

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

Ahlam Said Maroof*

Received on: 23/4/2008

Accepted on:31/12/2008

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 square root of initiator concentration $[I]^{1/2}$. Gravimetry technique is used for determination of the rate of polymerization, and viscometry is used for determination of average of polymerization. The uv- visible spectrophotometry is used to determine the rate constant of initiator decomposition (k_d). 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 (سالساليدهايد) 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 طردياً 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_d) ومن ثم ايجاد قيمة الثابت الحركي $k_p / k_t^{1/2}$ (حيث ان k_p و k_t هما ثابتا سرعة التكاثر والانهاء على التوالي).

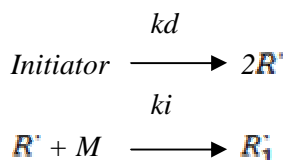
Introduction:-

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, a large number of monomer molecules are "consumed" for each active site introduced into the system. In chain reaction polymerization we may recognize four distinct types of processes.

They are (1) :

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

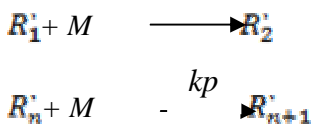


Where R^* is an initiator free radical.

M is a molecule of monomer.

k_d & k_i is the rate constant of Initiator

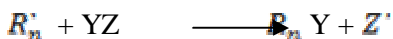
2- chain propagation – the addition of monomer molecules to the active chain end, accompanied by regeneration of the terminal active site.



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

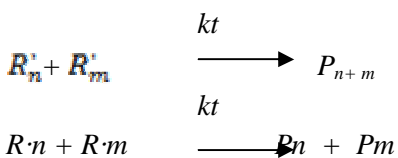
K_p is the rate constant for propagation.

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.



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

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



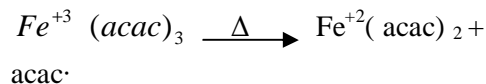
Where P_n is the final inactive polymer.

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 decomposition rate on the temperature which determines the usefulness of the compound as an initiator. Such thermal decompositions usually yield two free radicals from one initiator molecule by first –order reaction process (2).

The ability of certain metal chelates 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 :-

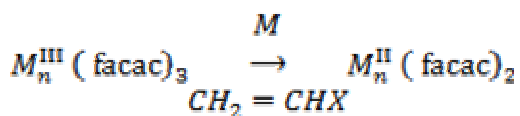


Several transition metal acetylacetonate complexes were tested as thermal initiators of the polymerization of styrene at 110 c° (4) , the following order of reactivity emerged:-

$Mn^{III} > Ce^{IV} > Co^{III} > Fe^{III} > Al^{III} = Cr^{III} = sty. > VIII$

$Mn^{III} (acac)_3$ 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 and 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 :-



Saleh and Aliwi(6) studied the thermal polymerization of styrene by anoval type of metal chelate complex: chloro-oxo-bis[N-(4-bromophenyl) saliylideneimine] vanadium(v)= VD(BrC₆H₄NCHOC₆H₄Cl)₂ Cl

AliWi and Al-Hayali (7) studied the thermal polymerization of MMA by Manganese III dithio carbamate 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(Brc₆H₄N:CHOC₆H₄)₂OCH₃ (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 :

Styrenen 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 hour .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

by repeated washing with distilled, then the monomer was dried over calcium hydride for 24 hours. The styrene was filtered and fractionally 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 purging 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).

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

where [m]= is the initial monomer concentration.

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

t= time of reaction in second.

2- viscometry:

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

$$|\eta| = k * M_n^{-\alpha} \quad \text{--- 2}$$

|\eta| is the intrinsic viscosity and \alpha and k are constant for a given polymer-solvent system at particular temperature. For poly Styrene⁽¹⁶⁾.

$$|\eta| = 2.0 * 10^{-5} * M_n^{0.74} \quad \text{--- 3}$$

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.

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

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 → 0).

$$\frac{h_{sp}}{c} = |\eta| + k |\eta|^2 c \quad \text{--- 5}$$

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 nm (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_{∞}), the solution was given prolonged irradiation for at least 10 half lives of the rate of initiator (about 6 hours).

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

$$\ln(a-x) = \ln a - k_a t \quad \text{---6}$$

Where:

a = concentration of initiator before irradiation.

x = the concentration of initiator after irradiation.

t = time of irradiation of initiator solution.

