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Transition Metal Chelates as Initiators of Vinyl Polymerization

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Transition Metal Chelates as Initiators of Vinyl Polymerization

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ABSTRACT

Recent information on the use of transition metal chelates as initiators of free radical polymerization of vinyl monomers is supplied. Chelates of various kinds and of various coordination numbers, derived from transition metal ions such as Mn(II), Mn(III), Co(II), Co(III), Fe(II), Fe(III), Cu(I), and Cu(II) with a multitude of both monomeric and polymeric ligands, are taken into consideration. The efficiency of the individual chelates toward radical polymerization of vinyl monomers under variable reaction conditions are discussed. The co-catalytic activity of some chelates in photopolymerization and peroxide initiated vinyl polymerization is accounted for. The kinetic results and spectroscopic evidence leading to the mechanistic details of individual paths of initiation of polymerization are discussed.

INTRODUCTION

Transition metal ions in their higher valency states such as Ce(IV), Cr(VI), Co(III), Mn(IV), Mn(III), Fe(III), and Cu(II) either alone or when coupled with easily oxidizable organic substrates have been found to be effective initiators of vinyl polymerization. The field has recently been reviewed by Nayak et al. [1]. In most of the systems involving the transition metal ions and organic substrates, the initial formation of a complex between the metal ion and the organic substrate, whose decomposition yields the initiating free radicals, have been suggested. But so far no interest seems to have been paid toward the review of free-radical initiated vinyl polymerization initiated by transition metal chelates. The present report gives a detailed recent information on the use of transition metal chelates.

It is now almost 19 years since it was found that certain metal chelates with O,O donor atoms in the ligand molecule yield free radicals on thermal decomposition [2]. Since then the interest of many authors has been concentrated on the study of the kinetics and mechanism of initiation of radical polymerization of vinyl and diene monomers under the effect of metal complexes. Initiating particles are believed to be the ligand radicals formed, i.e., under homolytic scission of the metal-oxygen bond in metal acetylacetonates. At the same time the formal valency of the metal is reduced by one. The reduction of the metal ion was confirmed by spectroscopic measurements.

MANGANESE CHELATES

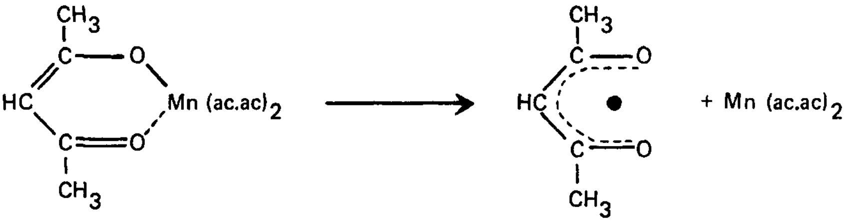
A number of complexes of manganese have been successfully prepared and their catalytic behavior to initiate vinyl polymerization has been investigated both in aqueous and nonaqueous media.

Mn(III)-Acetylacetonates

In 1965 Kastning et al. [3] reported the catalytic activity of various metal acetylacetonates [$Me(ac.ac)_3$] to initiate vinyl polymerization, and showed some excellent selectivities and stereospecificities of their polymerization. Their results were reexamined by Otsu et al. [4] and some questionable results were reported. The use of metal acetylacetonates as free radical initiators has been reported by a number of other workers [5-8]. It was found that among all the metal acetylacetonates, Mn(III) acetylacetonate was much more effective for radical homopolymerization and copolymerization of vinyl monomers both in aqueous and nonaqueous media.

Initiation Mechanism

From the kinetic results and study of the structure of the resulting polymer, it was clear to the authors [4] that $Mn(ac.ac)_3$ could induce ordinary radical polymerization of vinyl monomers and did not give any stereospecificity of the resulting polymers. These observations did not coincide with those reported by Kastning et al. [3]. The initiation mechanism put forward by them is identical with that proposed by Arnett et al. [2], which is considered to occur through the homolysis of the metal-oxygen bond with the simultaneous reduction of the valency of manganese by one:



The mechanism was supported by Bamford et al. [5] from the observed rate equation; $R_p = K'[\mathrm{MMA}]$ in the case of the polymerization of methyl methacrylate.

According to the above mechanism, the acetylacetonate radical must be produced as the initiating radical and at the same time the central metal ion of $\mathrm{Mn(ac.ac)_3}$ must be reduced. Both possibilities were found to be true. The former possibility was supported by the infrared spectrum of low molecular weight polystyrene obtained by Mn(ac.ac). The latter interpretation was supported from the change in color of the polymerizing mixture involving styrene and $\mathrm{Mn(ac.ac)_3}$ from blackish brown to yellowish brown.

Izawa et al. [6] pointed out that in nonpolar solvents the production of acetylacetonate radical was not observed and accordingly suggested that the monomer molecule must participate in the homolysis of $\mathrm{Mn(ac.ac)_3}$, i.e., in the initiating radical production step:

$$\mathrm{Mn(ac.ac)_3} + \mathrm{M} \rightleftharpoons [\mathrm{M}\ \ \mathrm{Mn(ac.ac)_3}] \longrightarrow \mathrm{(ac.ac)\text{–}M^{\bullet}} + \mathrm{Mn(ac.ac)_2}$$

Recently Bamford et al. [9] have shown that the Mn(III)-chelate of trifluoroacetylacetonate (fac.ac) could initiate selectively the radical polymerization of vinyl monomers which were easily polymerized by an anionic mechanism. In this case the ligand anion dissociated from the chelate, was added with the monomer, and then one electron transfer occurred as follows:

$$\mathrm{Mn(fac.ac)_3} \rightleftharpoons \mathrm{(fac.ac)^{-}Mn^{III}(fac.ac)_2} \xrightarrow{\mathrm{M}}$$

$$\mathrm{(fac.ac)\text{–}M^{-}Mn^{III}(fac.ac)_2} \longrightarrow \mathrm{(fac.ac)\text{–}M^{\bullet}} + \mathrm{Mn^{II}(fac.ac)_2}$$

Other evidence for such a complex formation has been obtained from recent observations by a number of workers on the polymerization of some aldehydes [10, 11] and cyclic oxides [12] through a coordinated anionic mechanism to give high polymers.

Mn(III) Chelate Containing Unsaturated Carboxylic Ligands

Studies on the kinetics of vinyl polymerization in the presence of Mn(III)-bis(acetylacetonate) carboxylate is of recent origin. The use of Mn(III)-tris-acetylacetonate (TAM) and saturated carboxylic acids as initiator of radical polymerization of methyl methacrylate and vinyl acetate was reported by a number of workers [13, 14]. But the use of Mn(III)-TAM and unsaturated carboxylic acids (acrylic, methacrylic, crotonic, maleic, etc.) chelates was for the first time reported by Pushkareva et al. [15]. They found that these chelates were active initiators of polymerization of methyl methacrylate (MMA) and styrene (St). A characteristic feature of bis-(acetylacetonates) of Mn(III) (BAAM) so obtained is that they undergo thermal decomposition with elimination of carboxylate ligands. This observation is quite different from that of carboxylate based on saturated acids and TAM, where decomposition of the species leads to the formation of an acetylacetone ligand [16]. The change in structure of the chelates by the introduction of unsaturated ligands affects not only their activity as initiators but also brings about selectivity with respect to monomers of different structure [17]. The new chelate was found to initiate radical polymerization of acrylonitrile (AN), MMA, vinyl acetate (VA), and St quite smoothly and effectively.

