

**[N,N-Ethylene bis (Salicylidene iminato)](benzoyl acetonato) Iron<sup>(111)</sup>  
as thermal initiator of methyl methacrylate polymerization**

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استخدام [ N,N - اثيلين ثنائي ( سالسيليدين اميناتو ) ] ( بنزويل اسيتو ناتو ) الحديد <sup>(111)</sup> كبادئ

حراري لبلمرة المثيل ميثاكريلات

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**Abstract**

The polymerization of methyl methacrylate(MMA) initiated by a mixed ligand complex , [N,N-Ethylene bis (Salicylidene iminato)](benzoyl acetonato) Iron<sup>(111)</sup> has been studied in bulk at 80°C .The rate order of polymerization is 0.5 with respect to initiator concentration and 1.5 with respect to monomer concentration .The activation energy and the kinetic are evaluated .According to the experimental results obtained a free radical mechanism has been proposed.

**الخلاصة**

تم في هذا البحث دراسة البلمرة الحرارية للمثيل ميثا اكريلات (MMA) بوساطة المعقد [ N,N - اثيلين ثنائي (سالسيليدين اميناتو)] ( بنزويل اسيتو ناتو ) الحديد <sup>(111)</sup> عند درجة حرارة 80 °م .وان رتبة سرعة البلمرة بالنسبة لتركيز البادئ هو (0.46) بينما كانت (1.5) بالنسبة لتركيز المونومر .تم حساب طاقة تنشيط الكلية للبلمرة والابتداء كما تم تشخيص الهيئة الفراغية للبولي مثيل ميثاأكريلات الناتج من البلمرة وتم اقتراح ميكانيكية البلمرة بالجذور الحرة.

## Introduction

Arnett and Mendelsohn <sup>(1)</sup> were first to report that certain metal chelates with o,o donor atoms in the ligand molecule yield free radical during thermal decomposition .Since then, the interest of many authors has been focused on the study of the kinetics and mechanism of initiation of radical polymerization of vinyl and diene monomers by metal chelates<sup>(2-13)</sup>. Various metal acetyl acetonates (acac) have been studied as initiators for vinyl polymerization. The homolysis of metal-oxygen bonds in metal chelates with the simultaneous reduction of the formal valency of the metal by one was found to be the initiation step<sup>(1-13)</sup> .While these reports indicated the importance of the central metal atom ,the striking influence of the ligand was very clearly indicated by the studies of Bamford <sup>(4)</sup> and Nishikawa <sup>(5)</sup> on metal chelates of various  $\alpha$  and  $\beta$  substituted acetyl acetonates. The mechanism of thermal initiation of MMA, styrene , and acrylonitrile by  $Mn(acac)_3$  and  $Mn(facac)_3$  complexes, were studied in detail by Bamford and Lind <sup>(3)</sup>. On other hand ,Indicator and Linder <sup>(6)</sup> reported that  $Cu^{11}$ ,  $Co^{11}$  and  $Fe(acac)_3$  enhanced the polymerization of MMA in presence of t-butyl hydroperoxide transition metal acetyl acetonates at 50°C was studied<sup>(7)</sup>.  $Co(acac)_3$  and  $Fe(acac)_3$  were proved to be effective thermal initiators for styrene and MMA polymerization ,respectively<sup>(8,9)</sup> .Bamford and co-workers <sup>(10)</sup> reported that  $Cu(acac)_2$  in conjunction with ammonium trichloroacetate initiates the polymerization of MMA at 80°C by free radical mechanism. Uehara and co-workers<sup>(11)</sup> studied the free radical polymerization of styrene ,MMA, and vinyl acetate at 70°C initiated by  $Mn(acac)_3$  in presence of pyridine derivatives as electron donors. It was observed that at 25°C, free radical polymerization of acrylonitrile in dimethyl sulphoxide solution (DMSO) is readily brought by  $Mn(acac)_3$  <sup>(12)</sup>. A mechanistic study of vinyl polymerization by  $Cu^{11}$  (1,3-diaminopropane) /  $CCl_4$  in DMSO solution was demonstrated by Kimura and co-workers<sup>(13)</sup>.