A_{∞} = Absorbance of initiator before irradiation.

$$a-x = A_t - A_{\infty} \quad \text{---7}$$

$$\ln(A_t - A_{\infty}) = \ln(A_{\infty} - A_{\infty}) - k_a t \quad \text{---8}$$

Thus a plot of $\ln(A_t - A_{\infty})$ with versus variety irradiation time (t) gives a straight line with slope equal to $k_a(a - 1)$.

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 measurement Copenhagen-CDM83 was used.

6- Flame atomic absorption apparatus shimadzu-760G was used.

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

Results and Discussion:-

1- Characterization:

The ligand and its complex was characterized by IR spectroscopy, molar

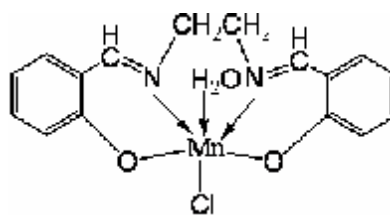
conductivity measurement, flame atomic absorption apparatus and Ion selective electrode all characterization data in Table(1),(2),(3) and figure (1).

In the IR spectra of the free ligand and its complex $\nu_{\text{C=N}}$ 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 Manganese (III) complex indicates that the OH group has become deprotonated and bonded to the metal ion as $\nu_{\text{O(17-18)}}$, New bands appeared at 462.9, 441.7, 351 and 505.3 cm^{-1} which could be attributed to the M-O(19), M-N(20), M-Cl(21), M-H₂O.

Fig.(1) shows the relation between the molar conductivity (Λ_m) ($\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-1}$) and the square root of the Schiff base complex concentration not linear. It indicates that the chelate complex weak electrolyte in solution so the chloro atom inner sphere coordinate⁽³³⁾.

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

Therefore we suggest that the structure of complex.



2- kinetics of Thermal initiation: the complex chloro[bis(salicylaldehyde) ethylene-diiminato] aqua manganese (III) was used as initiator it

was readily initiate the polymerization of styrene at 80°C.

The rate of polymerization of about $0.7 \times 10^{-6} \text{ mol. l}^{-1} \text{ s}^{-1}$ 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⁾.

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

it was found

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

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

The value of $k_p/k_t^{1/2}$ 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 $k_p/k_t^{1/2}$ 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 η_{sp}/c and conc. By applying equations(5), (3) was used to determine the molecular weight of polymer(27).

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

Measurement of the number average

degree of poly. \bar{Dp} of polystyrene was

found $\bar{Dp} = 3 \times 10$

from the relation(11) (27) .

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

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)respectively.

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 indistinguishable 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 there is a little 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, a series of wavelength 355 nm has been selected for this purpose. The value of $(A_t - A_\infty)$ decreases exponentially with the reaction time corresponding to the first order (31) chelate decomposition and consistent values for the first order rate constant (k_a) were obtained. (fig.10) shows the variation of $\ln(A_t - A_\infty)$ of manganese chelate in styrene solution with time of heating at 80 °C and k_a found $4.5 \times 10^{-2} \text{ s}^{-1}$ when the concentration of initiator was $2.6 \times 10^{-4} \text{ mol.l}^{-1}$. The rate of thermal decomposition of chelate manganese was found $1.2 \times 10^{-5} \text{ mol.l}^{-1} \cdot \text{s}^{-1}$ according to the equation(12):

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

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 80°C.

Reference:

- [1] MOSD, G., and Solomon, D.H., The chemistry of free Radical Polymerization, Oxford (U.K.) and Rarr-ytown, N.Y., Pergamon, 1995.
- [2] KUBISA, P., "Radical Polymerization with Reversible Deactivation of active Species", Polymery, 2000, 45(11-12).
- [3] E.M. Arnett and M.A. Mendelson, J. Amer. chem. Soc. 1962, 84, (3821).
- [4] R. G. Charles and M. A. Pawlikowski, J. Phys. Chem. 1958, 62, (440).
- [5] C. H. Bamford and D.J. Lind, Proc. Roy. Soc., A. 1968, 302, (154).
- [6] Saleh, N.J., and Aliwi, S. M. , Eng. , and Tech., No.3 1998, 17, (283).
- [7] Al-Hayali, A. H. , M. Sc. Thesis, Mustansiriah University, Baghdad 1999.
- [8] Aliwi, S. M. and Al-Hayali, A.H., Al-Mastansir-iah J.of Sci., Vol. 11, No. 87, 2000.
- [9] Siemeling, u., Kolling, L., Kuhnert, O. Neumann, B., Stammler, A., Stammler, H., G., Stammler, G., Fing, Kaminsk E. Kiefer, A, R. R. ZAAC, Vol.629, ISSUE 2002, (781-792).
- [10] Manmeekur, M and Sirrastara, A. K., J. of macromolecule Sci. Part-c polyreview, vol.42, No.4, 2002, (481-512).
- [11] Saleh, N. J., Eng. And Tech., vol.23 No. 5(2004), 198.
- [12] L. G. Marzilli, P. A. Marzilli and J. Amer. Chem. Soc. 1971, (93), 1374.