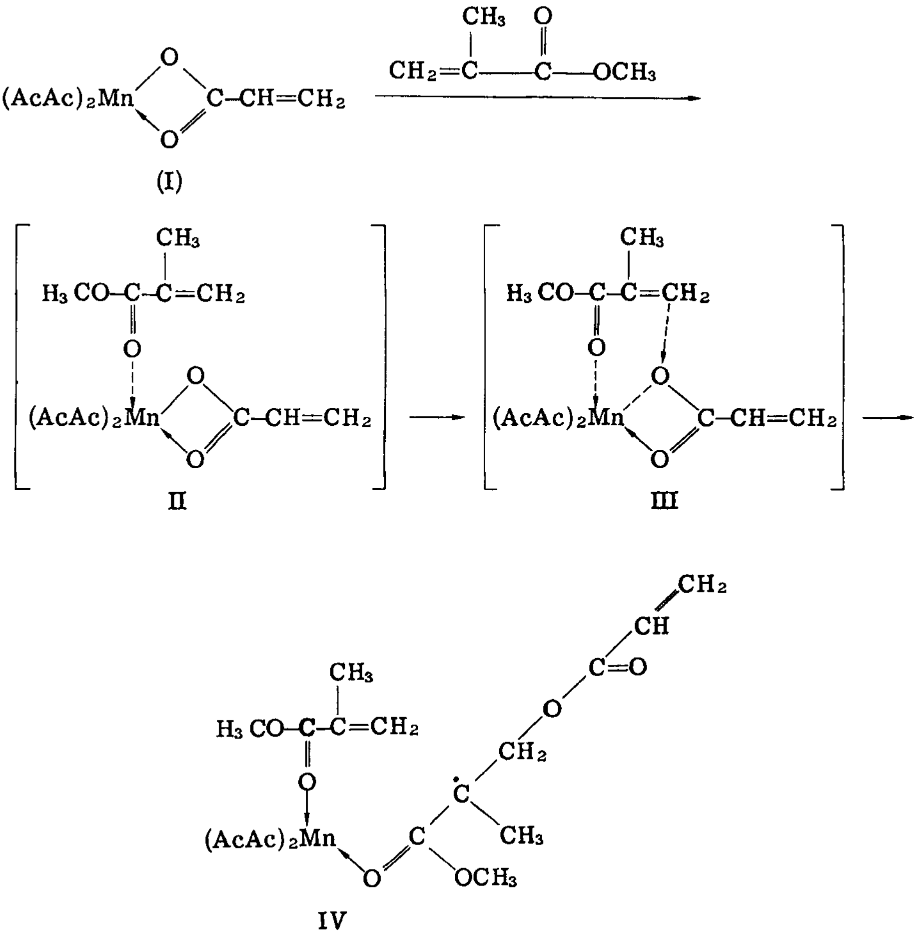
Reaction Mechanism and Rate Law

The rate of polymerization (R_p) with respect to the initiator was found to be close to 0.5, which confirms the free-radical nature of the process. The order with respect to monomer was 1.35 for St and 1.50 for MMA. This dependence of the rate on monomer concentration is different from the usual relationship in free-radical polymerization under the influence of acetylacetonates of metals [3, 14] and has been explained by participation of the monomer in the initiation stage. The following rate expressions were derived for the total polymerization rate.

$$R_{p90^\circ} = 4.0 \times 10^{-4} [\text{BAAM}]^{0.5} [\text{MMA}]^{1.35}$$

$$R_{p60^\circ} = 2.4 \times 10^{-4} [\text{BAAM}]^{0.58} [\text{MMA}]^{1.5}$$

The results of the kinetic investigation of polymerization of some monomer in bulk under the influence of BAAM showed that the rate is strongly dependent on the nature of the monomer and decreases over the series acrylonitrile > butyl acrylate > methyl methacrylate > styrene ≫ vinyl acetate. This series differs from the order of the reactivities of the monomers in the presence of TAM and saturated carboxylate derivatives. It has been explained that BAAM decomposes with elimination of the carboxylate ligand. It is probable that the rupture of the metal-oxygen bond is preceeded by the polar transition state which favors the addition of monomers that have a high electron accepting capacity (AN, BA, MMA). The high electron density at the double bond of vinyl acetate explains its lower rate of polymerization. In the case of styrene, a decisive part is played by the high polarizability factor (1.26) because of conjugation in the monomer. The following series of equations has been suggested by the authors [17] to describe initiation in the presence of BAAM:



A characteristic feature of the mechanism is the coordination step of the monomer (State II) and the subsequent reaction within the complex (State III) which occurs only with monomers of suitable structure. It is Stage III that is responsible for the selective behavior of the chelate. A similar proposal has been put forward by Bamford et al. [18] on the nature of the selective action of Mn(III)-tris-acetylacetonate in the polymerization of vinyl monomers.

Other Mn(III) Chelates

Apart from the Mn(III) chelates discussed above, there are some other reports [19-22] concerning the radical polymerization of vinyl monomers by other Mn(III) chelates. Okimoto et al. [22] have reported the catalytic behavior of Mn(III)-triethylene tetramine toward radical polymerization. Recently Gnanasundaram et al. [23] reported the kinetics of polymerization of acrylamide and methacrylamide initiated by the Mn(III)-diethanolamine complex at pH 0.9. The free radical nature of the reaction was inferred from the absence of any induction period in the deaerated system and the presence of a long induction period in the undeaerated system. The rate of polymerization was followed by bromometry and was found to be directly proportional to the first power of the monomer concentrations for both acrylamide and methacrylamide. The rate of complex disappearance was followed spectrometrically and was found to be proportional to the 0.5 power of the complex concentration for acrylamide and the 0.3 power for methacrylamide.

The following kinetic scheme was proposed to explain the experimental results. At pH 0.9 the complex decomposes to give a Mn(II) species and the radical $(C_2H_4OH)_2N^{\bullet}$, which adds to the monomer and initiates polymerization. The rate expression was derived as

$$R_p = k_p \left(\frac{k_r}{2k_{t_1}}\right)^{1/2} [\text{complex}]^{1/2} [M]$$

where M = acrylamide and methacrylamide.

COBALT CHELATES

Because of the ease of preparation and stability of cobalt chelates, considerable attention has been paid to them in the study of substitution, oxidation and hydrolysis reactions. A few examples of Co(II) and Co(III) complexes initiating vinyl polymerization are provided in the recent literature [4, 24-27].

Cobalt(II) System

(1) The important observation was made by Otsu et al. [24] that the binary system of pentacyano cobaltate(II) and some organic halides were effective as initiators of vinyl polymerization of MMA.

The polymerization of MMA was carried out in the presence of such organic halides as CCl_4, $CHCl_3$, CH_2Cl_2, $CHBr_3$, CHI_3, $CH_2{=}CH{-}CH_2{-}Cl$, $CH_2{=}CH{-}CH_2{-}Br$, $C_6H_5{-}CH_2{-}Cl$, and $C_6H_5{-}CH_2{-}Br$. From the results and the percent yield of the polymer (PMMA), they concluded that the initiating activity of these systems is dependent on the types of organic halides. The percent yield increases in the order $CH_2Cl_2 < CHCl_3 < CCl_4$; $CHCl_3 < CBr_3 \simeq CHI_3$; $R{-}Cl < R{-}Br$. This order is in good agreement with the decreasing order of bond dissociation energy of the carbon-halogen bond in organic halides [28], as well as with the order of radical formation due to a one electron transfer reaction as proposed by Halpern et al. [29].

$$[Co(CN)_5]^{3-} + R - X \longrightarrow R^{\cdot} + [Co(CN)_5X]^{3-}$$

(2) Bis(diethanolamine) cobalt octahydrate. Sundaram et al. [27] found that sodium bis(diethanolamine) cobalt octahydrate at pH 1.6 quite effectively decomposes via a homolysis path which can initiate polymerization of acrylamide and methacrylamide. There was polymerization at pH 4. Various kinetic aspects of the polymerization have been studied by the authors between 30 and 60° C. It was found that at pH 1.6 the rate constant of decomposition of the complex obeys the relationship

$$K = \frac{2.303}{t} \log \left(\frac{D_0 - D_\alpha}{D_t - D_\alpha} \right)$$

where D_0, D_t, and D_α are the optical densities of the complex solution at the beginning, after time t, and after 48 h, respectively.

The rate of polymerization (R_p) was found to be proportional to the first power of monomer concentration for both monomers whereas the rate was 0.3 order with respect to the initiator concentration in the case of acrylamide and 0.67 order in the case of methacrylamide.

From the kinetic results the following reaction scheme has been suggested.

(a) Radical Production:

$$[Co(DEA\text{-}2H)_2]^- + 2H_3{}^+O + H_2O \xrightarrow{k_r} [Co(DEA\text{-}2H)(H_2O)_3]^+ + (C_2H_4OH)_2N^{\cdot}H$$

where DEA = diethanolamine [bis(2-hydroxyethyl)amine].

(b) Initiation:

$$(C_2H_4OH)_2\dot{N}H + M \xrightarrow{k_i} M^{\bullet}$$

(c) Propagation:

$$M^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet}$$

$$M^{\bullet}_{n-1} + M \longrightarrow M_n^{\bullet}$$

(d) Termination

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_{t_1}} M_{n+m}$$

$$M_n^{\bullet} + [Co(DEA\text{-}2H)_2]^- \xrightarrow{k_{t_2}} \text{polymer}$$

$$M_n^{\bullet} + [Co(DEA)\text{-}H)_2]^+ \xrightarrow{k_{t_3}} \text{polymer}$$

$$M_n^{\bullet} + (C_2H_4OH)_2\dot{N}H \xrightarrow{k_{t_4}} \text{polymer}$$

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_{t_5}} M_n + M_m$$

Assuming that termination takes place by mutual combination (k_{t_1}), the rate expression has been calculated to be

$$R_p = k_p \left(\frac{k_c}{2k_t}\right)^{1/2} [H^+][I]^{1/2}[M]$$

Cobalt(III) System

(1) Polymerization by pentacyano cobaltate(III). Pentacyano cobaltate(III) chelates have been found to initiate bulk polymerization of such vinyl monomers [24] as AN, St, MMA, and VA quite smoothly and effectively. In these cases the polymerization systems were

heterogeneous because the organo cobalt concerned was insoluble in the polymerizing mixture. From the results of homopolymerization and copolymerization the following mechanism for initiation was suggested:

$$[C_6H_5{-}CH_2Co(CN)_5]^{3-} \longrightarrow C_6H_5{-}\dot{C}H_2 + [Co(CN)_5]^{3-}$$

$$C_6H_5{-}CH_2^{\bullet} + M \longrightarrow C_6H_5{-}CH_2{-}M^{\bullet}$$

An interesting finding is that the benzyl radical can initiate the radical polymerization of VA which is known to be a less reactive monomer [30].