Thermal polymerization of MMA by  $Mn^{11}$  dithiocarbamate complexes was studied <sup>(14-16)</sup>. Vanadium (v) chelate complexes, such as  $Vo(QoCH_3)$  ,  $Vo(C_9H_5)_3$  ,  $VoQ_2(C_3H_7)$ ,  $Vo(COPH)_3$ ,  $Vo(OSiph_3)_3$  and  $Vo(OC_2H_3)_3$  (where Q =8-hydroxy quinoline ,  $C_9H_5$  = indenyl ligand ) as photo initiators for the polymerization of MMA monomer.

Saleh<sup>(21-23)</sup> have reported Vanadium (v) chelate complexes derived from Schiff bases ,such as Chloro-oxobis (N-(4-bromophenyl) salicylidene iminato) Vanadium(v) ( $VoL_2Cl$ ) and

VoL<sub>2</sub>OCH<sub>3</sub>. These compounds have been used as photo and thermal initiators of MMA and styrene.

Siemeling and co-workers have investigated complexes with two different types modified imido and phosphaneiminato ligands these complexes are used for the co-polymerization of the polar olefins; MMA, AN, and vinyl acetate<sup>(24)</sup>.

In the present work we have studied the thermal polymerization of MMA at 80°C by a mixed ligand complex [N,N-Ethylene bis (Salicylidene iminato)](benzoyl acetonato) Iron<sup>(111)</sup>.

## 2-Experimental

### 2.1 Materials

Method described by Bamford and <sup>(3)</sup> was adopted for the purification of monomers .Analar benzene (B.D.H.Ltd) was dried before distillation .Analar methanol (B.D.H.Ltd) was used without further purification.

[N,N-Ethylene bis (Salicylidene iminato)](benzoyl acetonato) Iron<sup>(111)</sup> [ FeSalen Ba ] was prepared in a method similar to that described by Podder and Biswas <sup>(25)</sup> . For prepared [CoSalen acac], solution of 0.0025 mole (Salen-H<sub>2</sub>) bis (Salicylaldehyde) ethylene diimine and 0.005 mole NaOH in absolute ethanol was added with stirring to 0.0025 mole of Fe(acac)<sub>3</sub> dissolved in absolute ethanol and left ½ hour .A red –orange precipitate was formed ,filtered and then washed with dry ethanol solvent ,the precipitate was dried under reduce pressure at room temperature and stored in dark dry place.

### 2-2 Technique

A Gravimetric method was employed to determine the rate of polymerization( $\omega$ )<sup>(26)</sup>. Pyrex tube 15 cm, in length, 1.5 cm in diameter, 10 cm<sup>3</sup> capacity was used in polymerization process. The tube was connected to an nitrogen gas purging system in order to remove the dissolved air, bubbling MMA<sup>(26)</sup> with saturated nitrogen gas (purity 99.9) for 20 minutes. The reaction tube was protected from light using aluminum foil and placed in a bath at 80°C .Average rates of polymerization were measured gravimetrically by precipitation of the polymer in 50 fold of pure ethanol, and the rate of polymerization was calculated as follows;

$$\omega = -\frac{\partial [M]}{\partial t} = \frac{[M_0] \times \text{conv} \%}{100 \times t(\text{sec})} \dots\dots\dots(1)$$

Where  $[M_0]$  = the initial monomer concentration,  $\text{conv}\%$  is the percentage of conversion of monomer to polymer,  $t$  = time of reaction (in second). The number average molecular weight of polymer (PMMA) was generally determined at  $30^\circ\text{C}$  using Mark-Houwink equation<sup>(27)</sup>, values of  $k$  and were taken from reference<sup>(28)</sup>. Infra-red spectra were recorded with a Pye–Unicam SP3-100. IR-spectrophotometer using KBr disk technique. Hitachi U-2000 double beam UV-Visible to measure the changes in initiator concentration and spectra during the polymerization process.