- [13]A. C. Faberetti, F. Forghier and C. Preti, *Inorge. Chem.. Ata*, 1984, (86), 127.
- [14]Semour, R. B., and Carraher, C.E., *Polymer chemistry*, 2nd ed. New York Dekker. 1998 chaps. 9.
- [15]Billmyer, F. W., JR, *Text-book of polymer Science*, 3rd. New York: Wiley. 1984 chaps.1,8.
- [16]E.A. Collins "Experimental in polymer science", John wiley and sons, New York 1973.
- [17]Nishinaga, A., Tsutsui, T., Moriyama, H.; Wazaki, T.; Mashino, T.; Fujii, Y.J. *Mol. Catal.* 1993.83,117.
- [18]Kervnen, K.; Lahtineu, P., Repo, T.; Svahn, M.; Leskela, M. *catal. Tody* 2002,75,183.
- [19]K.N. Thimmaiah, G.T. Chandraappa, Winston D. Lloyd and Cyril Parkanyi, *Inorganic chimica acta* 1985, 107, 1-4.
- [20]A. Jassim, A. J. Abdul-Ghani and G. A. Alwan, *I. J. of chem*, 27, No.1,2001,135- 1-4.
- [21]Lallan Mishra, Ashok Kunar, padey and Rajendre Parsi Singh, *J. India of chem.* 31A, 1992,195-198.
- [22]S.M. Aliwi, M.Sc. Thesis, Univ. of Liverpool (1974).
- [23]Fischer, H., "The Persistent Radical Effect; A Principle for Selective Radical Reactions and living Radical Polymerizations" *chem. Rev.*, 2001,101,3581.
- [24]G. B. Burnett, *J. chem.. Soc.*, 1950, (46),772.
- [25]C.H. Bamford and A.N. Ferrar, *J. chem.. soc., Fara-day Trans., I*, 1972, (68) 1243.
- [26]S.M. Aiw and C. H. Bamford, *J. Photochem. And Photobiol., A*, 1989, (47),353.
- [27]Sperling, L. H., *Introduction to Physical polymer Science*, 3rd ed. New York: Wiley Interscience, 2001.
- [28]A.T. Casy. D.J. Macky and R.L. Matin, *Aust. J. chem.*, (25),1972, 477.
- [29]S. M. Abdulla, A.H, MSc. Thesis, Mustansirih University, Baghdad 1999.
- [30]S.M. Aliwi and A.H. AL-Hayali, *AlMustansirih J.of sciences* vol. 11, No. 87,(2000).
- [31]Allen P.M., and Patrick, C.R. *Kinetics and Mechanisms of polymerization Reaction*. New York: Wiley chaps. 2,3,7, 1974.
- [32]Mishra M. K. and YACEI, Y., *Handbook of Radical Vinyl polymerization*, New York: Dekker, 1998.
- [33]S.A. Kettle, *coordination compounds*, Thoms Nelson, London, 3,186,212(1975).

**Table (1) characterization data for free Schiff base and its 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%	$R \times 10^{-5}$ $mol.l^{-1}.s^{-1}$	$[I] \times 10^{-5} mol.l^{-1}$	$\frac{kp}{kt^{1/2}} \times 10^{-4}$ $(mol^{-1/2}.l^{3/2}.s^{-1/2})$
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