Further, pentacyano cobaltate(III), when coupled with an organic halide such as benzyl bromide, has been found to be much more effective than pentacyano cobaltate(III) alone, i.e., the polymer yield in the presence of benzyl bromide increased more than that in the absence of the halide, suggesting that pentacyano cobaltate(II), which resulted from the decomposition of pentacyano cobaltate(III), reacts further with benzyl bromide:

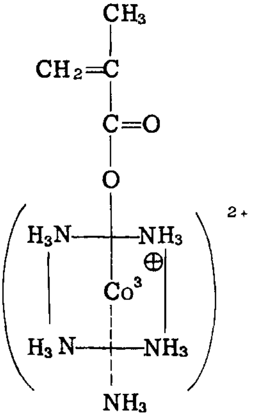
$$[C_6H_5{-}CH_2Co(CN)_5]^{3-} \longrightarrow C_6H_5{-}CH_2^{\bullet} + [Co(CN)_5]^{3-}$$

$$[Co(CN)_5]^{3-} + C_6H_5{-}CH_2{-}Br \longrightarrow C_6H_5{-}CH_2^{\bullet} + [Co(CN)_5X]^{3-}$$

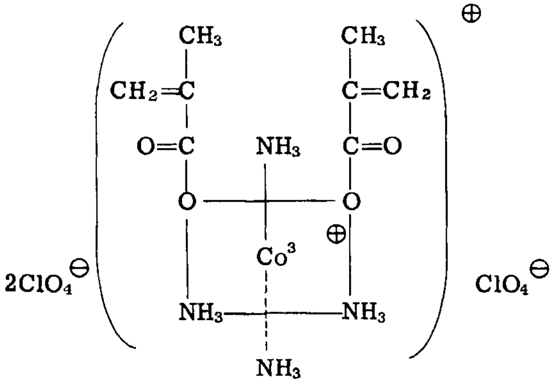
(2) Radical polymerization of methacrylic acid coordinated to Co(III) complexes. Many examples of specific functionalities of metal complexes attached to macromolecular chains have been demonstrated. Of course, these functionalities should be closely related to the configurational, sequential, and other structures of macromolecular ligands. However, metal complex polymers, usually obtained by a coordination reaction between polymer ligand and metal complex, raise many difficulties for the analyses of their detailed structures. On the other hand, polymers obtained by polymerization of monomers coordinated to the metal complex could give suitable models for understanding the specificities of metal complexes in the macromolecular domain. However, radical polymerization of vinyl monomers coordinated to a transition metal complex of the so-called Werner type have never been studied because of their inhibiting effect in the process of polymerization. In contrast to this, several kinds of monomers attached to π-metal complexes as ferrocenyl and tricarbonyl phenyl groups have been polymerized and their reactivities have been discussed [31].

These studies led Osada [25] to study what kind of influence the reactivity of methacrylate monomer would be subjected to on account of the coordination of a metal complex to the conjugated system.

For this purpose radical homopolymerization and copolymerization of methacrylic acid (MAA) coordinated to amine cobalt(III) complexes, methacrylato pentamine cobalt(III) perchlorate (a), and cis-dimethacrylato tetramine cobalt(III) perchlorate (b) were carried out in aqueous medium.



(a)



(b)

A report briefly describing that these two monomers could be successfully polymerized by a free radical mechanism and their configurational effects on the resulting polymers has appeared elsewhere [32].

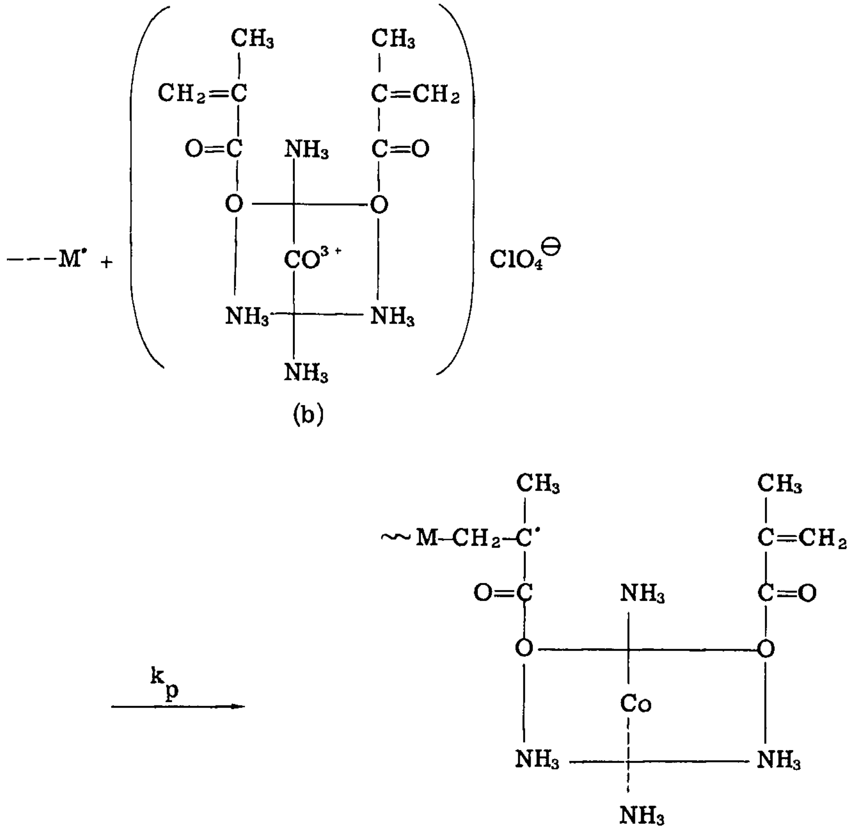
The radical homopolymerization of the metal monomers (a) and (b) and their copolymerization with MAA were carried out at pH 3 or 7 using persulfate-thiosulfate redox initiator. It was found that (a) could be successfully homopolymerized at pH 3 although the product contained a certain amount of monomeric units of MMA. On the other hand, the homopolymerization of (a) at PH 7 and that of (b) at pH 3 gave no polymeric product.

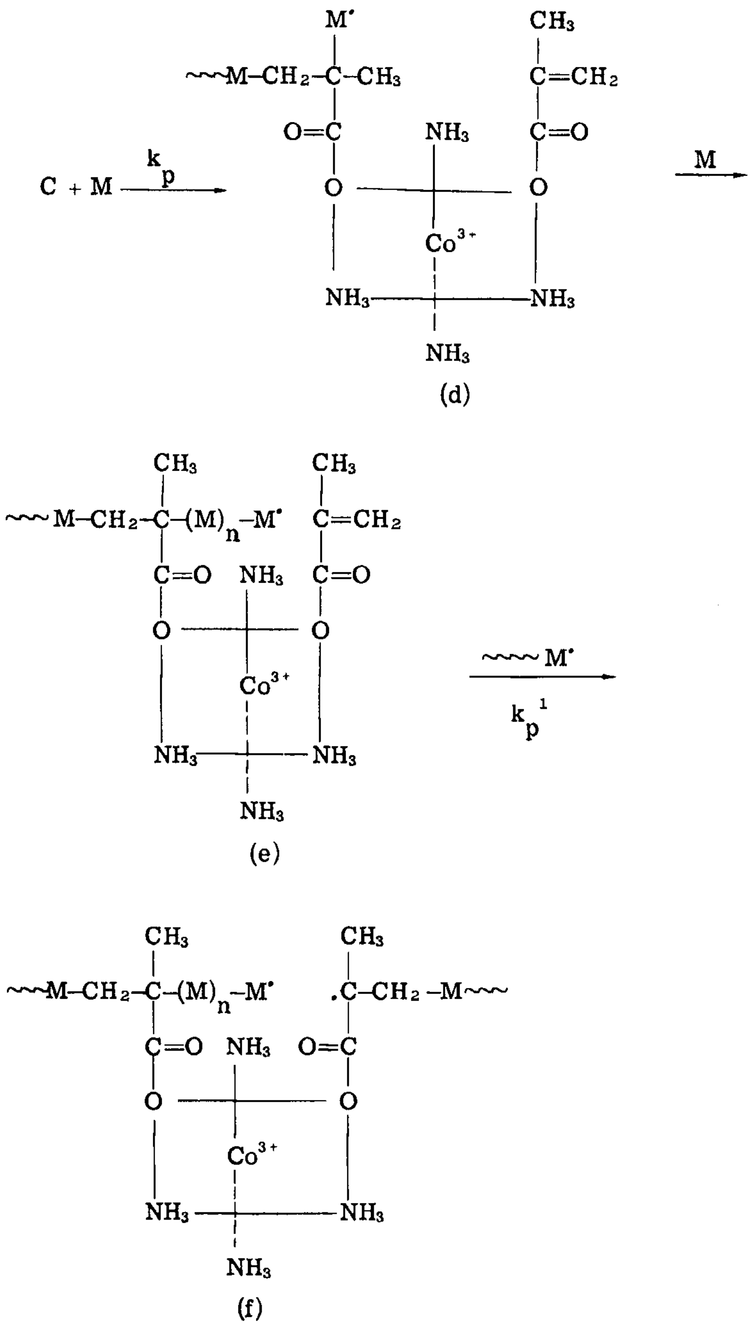
From the observed rate and spectral measurement it was evident that the metal complex monomer becomes incorporated more easily into the macromolecule at pH 7 than at pH 3. This might be due to electrostatic interactions between the reaction species (monomers and growing radicals). At pH 7 most MMA molecules are ionized (pK_a = 4.36) and this facilitates the incorporation of the positively charged metal complex monomer due to electrostatic interaction. At the same time, the addition of methacrylate anion to its radical would become unfavorable owing to electrostatic repulsion. The fact that (a) and (b) can be incorporated into the macromolecules to more than 50% means that sequences consisting of at least two monomeric units of (a) or (b) can be realized in spite of the extraordinary bulky group of the complex.