### 3-Results and discussion

The polymerization of MMA using FesalenBa was inhibited by hydroquinone, thus clearly establishing the free radical nature of the process. The MMA polymerization with FesalenBa was investigated in bulk. The average rate of polymerization ( $\omega$ ) increased with concentration of the initiator. Figure(1) illustrates the plots of  $\log \omega$  vs  $\log [FesalenBa]$  at constant monomer concentration and temperature the straight lines in Figure (2) between  $\log [FesalenBa]^{1/2}$  and ( $\omega$ ), gives initiator order of 0.46 in bulk at  $80^\circ\text{C}$ , suggesting bimolecular termination of growing polymer radicals and giving additional support to the free radical nature of the reaction. Results shown in Figures (1,2) illustrate that no inhibition or retardation is observed in the present initiating system, and the polymerization is considered to be obtained by Arentt<sup>(1)</sup>, Bamford and Lind<sup>(3)</sup>, Aliwi<sup>(29)</sup>, Thiagarajan and co-workers<sup>(30)</sup>, Abeer<sup>(16)</sup> and Saleh<sup>(21-23)</sup>, in polymerization of MMA by Azo bis iso butyronitrile (AIBN),  $Mn(acac)_3$ ,  $VO(acac)_2Cl$ , CosalenBa,  $Mn(1,1)$  dithiocarbamate and Chloro –oxo bis (N-(4-bromophenyl) salicylidene iminato) Vanadium (v) ( $VO_2Cl$ ) and ( $VO_2OCH_3$ ) respectively.

Dependence the rate of polymerization ( $\omega$ ) on the monomer concentration was determined at  $80^\circ\text{C}$ , constant chelate concentration  $5 \times 10^{-5}$  mole/L and variable monomer concentration  $[M]$  with benzene as diluents. The rate of polymerization ( $\omega$ ) is exhibited in Fig (3). The monomer order is closed to 1.5, indicating the involvement of the monomer in the initiation step. This result is in good agreement with result obtained by Uehera & co-workers<sup>(8)</sup> obtained an order of 1.5 for the thermal polymerization of styrene by  $Cu(acac)_2$  at  $80^\circ\text{C}$ . Prabha and Nandi<sup>(9)</sup> obtained an order of (1.5) for thermal polymerization of MMA at  $70^\circ\text{C}$ . Bamford and Lind<sup>(3)</sup> also reported that the order of MMA is (1.5) by  $Mn(acac)_3$  at  $80^\circ\text{C}$ . The same authors obtained an order (1.5) for thermal polymerization of styrene in benzene and (1.2) in ethyl



acetate when thermally initiated at 80°C using Mn(acac)<sub>3</sub>. Thiagarajan and co-workers<sup>(30)</sup> also obtained the order of (1.44) for the polymerization of MMA by CoSalen Ba at 80°C. N.J.Saleh<sup>(23)</sup> obtained the order of MMA at 80°C is (1.8) by methoxy-oxo bis (N-(4-bromophenyl) salicylidene iminato) Vanadium (v) and A.H.Mustafa<sup>(16)</sup>(≈2) by Mn<sup>111</sup>dithiocarbamate at 80°C. All these authors suggested that complex formation between the chelate and monomer undergoes a thermal oxidation-reduction reaction.

The kinetic parameter  $k_p / k_t^{1/2}$  ( $k_p$  and  $k_t$ ) being rate constants of propagation and second order termination respectively, this parameter was calculated from the following relation<sup>(29)</sup>.

$$\left( \frac{k_p}{k_t^{1/2}} \right) = \frac{1}{[M]} \times \left[ \omega D_p \times \frac{2+y}{2(1+y)} \right]^{1/2} \quad (2)$$

$y$  =ratio of  $k_{tc}/k_{td}$ , ( $k_{tc}$  &  $k_{td}$  termination constants by combination, and by disproportionate respectively),  $y = 0.77$  at 80°C<sup>(16,31)</sup>. Mean value of  $K_p / K_t^{1/2}$  was found to be equal to 0.145 mol<sup>1/2</sup>.s<sup>-1/2</sup>. This value of  $K_p / K_t^{1/2}$  for this initiator is close to from that obtained by Arentt<sup>(1)</sup> (0.109) for the polymerization of MMA at 77°C using AIBN as initiator, Bamford & Lind<sup>(3)</sup>(0.17), Thiagarajan & co-workers<sup>(30)</sup> (0.174) and N.J.Saleh<sup>(23)</sup> (0.1).

### Detection of polymer tacticity

The tacticity of polymer chain produced thermally using the initiator presented in this work was detected by infrared spectrophotometry and it is found to have atactic configuration. The IR-spectrum of polymer film is similar to that reported for atactic PMMA<sup>(32)</sup> produced by peroxide di benzoyl as initiator. Thus it is concluded that the radical species is completely detached before the initiation process and the rest of coordination Iron complex is not



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involved in the initiation step or propagation process. Therefore there is no change of any stereo regularity of MMA repeating units in the polymer chain<sup>(16,23)</sup>.