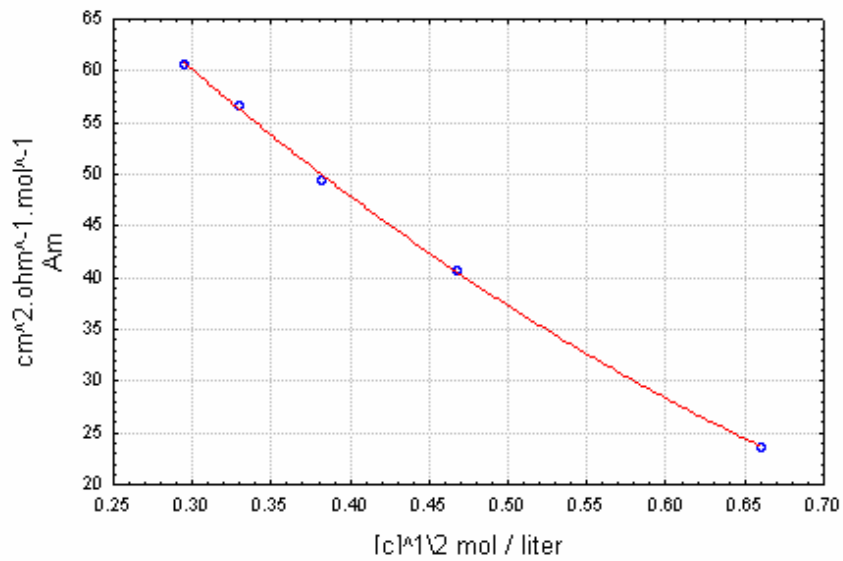


Figure (1) Relation between molar conductivity and square molar conductivity (Λ) & square root of concentration $[c]^{1/2}$

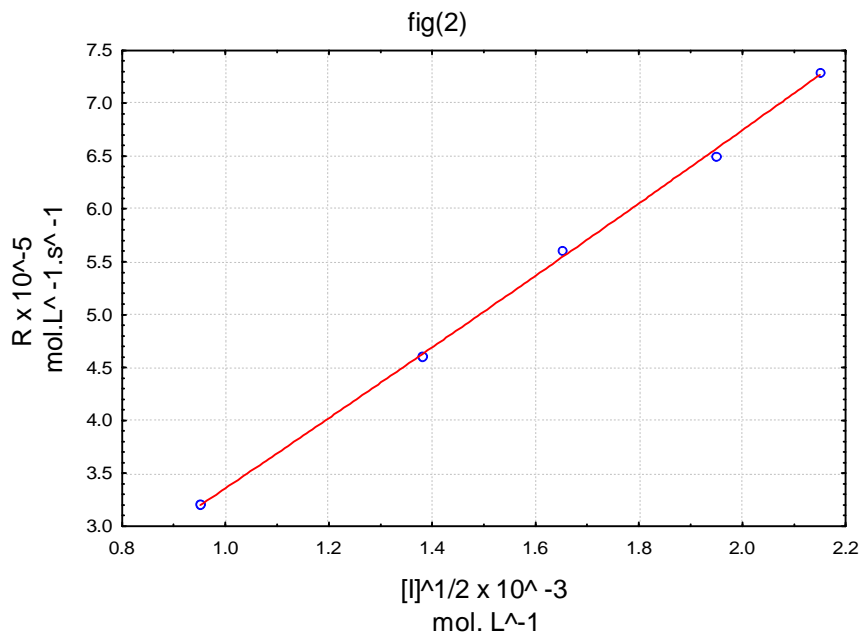


Figure (2) Relation between rate Polymerization and square root of the chelate con. at constant monomer con.