The copolymerization of (b) with methacrylic acid can be written in two possible ways.

Case 1

The growing chain reacts with only one of the two coordinated methacrylato residues in (b). The subsequent addition to the coordinated radical (c) takes place with another molecule of the monomer, etc. The methacrylato residue in the resulting macromolecule (d) may undergo cross-linking in the further course of the reaction.



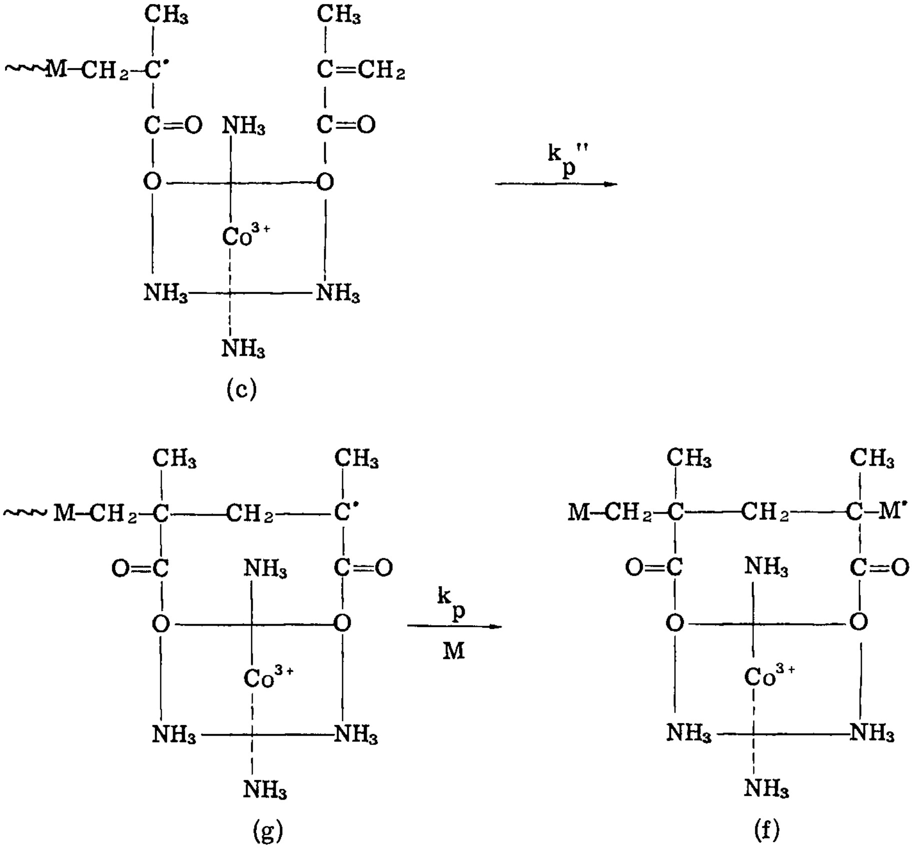

C + M
k
p
M
~~~~ M•
k
p
1
M•
~~~M–CH2–C–CH3
O=C
C=CH2
C=O
CH3
NH3
O
Co3+
NH3
(d)
~~~M–CH2–C–(M)n–M•
(e)
.C–CH2–M~~~
(f)
~~~~

where M = monomer, M• = growing radical end, and k_p and k_p^1 = apparent rate constant of propagation.

Case 2

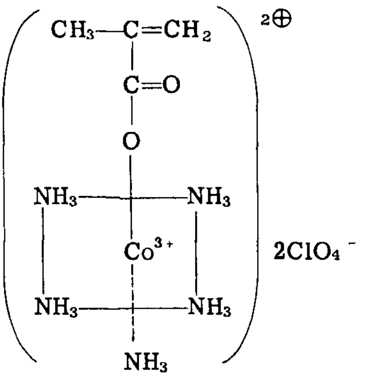
An intramolecular addition of a second methacrylate residue to the coordinated radical (c) takes place. This case will be realized when the reactivity of the second methacrylato residue is increased by the influence of the growing radical in the same complex or when the second methacrylato residue is sterically more favorable for the addition than the other molecules of the monomer.

The authors in their investigation could not reach a conclusion as to which sequence is true.

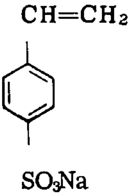


where $k_p'' > k_p$.

(3) Radical copolymerization of methacrylic acid coordinated to the Co(III) complex with other vinyl monomers. Osada et al. [26] synthesized a new type of alternative copolymer having -(ABA)- sequences obtained by radical polymerization of methacrylato pentamine cobalt(III) perchlorate (A) with sodium styrene sulfonate (B) in aqueous medium.



(A)

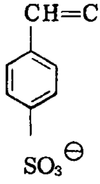


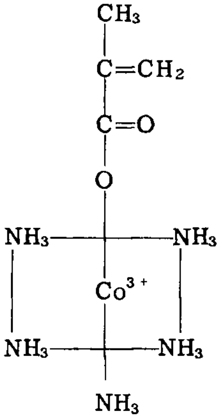
(B)

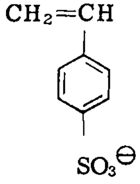
The radical copolymerization was carried out in aqueous medium at pH 1 at 50°C in an argon atmosphere using $K_2S_2O_8$ as initiator. Mixing aqueous solutions of both monomers produced an insoluble complex. By heating the complex at 50°C in aqueous perchloric acid, a homogeneous solution was obtained. The copolymerization of every system was accompanied by precipitation of the copolymers. From the results it was clear that the copolymers obtained contain 60-70% of a monomeric unit of sodium-styrene sulfonate in the range of a monomer feed from 20 to 80%. On the basis of this it was considered that the mole ratio of the monomeric units of (B) and (A) in these copolymers is 2:1. Alternative sequences such as –B–A–B– are reasonable, when ion-pairs like (c) are considered in the process of propagation. Due to their hydrophobic character, the formation of such ion-pairs in aqueous medium is more probable than that of ion-pairs of monomers with each counterion.

(4) Co(III)-acetylacetonates. The ability of various metal acetylacetonates to initiate radical polymerization and the mechanistic path of initiation were reported by Otsu et al. [4]. They observed that among all the metal-acetylacetonates, Mn(III)-acetylacetonate was much more effective, after which comes Co(III)-acetylacetonate. The rate of polymerization obeys the same rate equation as for Mn(III)-acetylacetonate:

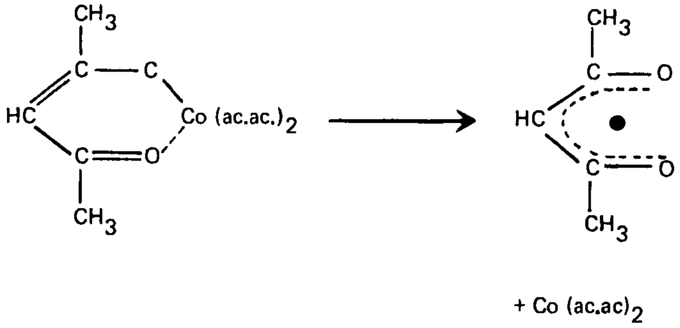
$$R_p = K^1 [M]$$


(B)


(C)


(B)

The initiating radical from the chelate is the same as in the case of Mn(III)-acetylacetonate, i.e., the acetylacetonate radical.