### Activation energy

Values of  $\omega$  at various temperatures were determined at fixed concentrations of monomer and in initiator. Figure(4) shows the Arrhenius plot of reciprocal absolute temperature with values of  $\ln \omega$  at various temperatures .From fig(4),the overall polymerization activation energies( $E_T$ ) was deduced from the slope of this plot. It was found to be equal to 9.174 Kcal/mol .

The activation energy for initiation process was calculated by using the following equation(4,30):

$$E_T = (E_p - E_t/2) + E_i/2 \dots\dots\dots 3$$

Where( $E_i$ ,  $E_p$  &  $E_t$  ) activation energy of initiation , propagation and termination respectively. The value of  $(E_p - E_t /2)$  is equal to (4.6 kcal/ mol) for the polymerization of MMA at 80°C <sup>(16,23,30,33)</sup>.From this value and the value of  $E_T$  then  $E_i$  is deduced and found to be 9.147 kcal/mol. The values of  $E_T$  and  $E_i$  agrees well with these reported for thermal polymerization of MMA by Mn (tfac)<sub>3</sub> as initiator [ $E_T$ = 12.5;  $E_i$ = 15.8 kcal/mol ]and for Mn(ppd)<sub>3</sub>( $E_T$  =11.0.,  $E_i$  =12.9 kcal/mol)and for Mn(acac)<sub>3</sub> ( $E_T$  =17.7 ;  $E_i$  =26.6kcal/mol)(3) .and A.H.Mustafa<sup>(16)</sup> ( $E_T$ =10.27-14.51; $E_i$ =11.34-19.82kcal/mol)when used n<sup>111</sup>dithiocarbamate at 80°C as initiators and N.J.Saleh<sup>(23)</sup>( $E_T$ =10.2 ; $E_i$ =15.35kcal/mol) .Thinagarajan and co-workers <sup>(30)</sup> ( $E_T$  =10.9;  $E_i$  =11.0 kcal/mol when used CosalenAc as initiator and  $E_T$  =7.3 ;  $E_i$ = 3.8 kcal/ mol when used CosalenBa as initiator for thermal polymerization of MMA by a dilatometric technique at 80°C.

### Mechanism

Based on x-ray crystal structure ,Bailey <sup>(34)</sup> showed that the quadridentate Salen ligand [N,N-Ethylene bis (Salicylidene iminato) adopts a significantly strained non-polar configuration and the Co-O bonds of the Salen part are shorter and stronger than the benzoylacetate part in CoSalen Ba. Thus it may be

concluded that the Salen ligand although strained may not easily come out as a radical .The discussion indicates that ,in the monomer moiety ,the FeSalen Ba decomposes into a planar(Salen) Fe(II) and benzoyl acetate radical .Accordingly, a two –stage initiation step is formulated<sup>(30)</sup>:

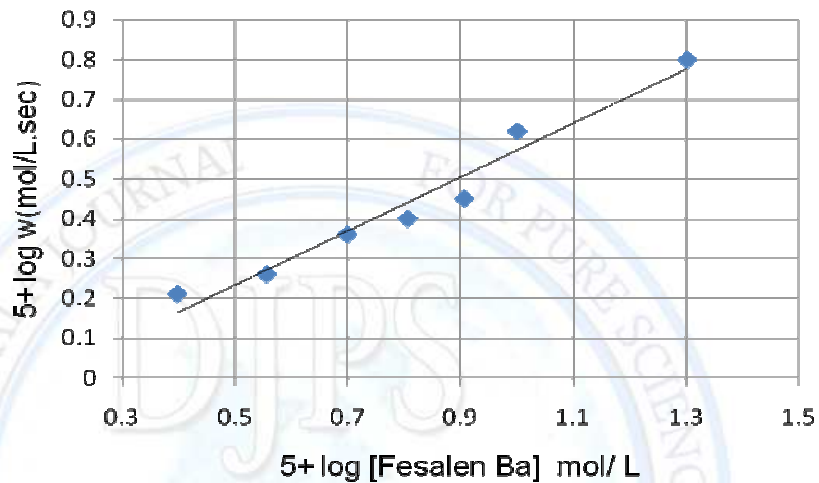


Fig 1: Dependence of log w on initiator concentration at 80 ° C

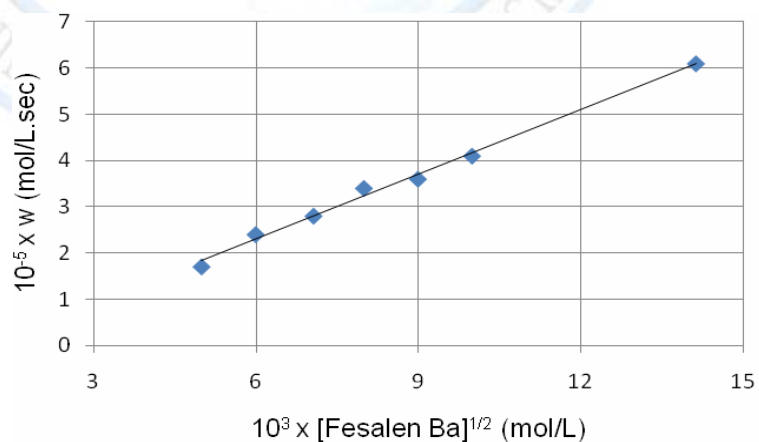


Fig 2: Dependence of average rate of MMA polymerization (bulk) on the square root of complex conc. at 80 ° C [M]= 9.2 mol/L



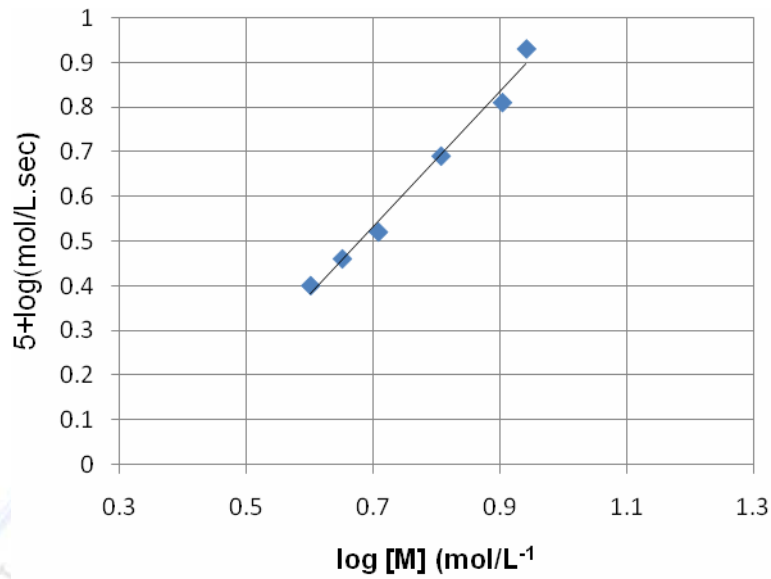


Fig 3: Rate of Polymerization at 80°C as a fuction of monomer Concetration (benzene is used as diluent)

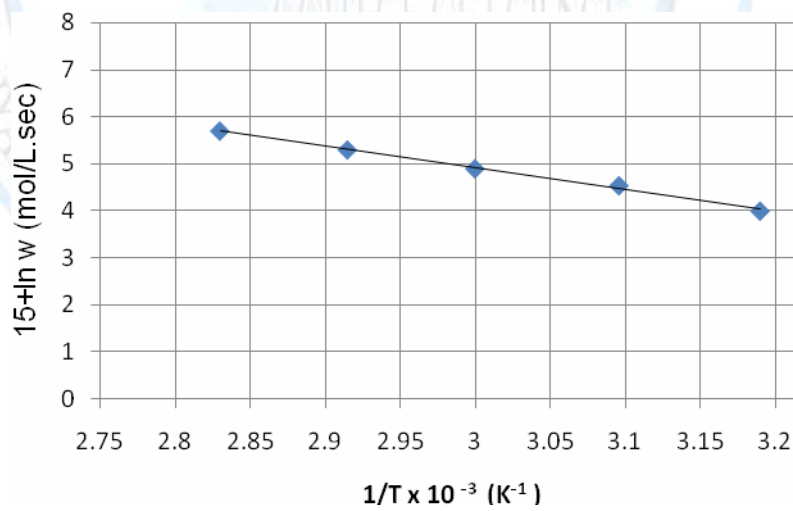


Fig 4 : Arrhenius plot of reciprocal absolute temperature with values of Ln ω at various temperatures  
 [I] = 5x10<sup>-5</sup> mol/L , [M] = 9.2mol/L

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