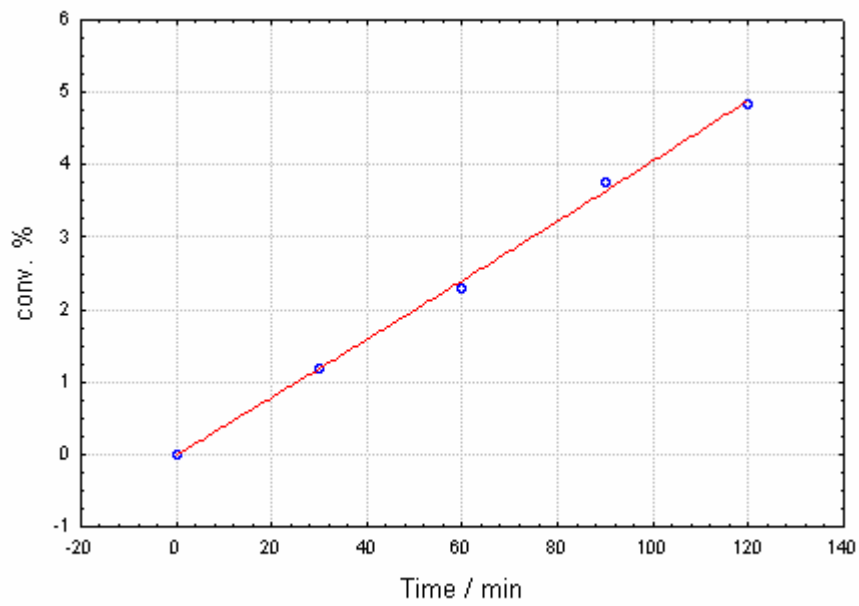


fig.(3) Relation between conversion percentage. And Time

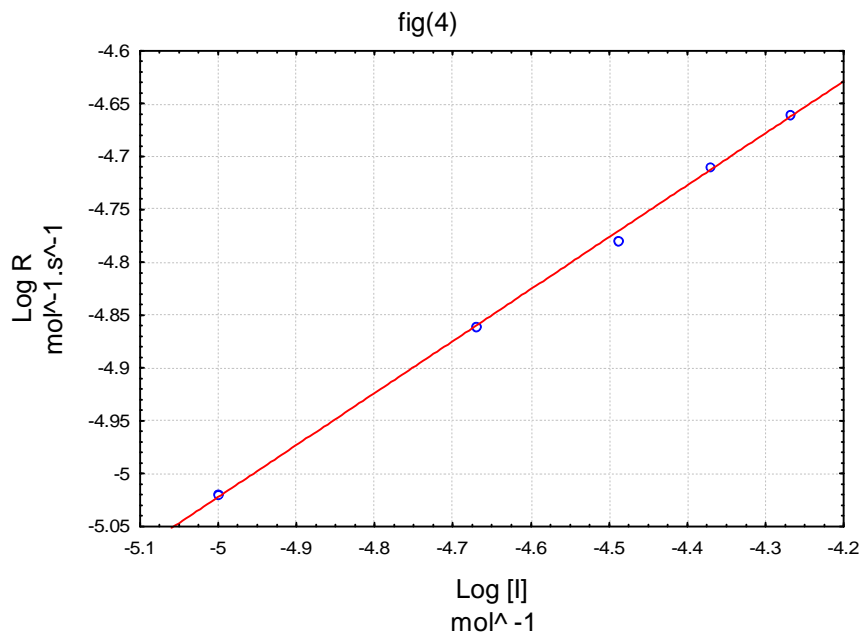


Figure (4) Relation between logarithmic rate of polymerization at 80°C logarithmic initiator con.

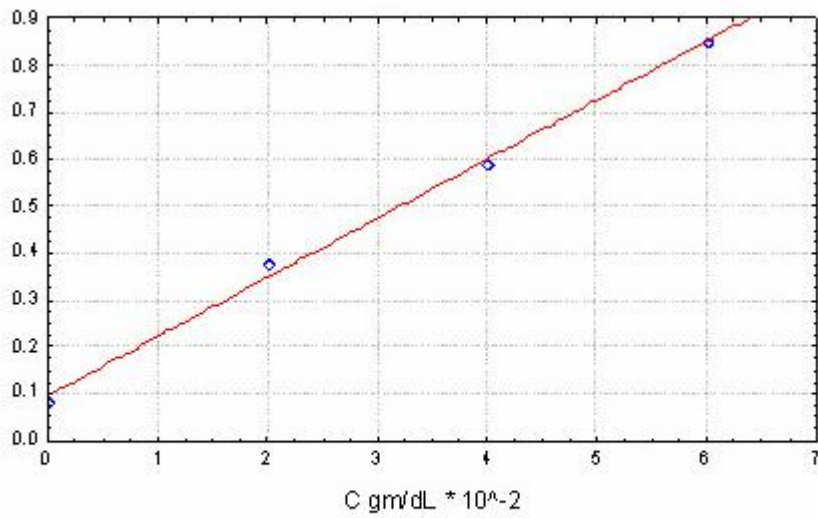


FIG (5) Relation between the intrinsic Viscosity to the Conc. of polymer Sol. And Conc. of polymer in gm.dL⁻¹