Fe(II) AND Fe(III) CHELATES

Metal chelates, especially metal-acetylacetonates, constitute a well-explored field [3-5, 20, 33-37] which has attracted the attention of chemists during the last few decades. A few reports have appeared regarding iron-chelate-initiated polymerization of vinyl monomers. Included in the reports are Fe(II)-acetylacetonate [38, 39], Fe(III)-dipivaloylmethide [40, 41], photopolymerization initiated by Fe(III)-salt saccharide systems [42, 43], tris-(phenanthroline)-Fe(III) complex [44], and iron-complexes of aromatic nitriles [45].

(1) Fe(II)-bis(acetylacetonate) system. The activity of bis-acetylacetonato-Fe(II) in initiating the radical polymerization of

vinyl monomers was recognized by Allen et al. [38]. Subsequently they observed that the activity of the complex toward vinyl polymerization is attributed to the presence of the ferric complex. The authors prepared a pure sample of Fe(ac.ac)$_2$ and found that its initiating abilities differ strikingly from Fe(III) (ac.ac)$_3$ [39]. Fe(II) (ac.ac)$_2$ is an extremely inefficient initiator of MMA polymerization. It is so inefficient that the authors suspected that the activity is probably due to trace impurities. On the other hand, false Fe(ac.ac)$_2$ and Fe(ac.ac)$_3$ are relatively active initiators. Fe(II)(ac.ac)$_2$ thus loses its anomalous status conferred earlier [38] by the authors when they cited it as an exception to the rule that only acetylacetonato complexes of higher oxidation states of transition metals are active initiators of radical polymerization.

(2) Fe(III)-dipivaloylmethide system. The behavior of the chelate ferric-dipivaloylmethide, Fe(DPM)$_3$, in vinyl polymerization and the true path of initiation was investigated by Nandi et al. [40, 41]. The chelate was found to be effective for initiating the radical polymerization of methyl acrylate (MA), MMA, and St. A direct decomposition of the chelate to yield an initiating radical was thought to be improbable. Studies carried out by the authors refute the possibility of thermal decomposition of Fe(DPM)$_3$. The thermal decomposition studies on a dioxane solution of Fe(DPM)$_3$ in nitrogen atmosphere failed to record any change in the concentration over a period of 360 min at 70°C. The concentration was determined by measuring the optical density at 273 nm. Also, experiment carried out under oxygen did not show any oxygen uptake or change in concentration of Fe(DPM)$_3$. Attempts on the estimation of any ferrous species formed during the entire period of heating under nitrogen or oxygen indicated that no reduction took place. These observations regarding the inertness of Fe(DPM)$_3$ by the authors was supported by Arnett et al. [46], who reported that Fe(DPM)$_3$ is rather inert and does not initiate oxidation of hydrocarbons, like the acetylacetonate chelate of iron. All these lend support to the fact that direct decomposition of the chelate is not responsible for radical production.

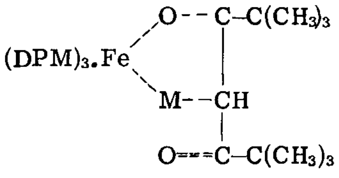
Another indication comes from the selectivity exhibited by the chelate. If, in fact, the chelate were responsible for the initiation of radical polymerization, then the chelate would not have discriminated among the monomers as supported by their results. The inability to do this weighs heavily against the possibility of direct decomposition. Moreover, this selectivity evidently suggests the involvement of the monomer in the initiation step.

It was thus suggested that there was formation of a new complex between the monomer and the chelate, and its subsequent decomposition yielded the initiating radical. This fact easily explains the selectivity of the chelate and a monomer order greater than unity. Spectral studies undertaken with different monomers as solvents and Fe(DPM)$_3$ as the solute show significant changes in the ultraviolet spectrum of the chelate. Thus, when the ultraviolet spectrum of the chelate was taken in solvents such as benzene, alcohol, chloroform, and carbon tetrachloride, the chelate gave its characteristic peak at 273 nm. In solutions of St, MA, and MMA, the previous peak shifted to 308 or 298 nm.

Sites of Interaction

The interaction between the chelate and monomer greatly affects the ligand part of the chelate as reflected from the perturbation of the $\pi \rightarrow \pi^*$ transition of the coordinated ligand. There are instances of the β-diketonates complexing with the solvent molecules [47]. Thus, for the chloroform solutions of Fe(ac.ac)$_3$, a trifurcated hydrogen bond involving the three oxygens of the chelate ring and the hydrogen of the chloroform has been suggested. Conditions like the geometrical array of atoms in the octahedral Fe(DPM)$_3$ and the spatial configuration of the unsaturated monomer with which the chelate interacts, render such a structure unlikely in this case, however. The direct interaction between the central metal ion of the chelate and the monomer also seems improbable, since this should have left the $\pi \rightarrow \pi^*$ transition of the coordinated ligand undisturbed.

These observations favor structure (I), where the chelate ring is appreciably pushed aside and probably opened up by the monomer.



(I)

where M = monomer. A similar route was also suggested by Bamford et al. [9, 48] for Mn(FAc.ac)$_3$-initiated polymerization.

Propagation and Termination

The propagation step in the Fe(DPM)$_3$-initiated system seems to be of the standard type. The values are in good agreement with those reported in the literature for other free radical systems. The overall energy of activation, rate of initiation, range of molecular weight, and rate of polymerization all point to a normal free radical step. The square-root dependence of R_p on the chelate concentration implies a bimolecular nature of the termination reaction.

All these conclusions derived from experimental data indicate a two-stage initiation step:

$$\mathrm{Fe(DPM)_3} + \mathrm{M} \longrightarrow \mathrm{Fe(DPM)_3}\text{----}\mathrm{M}$$

$$\mathrm{Fe(DPM)_3}\text{---}\mathrm{M} \longrightarrow \mathrm{R^{\cdot}} + \text{other species}$$

The detection of Fe(II) ion in the polymerization system and also when the chelate is heated in the presence of monomer establishes that the other species could be Fe(II) from the chelate. These two steps for the initiation yield an expression of the following form for R_i:

$$R_i = k_d[\mathrm{Fe(DPM)_3}\text{---}\mathrm{M}]$$

Consequently the rate of polymerization will be

$$R_p = k_p[\mathrm{M}](k_d/k_t)[\mathrm{Fe(DPM)_3}\text{---}\mathrm{M}]^{1/2}$$

This kinetic condition, which calls for a monomer order of 3/2 and an initiator exponent of 1/2, is satisfactorily obeyed by the $\mathrm{Fe(DPM)_3}$-initiated system.

(3) Photoinduced vinyl polymerization in the presence of iron chelate. Although the photopolymerization of vinyl monomers by Fe(III)-salt has received considerable interest during recent years [49-51], not much attention has been paid to the photopolymerization initiated by Fe(III) chelate, except for a few reports by Okimoto et al. [52-55]. These authors have reported the photoinduced vinyl polymerization of AN and acrylamide (AM) by Fe(III)-salt-saccharide systems. Stockmayer et al. [52] have studied the kinetics of photopolymerization of vinyl monomers with Fe(III)-salt-saccharide systems in aqueous medium and found that the accelerating effect caused by the addition of a saccharide to the reaction system containing Fe(III)-salt was mainly concerned with the initiation step, and the photochemical reaction scheme of Fe(III) ion with saccharide is quite similar to that of the redox reaction with the Ce(IV)-saccharide system [56].

Okimoto et al. [52-55] have studied various kinetic aspects in the photoinduced Fe(III)-salt-saccharide systems in vinyl polymerization. A number of ferric salts such as Fe(III)-nitrate, Fe(III)-perchlorate, Fe(III)-chloride, Fe(III)-ammonium sulfate, and potassium ferricyanide, coupled with a multitude of saccharides such as glucose, fructose, α-methyl-D-glucose, lactose, maltose, and sucrose, have been utilized for polymerization purposes. The effect of various neutral salts and additives such as methyl alcohol, ethyl alcohol, isopropyl alcohol, t-butyl alcohol, ethylene glycol, glycerol, cyclohexanol, cis-1,2-cyclohexane diol, formaldehyde, and butraldehyde on the polymerization process has been investigated.

From their kinetic results, the following reaction scheme for such systems has been suggested.

Polymerization Scheme

Although there exist some problems based upon heterogeneity of the polymerization system and the efficiency of photoabsorption, the complex formation between the Fe(III) ion and saccharide was clearly indicated spectrophotometrically, and consumption of both the Fe(III) ion and glucose during photoirradiation was confirmed. Similar complex formations of Fe(III)-gluconate [57] and sugar-Fe(III) [58] have been proposed. Further, it was reasonably assumed that at lower Fe(III) ion concentrations, mutual termination of the polymer radicals predominates, while at higher Fe(III) ion concentrations, termination of the polymer radicals by Fe(III) ion and/or reaction of a primary radical with Fe(III) ion becomes significant.

