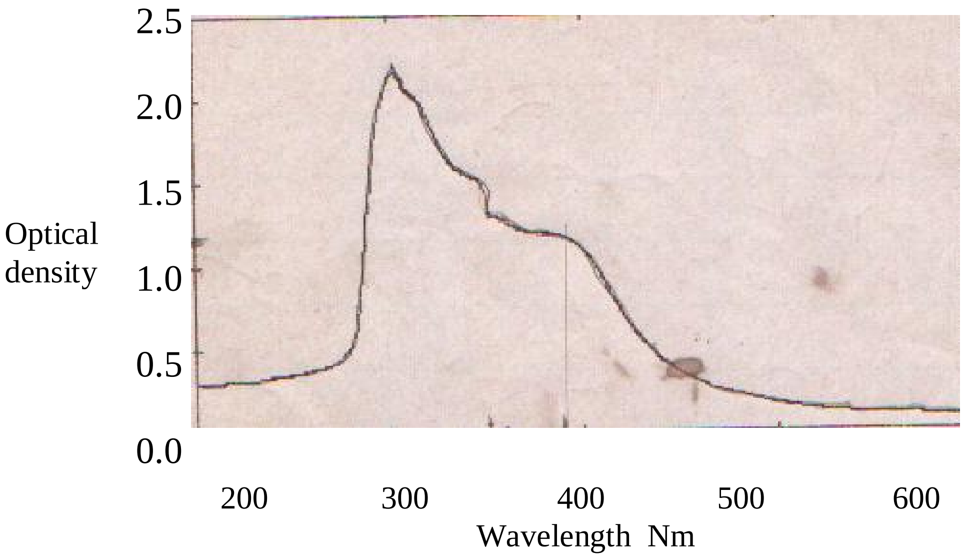

Figure (6 ) uv-visble absorption spectrum of manganese chelate in styrene

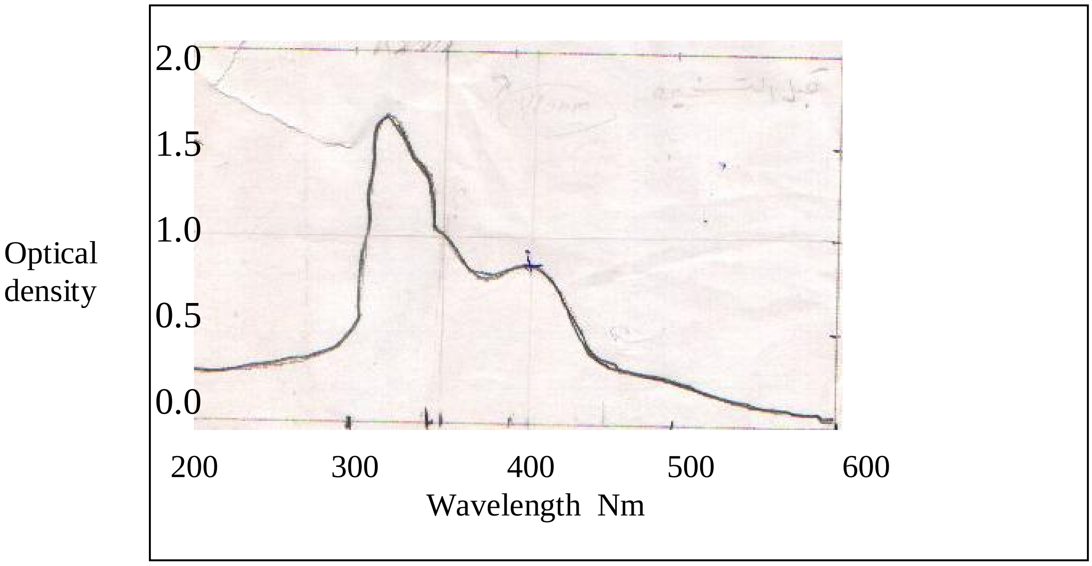

fig.(7): Fig. (6 ) uv-visble absorption spectrum of manganese chelate in styrene

Figure (8): uv-visble absorption spectrum of bulk

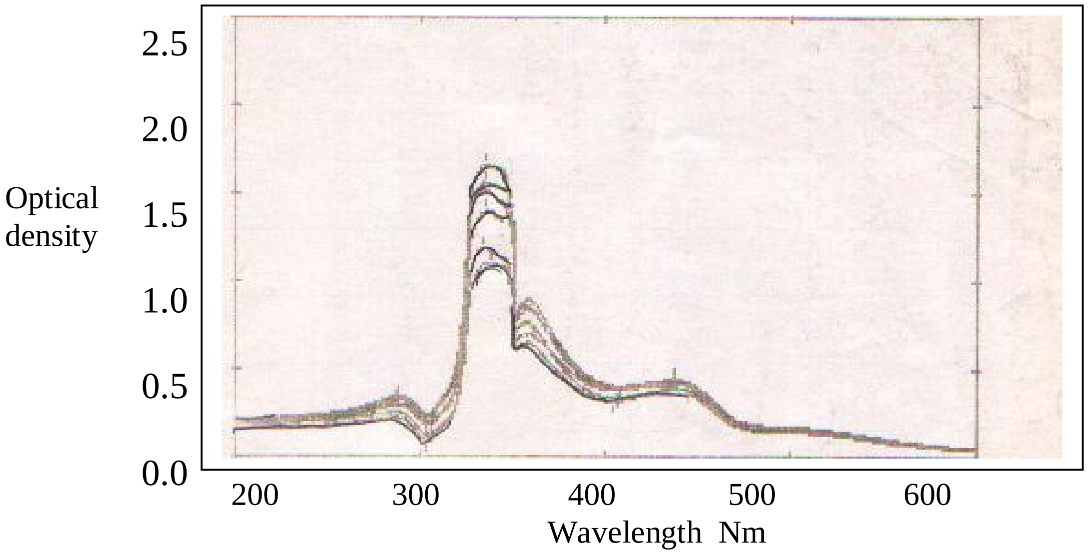

Figure ( 9): uv-visble spectrum of manganese chelate in styrene changes with time of irradiation at λ = 355nm