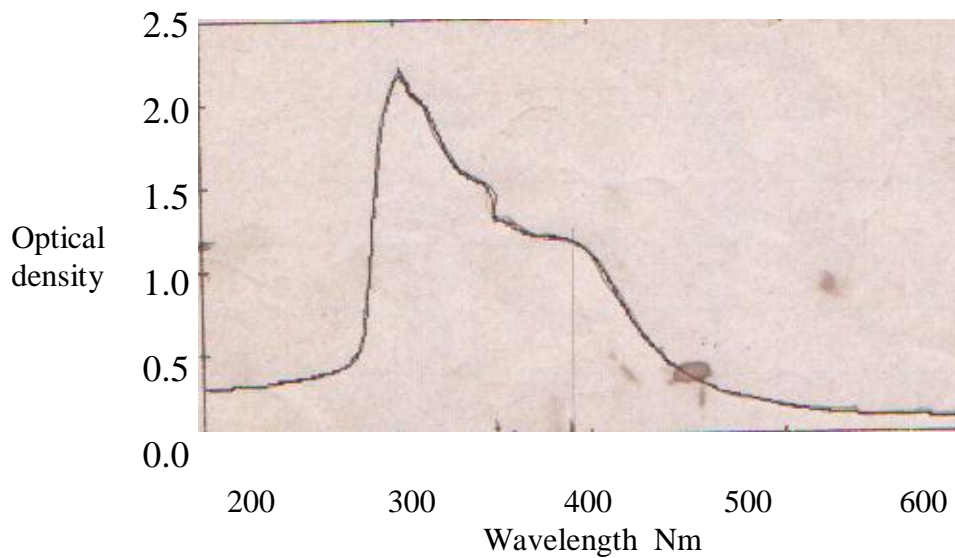


Figure (6) uv-visible absorption spectrum of manganese chelate in styrene

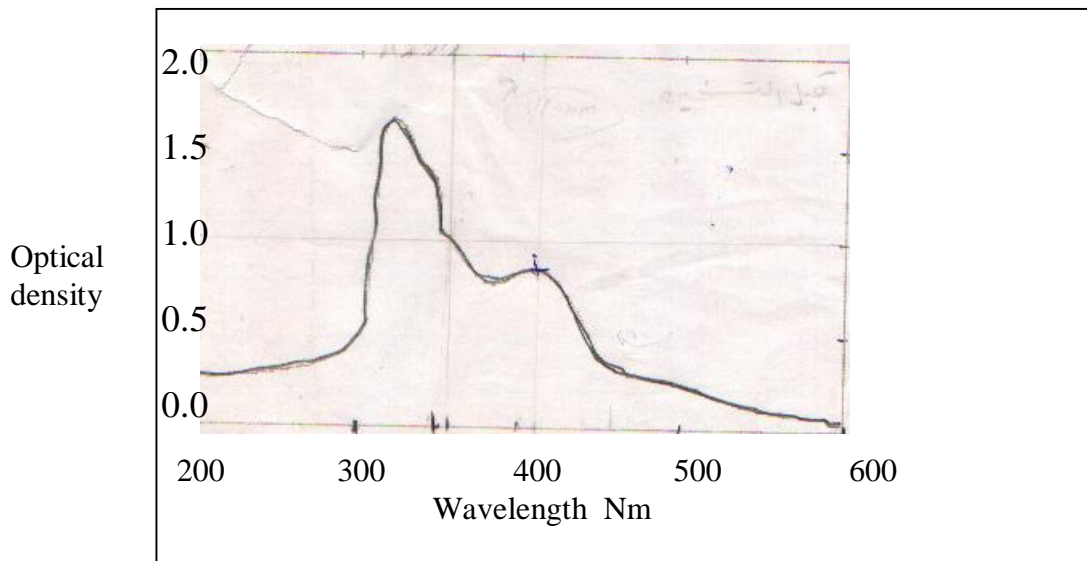


fig.(7): Fig. (6) uv-visible absorption spectrum of manganese chelate in styrene