Initiation:

$$\mathrm{Fe(III)} + \mathrm{SH} \overset{K}{\rightleftharpoons} \text{complex} \xrightarrow{h\nu} \mathrm{Fe(II)} + \mathrm{S}^{\bullet} + \mathrm{H}^{+}$$

$$\mathrm{S}^{\bullet} + \mathrm{Fe(III)} \xrightarrow{k_0} \text{inactive product}$$

$$\mathrm{S}^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{M}^{\bullet}$$

Propagation:

$$\mathrm{M}^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_2^{\bullet}$$

$$\mathrm{M}_2^{\bullet} + \mathrm{M} \longrightarrow \mathrm{M}_3^{\bullet}$$

$$\vdots$$

$$\mathrm{M}_{n-1}^{\bullet} + \mathrm{M} \longrightarrow \mathrm{M}_n^{\bullet}$$

Termination:

$$\mathrm{M}_n^{\bullet} + \mathrm{M}_m^{\bullet} \xrightarrow{k_{t_1}} \text{Polymer}$$

$$\mathrm{M}_n^{\bullet} + \mathrm{Fe(III)} \xrightarrow{k_{t_2}} \text{Polymer} + \mathrm{Fe(II)} + \mathrm{H}^{+}$$

where M = monomer, $\mathrm{M}^{\bullet}$ = monomer radical and $\mathrm{M}_n^{\bullet}$ ($\mathrm{M}_m^{\bullet}$) = polymer radical.

(4) Tris-(phenanthroline)-Fe(III) system. The interaction of polymer radicals with transition metal salts and complexes has been reported by various workers [59-63]. Although the transition metal ion-chelates have been found to be free radical initiators for vinyl polymerization, they sometimes also behave as inhibitors, i.e., they are capable of terminating polymer radicals. Such a phenomenon was reported by Chetia et al. [64] in the polymerization of styrene initiated by 2,2'-azobisisobutyronitrile (AIBN) in DMF at 60° C. The authors found that the tris-(phenanthroline)-Fe(III) complex has no accelerating effect on the polymerization process, i.e., it is incapable of interacting with AIBN, leading to its facile decomposition to generate initiating radicals, and this might have caused an enhancement in the rate. On the contrary, it was found to be an ideal retarder or inhibitor. It terminates the growing polymer radicals in a manner similar to that of transition metal salts like $FeCl_3$:

$$CH_2\text{–}Ph + [Fe(Phen)_3]^{3+} \xrightarrow[DMF]{k_z} \sim\sim\sim CH{=}CH\text{–}Ph$$

$$+ [Fe(Phen)_2]^{2+} + H^+$$

COPPER CHELATE

Like other transition metal ion chelates, various kinds of Cu(II)-chelates have been found to initiate radical homopolymerization and copolymerization, either alone or when coupled with organic peroxides and hydroperoxides. Examples of such reactions are cited below.

(1) Cu(II)-acetylacetone in t-butylhydroperoxide initiated polymerization of methyl methacrylate. The catalytic effect of Cu(II)-acetylacetonate, Cu(aa)$_2$, on t-butylhydroperoxide (TBHP) decomposition and peroxide-initiated polymerization was reported by Indicator et al. [65-67]. The polymerization of MMA and the decomposition of TBHP have been determined in the presence and as well as in the absence of Cu(aa)$_2$ in 1-chloroacetone and DMSO at 60° C. From the results obtained, the catalytic effect of Cu(aa)$_2$ was clearly evident for both mechanisms. Peroxide decomposition is faster in 1-chlorooctane than in DMSO but polymerization rates in DMSO are higher. The efficiency (f) of the chain reactions by TBHP decomposition is consequently about 5-10 times greater in DMSO than in 1-chlorooctane.

From the kinetic results the following rate expressions for TBHP decomposition (R_d), polymerization initiation rate (R_i), and rate of polymerization (R_p) in the presence of Cu(aa)$_2$ and the rate of polymerization ($R_p{}^0$) in the absence of Cu(aa)$_2$ for both solvents have been derived.

For 1-Chlorooctane:

1. $R_d = k_d[\mathrm{Cu(aa)_2}]^{0.32}[\mathrm{TBHP}]^{0.60}[\mathrm{MMA}]^{0.53}$

2. $R_i = fR_d$

3. $R_p - R_p{}^0 = k_p[\mathrm{MMA}]^{0.85}[\mathrm{Cu(aa)_2}]^{0.18}[\mathrm{TBHP}]^{0.29}$

$$= K[\mathrm{MMA}]^{1.0}R_i{}^{1/2}$$

For DMSO:

4. $R_d = k_d[\mathrm{Cu(aa)_2}]^{0.69}[\mathrm{TBHP}]^{1.0}[\mathrm{MMA}]^{1.0}$

5. $R_i = fR_d$

6. $R_p - R_p{}^0 = k_p[\mathrm{MMA}]^{1.5}[\mathrm{Cu(aa)_2}]^{0.30}[\mathrm{TBHP}]^{0.50}$

$$= K[\mathrm{MMA}]^{1.0}R_i{}^{1/2}$$

where R_d = TBHP decomposition

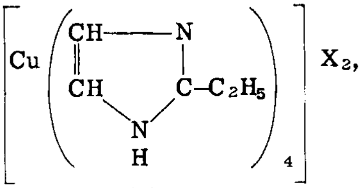
R_i = polymerization initiation rate

f = initiation efficiency

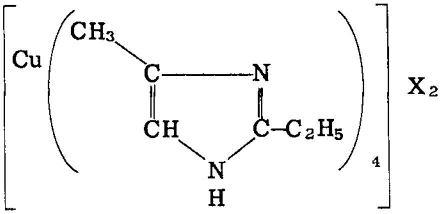
R_p = rate of polymerization in the presence of $\mathrm{Cu(aa)_2}$

$R_p{}^0$ = rate of polymerization in the absence of $\mathrm{Cu(aa)_2}$

(2) Cu(II)-imidazole complex initiated vinyl polymerization. In a series of interesting communications, Takemoto et al. [68-71] have shown that a system of Cu(II) ion and nylon 6, its oligomers, and several amine compounds are effective for radical initiation vinyl polymerization. The same authors have also noticed that Cu(II) complexes of some heterocycles, particularly imidazole and its derivatives, can initiate the free radical polymerization of acrylonitrile [72]. Imidazole is one of the metal binding groups both in natural metalloproteins (i.e., carboxypeptidase, myoglobin, and hemoglobin) and in metalloprotein complexes. A large number of Cu(II) complexes with imidazole and its derivatives were successfully synthesized [73].



(a)



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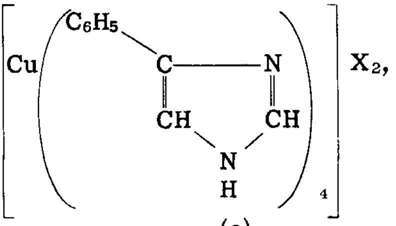

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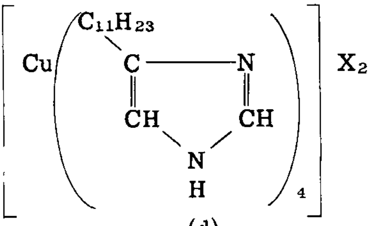

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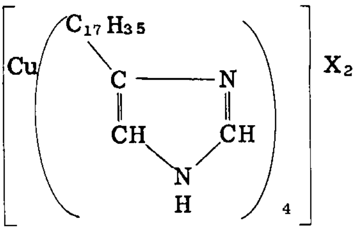


(e)

(where X = ClO_4, NO_3, Cl, and Br)

The kinetics of vinyl polymerization involving such Cu(II)-imidazole complexes has been investigated [74]. Some imidazole complexes of Cu(II) such as $[Cu(ImH)_2]X_2$ have also been found to initiate vinyl polymerization. The reactions were carried out in a DMSO medium. From the results obtained it was clear that the rate of polymerization depends on the kind of anion in the complex. In the case of NO_3^- and ClO_4^- the polymerization proceeded rather smoothly. However, in the case of halogen anions such as Cl^- and Br^-, polymerization could not be initiated. Further, it was found that the rate of polymerization (R_p) was directly proportional to the initiator concentration under the conditions that $[I] < 2 \times 10^{-2}$ M and $[I] > 2 \times 10^{-2}$ M, R_p with respect to [I] was 1/4. The following rate expressions were derived:

$$R_p = k[I][AN]^2 \qquad ([I] < 2 \times 10^{-2}\ \underline{M})$$

$$R_p = k[I]^{1/4}[AN]^2 \qquad ([I] > 2 \times 10^{-2}\ \underline{M})$$

These equations seem to be somewhat peculiar because free radical polymerizations generally satisfy the so-called square-root relationship. In order to explain such deviations, it was proposed that there is interaction between the AN monomer and the initiator complex followed by a monomolecular termination:

$$I + AN \xrightarrow{k_i} R^\bullet, \qquad V_i = k_i[I][AN]$$

$$\sim\sim AN^\bullet \xrightarrow{k_t} P, \qquad V_t = k_t[\sim\sim AN^\bullet]$$

In the stationary state,

$$\frac{d[AN^\bullet]}{dt} = k_i[I][AN] - k_t[\sim\sim AN^\bullet] = 0$$

$$[\sim\sim AN^\bullet] = \frac{k_i}{k_t}[I][AN]$$

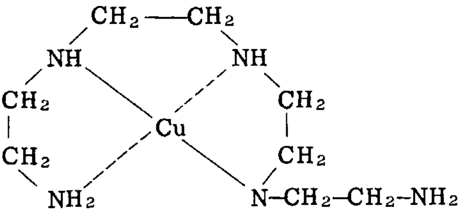
$$R_p = k_p[AN][\sim\sim AN^\bullet] = k_p\frac{k_i}{k_t}[I][AN]^2$$

Further information that the reaction proceeds via the complex formation between Cu(II)-chelate and AN with subsequent initiation to polymer was obtained by spectral evidence, where the reduction of Cu(II) to Cu(I) was determined by ESR measurement.