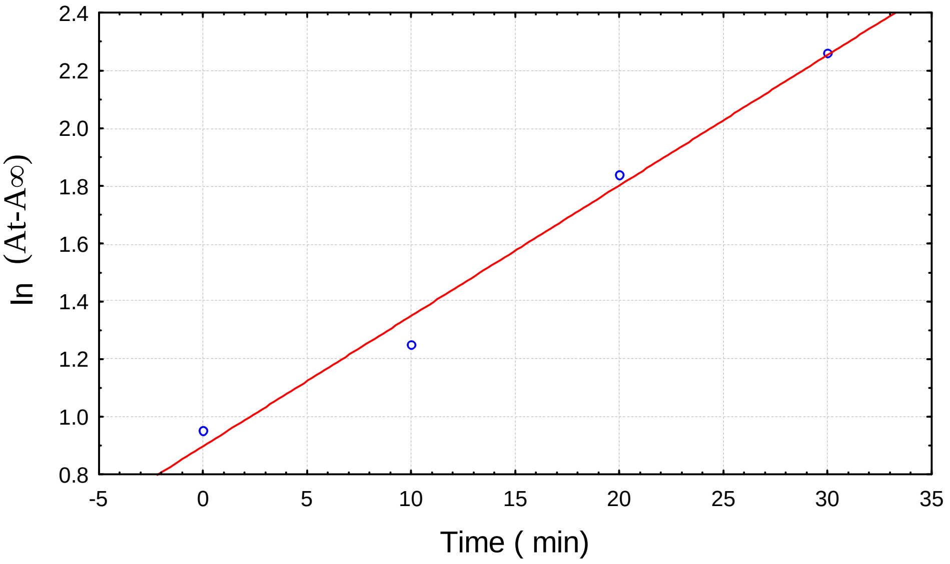

Figure ( 10) rariation of optical density at λ = 355 nm with time of irradiation

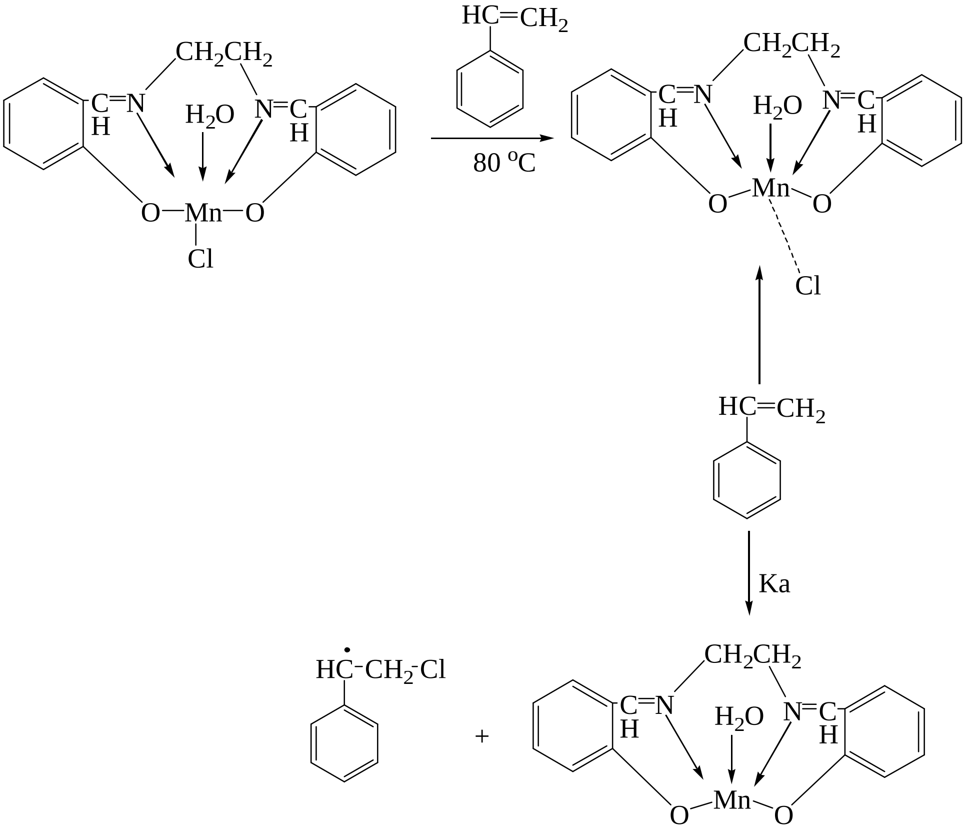

Fig.(11) reaction scheme might be suggested for the generation of the initiating chelate manganese (III) in styrene solution during heating at 80 c◦.

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*** Chemical Engineering Department, University of Technology/Baghdad**