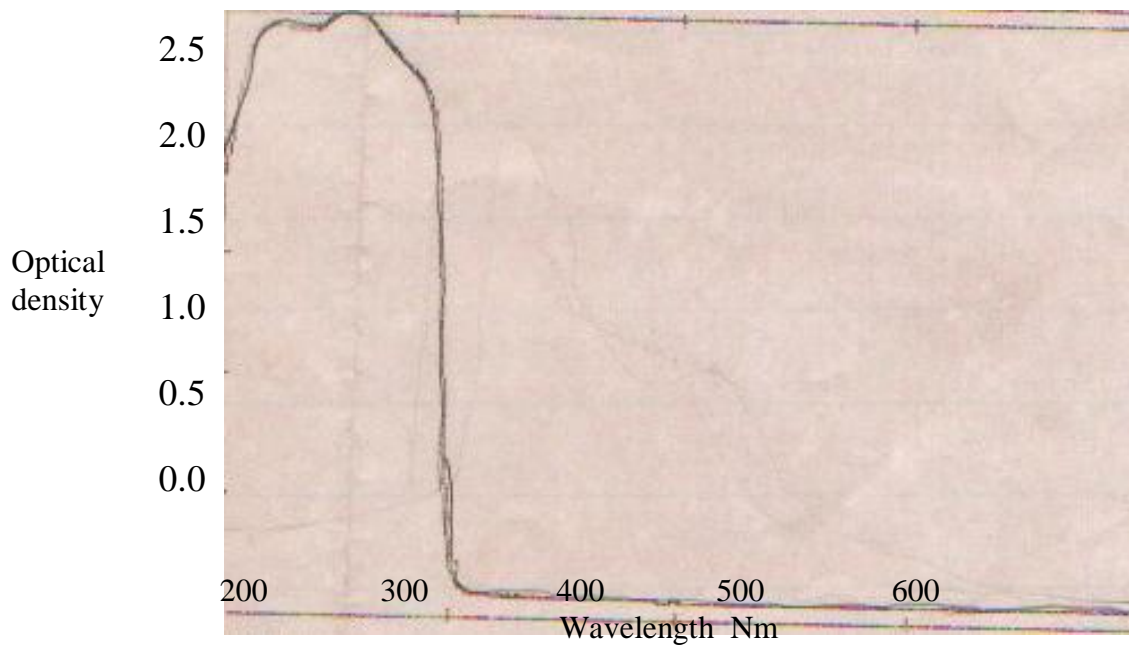


Figure (8): uv-visible absorption spectrum of bulk

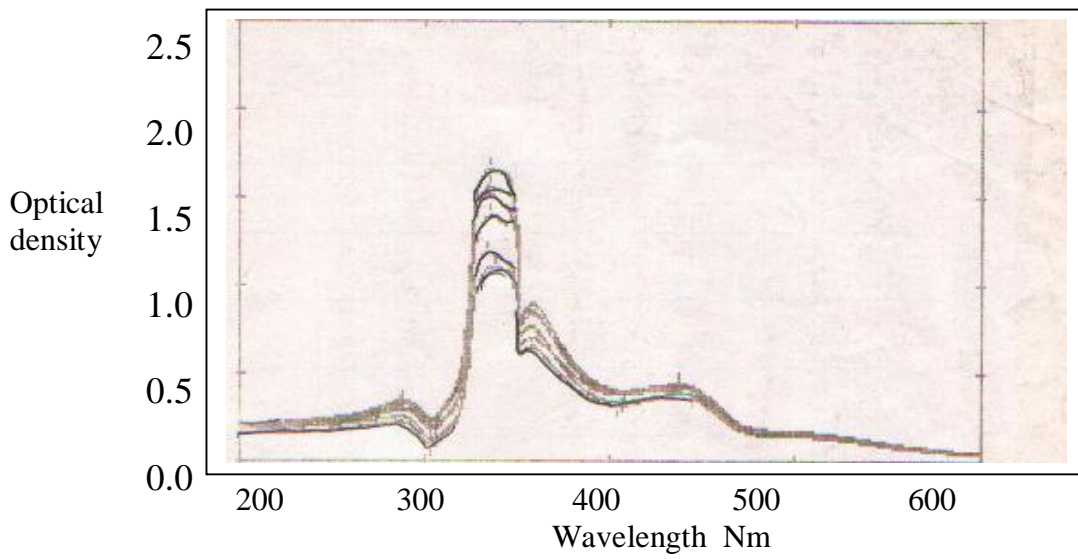


Figure (9): uv-visble spectrum of manganese chelate in styrene changes with time of irradiation at $\lambda = 355\text{nm}$