In order to get such information about the mechanism for the decomposition of imidazoles-Cu(II) complexes in some detail, ESR spectra for the $Cu(ImH)_4(NO_3)_2$/AN systems were measured at 60°C in sealed capillary tubes. In the spectral study four signals characteristic of the bivalent Cu(II) species were obtained. The ESR signals then decreased in intensity with an increase in time, and after 2 h they disappeared completely. These observations suggested that the paramagnetic Cu(II) complex was reduced to the diamagnetic Cu(I) complex during polymerization. Polyacrylonitrile (PAN) obtained by polymerizing AN by $Cu(ImH)_4(NO_3)_2$ was found to form a complex with Cu(I) as evident from spectral studies.

(3) Cu(II)-oligo(n)ethylene-(n + 1) amine systems. Takemoto et al. [68] have shown that nylon 6 can initiate the polymerization of MMA

and other vinyl monomers in CCl_4 via a free radical mechanism. The role of trace of metals for the initiating system in problem was also pointed out. In order to clarify the initiation mechanism of the system the polymerization of vinyl monomers was also investigated with the system Cu(II) ion and nylon 6 oligomers having a definite chemical structure in aqueous media. It was confirmed that the complex of the Cu(II)-amine type plays an important role in the initiation process. The substantial problems in these preceeding works, particularly the behavior of the Cu(II) ion, have been thoroughly investigated by the authors [70]. The vinyl polymerization was carried out in the presence of Cu(II) ion, oligon (n) ethylene (n + 1) amines as multident ligands, and CCl_4 in in order to clarify the relationship between the coordination character of the Cu(II)-amine complexes and their activity for initiating vinyl polymerization. Among the ligands used, trien seems to form the most reactive Cu(II)-complex, and the order of reactivity was found to be trien > tetraen > dien > en. These reactivities varied with the changing molar ratio of Cu(II) ion to amine. From the experimental results it was found that polymerization did not proceed if the reaction system was devoid of the Cu(II) ion. Also, polymerization could not proceed in the case where Cu(II) and amine were present in an equimolar ratio. On the contrary, the Cu(II)-tetraen system showed moderate activity even in the case where it was used in an equimolar ratio, probably because of the existence of a residual free amino group in the quinquidentate ligand:



For Cu(II)-dien and Cu(II)en systems, the maximum point of conversion shifted to a lower concentration of Cu(II) ion. These observations can be explained by the lower stability constants of bis-dien and bis-en-Cu(II) complexes as compared with those of trien and tetraen-Cu(II) complexes.

The following reaction mechanism was suggested. It readily explains all the experimental results.

$$\text{Cu(II)-trien} + \text{trien} \longrightarrow \text{(Cu(I)-complex} + (\overset{\bullet}{\text{t}}\text{rien})$$

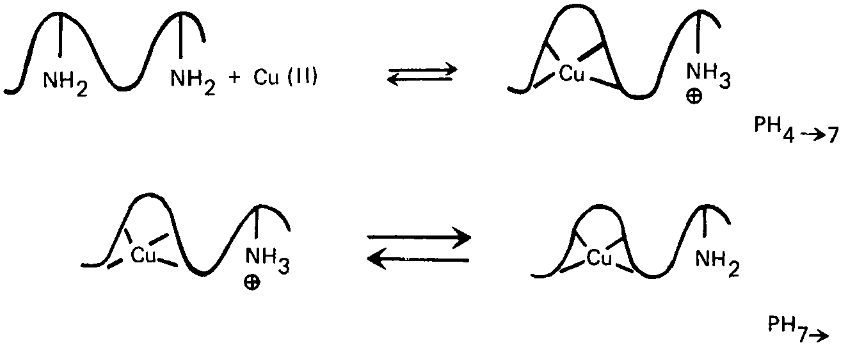
$$\text{trien} + CCl_4 \longrightarrow \overset{\bullet}{C}Cl_3 + \text{nonradical product}$$

$$\overset{\bullet}{C}Cl_3 + \text{AN} \longrightarrow \text{polymer}$$

The above mechanism is identical to that suggested by Smith et al. [75].

(4) Polyvinyl amine Cu(II) chelates. Recently there has been interest in the catalytic action of chelate polymers in connection with their chemical reaction in biological materials. Takemoto et al. [76, 77] observed that polyvinylamine-Cu(II) chelate is effective in initiating vinyl polymerization of AN, MMA, and St in the presence of CCl_4. Using the Cu(II) chelate of 1,3-diaminopropane, the initiation was also examined and compared with initiation by the polymeric chelate. Since the structure of the polymeric chelate was assumed to depend on the pH value of the reaction system and on the reaction temperature, the polymerization of the monomers was carried out at different temperatures and particularly in aqueous solution with different pH values.

From the results obtained under variable circumstances, the authors reached the following conclusions: The formation of Cu(II) complexes proceeds with a rise in the pH value of the reaction system and is completed near pH 7. After the complex is formed, dissociation of the free amino units subsequently occurs in the pH ranges from 7 to 10. Above pH 10 the concentration of the OH^- ion tends to increase.



This fact suggests that some free base might precipitate in the initiation mechanism above pH 10, where both the polymer chelate and the 1,3-diaminopropane chelate are active enough to initiate polymerization. A peak in the conversion curve at pH 8 was observed and was attributed to the structure of the polymeric chelate at that pH. The form of the polymeric chelate might change from a monodentate to a tetradentate chelate with a rise in pH value from 4 to 7. This might give rise to the concentration of polymer chains forming rounded structures around each metal atom. This was further confirmed by a viscosity change in the polymer chelate. The concentration of the polymer chain might promote the interaction between the metal complex and free amino units in the polymer chain. With pH changes from 8 to 10 the polymeric chelate becomes rigid. This might prevent the interaction between complex and free amine, so that the rate of polymerization tends to decrease. The following mechanism for initiation was suggested:

$$\mathrm{Cu(II)} + \mathrm{R{-}NH_2} \rightleftharpoons \mathrm{Cu(II)\ complex}$$

$$\mathrm{Cu(II)\ complex} + \mathrm{R{-}NH_2} \longrightarrow \mathrm{Cu(I)\ complex} + \mathrm{R{-}\overset{\bullet\,+}{N}H_2}$$

$$\mathrm{R{-}\overset{\bullet\,+}{N}H_2} \longrightarrow \mathrm{R{-}\overset{\bullet}{N}H} + \mathrm{H^+}$$

$$\mathrm{R{-}\overset{\bullet\,+}{N}H_2} + \mathrm{CCl_4} \longrightarrow \mathrm{R{-}NHCl} + \mathrm{\overset{\bullet}{C}Cl_3} \qquad (\mathrm{R^\bullet} = \mathrm{R{-}\overset{\bullet}{N}H} \text{ or } \mathrm{\overset{\bullet}{C}Cl_3})$$

$$\mathrm{R^\bullet} + \mathrm{M} \longrightarrow \mathrm{R{-}M_1{}^\bullet}, \text{ etc.}$$

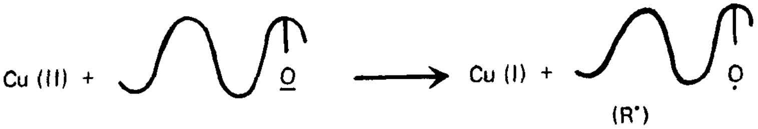
(5) Polyvinyl alcohol-Cu(II)-chelates. The efficiency of polyvinyl alcohol-Cu(II) chelate to initiate vinyl polymerization in CCl_4 medium was noticed by Takemoto et al. [78, 79] and by Enmons [80]. The polymerization initiated by 1,3-propane diol-Cu(II) chelate was also examined and the results were compared with the case in which the polymer chelate was used. Since the structure of the polymer chelate was thought to depend on the condition of polymerization on the metal-ligand mole ratio, the temperature, and the pH value of the initiator system, polymerization was carried out under different reaction conditions. The pH dependence of the polymerization was investigated with the aid of the titration data of a poly(vinyl alcohol)/Cu(II) solution.