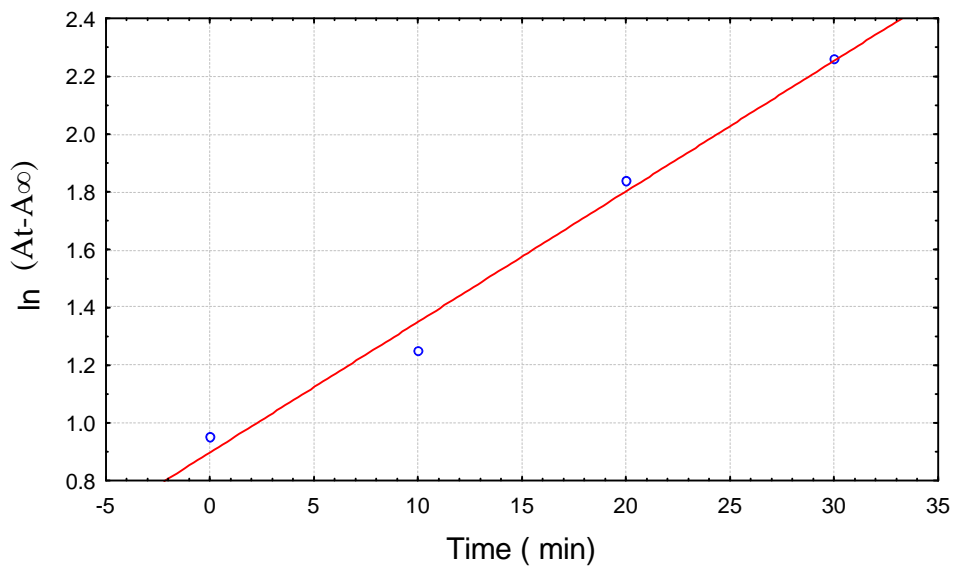


Figure (10) rariation of optical density at $\lambda = 355\text{ nm}$ with time of irradiation

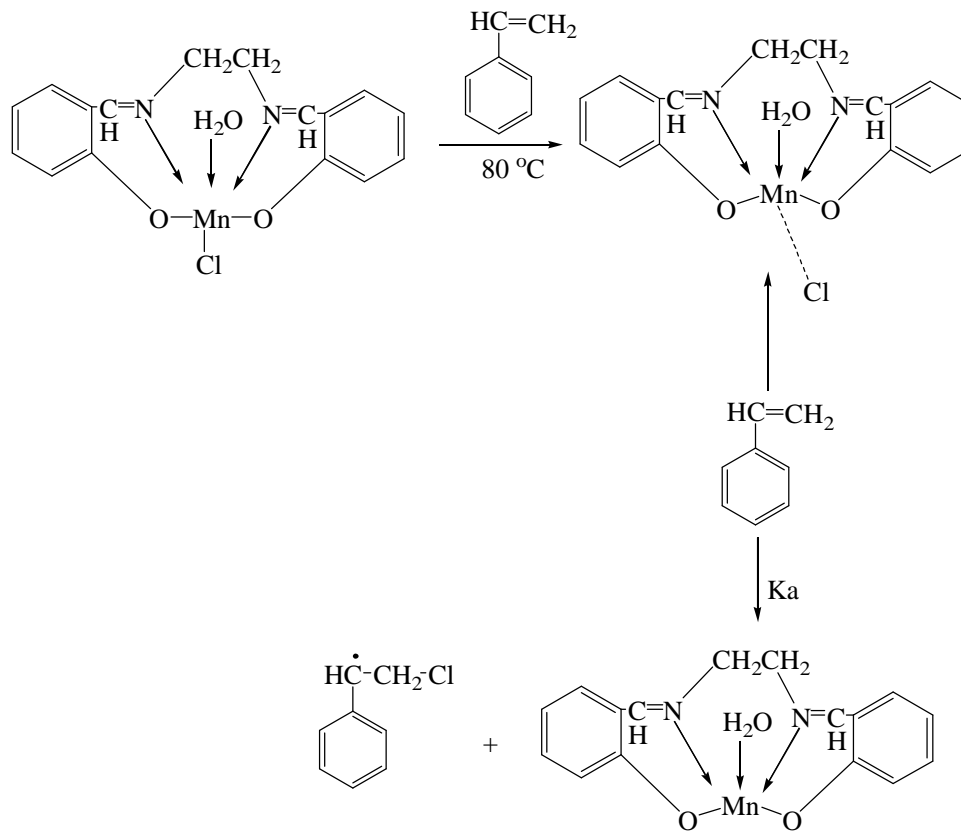


Fig.(11) reaction scheme might be suggested for the generation of the initiating chelate manganese (III) in styrene solution during heating at 80 c°.