From the experimental results it was found that the order of reactivity of the monomers is MMA > St ≫ AN. For the behavior of the initiation of poly(vinyl alcohol)-Cu(II) chelate it was assumed that the formation of the Cu(II)-chelate is started with a rise in the pH value of the initiator system and is completed at about pH 8.

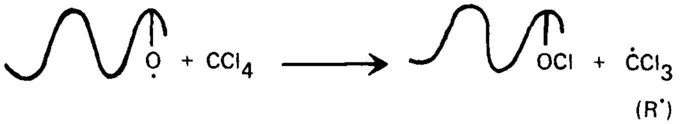
From the result of the titration study reported, the molar absorptivity and the intrinsic viscosity of poly(vinyl alcohol)-Cu(II) chelate solution were computed, from which it was clear that the formation of the chelate was nearly completed at about pH 8. After completion of the Cu(II) chelate formation, precipitation of the polymer chelate begins to occur gradually above pH 8. Above pH 10 the concentration of OH^- ion tends to increase in the initiator system. In other words, in the pH range from 5.6 to 8 the conversion increases with a rise in concentration of poly(vinyl alcohol)-Cu(II) chelate. In the pH range from 8 to 10 the increase in conversion is temporarily retained owing to precipitation of the polymer chelate. The authors could not explain why the conversion shows a drastic increase above pH 10, i.e., how the OH^- ions present in excess may participate in increasing the rate of polymerization.

At near pH 10, no effect of neutral salt was observed because the polymer chelate was rigid enough and the initiation reaction might be caused by an intramolecular reaction in the polymer chelate, as pointed out by Shirai et al. [81].

However, at pH 5.6 the polymerization was initiated only in the absence of neutral salts. Conformational changes are expected in many polyelectrolytic solutions by adding the salt to a solution of the polyelectrolytes. These changes are reflected in the viscosity behavior of the solutions [82]. Due to these considerations as well as to the fact that no chelate formation was observed at pH 5.6, the initiation at pH 5.6 without neutral salt was assumed to be an intramolecular reaction:



The radical formed at pH 5.6 might initiate polymerization or it can interact with CCl₄ to yield the trichloromethyl radical which can also initiate polymerization:



$$M + R^{\bullet} \longrightarrow R - M_i$$

These conclusions were supported by spin trapping and gelation studies [79].

(6) Cu(II)-chelate-cumene hydroperoxide (CHP) system. It is well known that metal compounds can affect the course of the free radical process. In the free radical polymerization of vinyl and diene monomers, metal compounds are widely used in conjunction with organic peroxides and hydroperoxides as components of a redox system. The

participation of a given metal ion in the free-radical process is also strongly influenced by other factors such as the kind of ligand which is bound to the metal ion and by the presence of complexing agents in the reaction system [83, 84].

Quite a large number of papers by Barton et al. [84-87] have appeared in this field. They have reported on the influence of various metal complexes and complexing agents on the course of cumene hydroperoxide decomposition in nonaqueous solutions. The rate of cumene hydroperoxide decomposition in the presence of Cu(II)-acetate was significantly affected by the addition of amino alcohols into the reaction system. It was suggested that the decomposition of cumene hydroperoxide took place via a complex formed between the components of the reaction system. However, the individual components of the catalytic system did not accelerate the decomposition reaction, provided they were applied separately.

It was noticed by the authors that the rate of MMA polymerization is essentially higher in the system CHP/Cuac/2-aminoethanol (AE) than in other systems, whereas the system Cuac/AE does not initiate the polymerization of MMA at all. Further study was also conducted to find the influence of a number of amino alcohols such as 2-N-(2-aminoethyl)aminoethanol (AEE), 1-amino-2-propanol (AP), AE, 2-diethylaminoethanol (DAE), 2,2'-iminodiethanol (IDE), 2-dibutylaminoethanol (BAE), 2,2'-N-phenyliminodiethanol (FDE), and 2,2',2''-nitrilotriethanol (NTE). It was found that the efficiency of the initiating system is higher if an amino alcohol with a greater number of nitrogen atom is used (AEE), whereas the number of alcoholic groups in an amino alcohol influences this efficiency to a much lesser degree (IDE in comparison with AE). From a study of the rate parameters under variable conditions, especially at variable temperatures, the following mechanism for the reaction was suggested.

Copper acetate is known to exist in nonpolar solvents primarily in the form of its dimer. After the addition of amino alcohol it can dissociate into the monomeric form, i.e., the equilibrium expressed by Eq. (1) is shifted to the left side:

$$2\text{Cuac} \xrightleftharpoons{K_A} (\text{Cuac})_2 \tag{1}$$

This fact is experimentally supported by ESR measurements [85] as well as by spectroscopic studies. After the addition of AE to Cuac solution, the absorption band at 340 nm, which according to the literature [88] corresponds to the Cu–O band in binuclear complexes, has disappeared in the spectrum of Cuac at an AE:Cuac ratio of 0.5:1. The disappearance of this band was observed in methanol, benzene, and MMA. However, although a new absorption band at 350-360 nm simultaneously developed in methanol, it does not appear in benzene or MMA in which only a shift in the absorption maximum in the visible region toward shorter wavelengths (d-d transition) is observed. This shift depends on the concentration of the AE added.

The results obtained by the study of CHP decomposition in the presence of Cuac and AE as well as by the study of MMA polymerization initiated by the system CHP/Cuac/AE, after confirmation with some data known from the literature concerning complex formation from Cuac and various ligands, allowed the authors to express an idea about the creation of a complex between Cuac and AE "in situ."

$$\text{Cuac} + \text{A}^{\bullet}\text{E} \xrightleftharpoons{K_L} \text{Cuac(AE)} \qquad (2)$$

Further, in the presence of CHP a complex of Cuac, AE, and CHP can be formed, which is a precursor of catalytic CHP decomposition, the product of which initiated MMA polymerization by the usual radical mechanism.

(7) Cu(II)-2-aminoethanol system. It is now almost 19 years since it was found that certain metal chelates with O,O donor atoms in the ligand molecule yield free radicals on thermal decomposition [89]. Since then the interest of many workers has been concentrated on the study of the kinetics and mechanism of initiation of radical polymerization of vinyl monomers under the effect of metal chelates as discussed previously.

The selectivity of Cu(II)-2-aminoethanolate toward radical polymerization of vinyl monomers was reported by Barton et al. [90]. They found that Cu(II)-2-aminoethanolate (Cumea) initiates the polymerization of MMA but not that of St and AN. From the polymerization results it was found that Cumea is not an inhibitor of the free radical polymerization of MMA and St and that it acts as an inhibitor only for some monomers i.e., it is a selective initiator. Cumea also acts selectively in polymerization initiated by AIBN. The addition of Cumea into the system MMA-AIBN enhances the rate of polymerization as compared with the rate in the system MMA-AIBN without Cumea. The square of the rate of polymerization in the combined system is approximately equal to the sum of the squared polymerization rates in the MMA-AIBN and MMA-Cumea systems, suggesting that here initiation by AIBN and by Cumea is additive in this case without further influence of Cumea on polymerization. On the contrary, the rate of polymerization in the system AN-AIBN will be retarded by the addition of Cumea. The addition of free ligand AE to the system Cumea-vinyl monomer enhances the rate of polymerization in the case of MMA and St. Although no polymerization in the system Cumea-AN was observed, the reverse is true for the system Cumea-AN-AE.

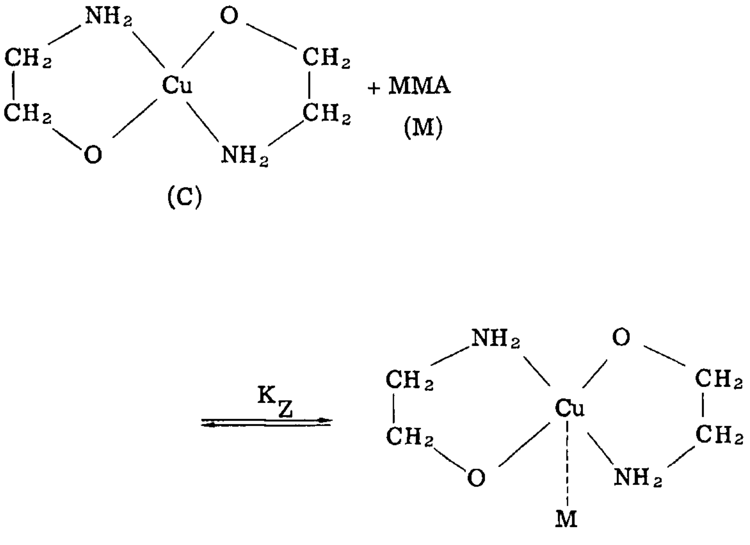
The polymerization reactions were studied under variable conditions. The effect of a number of amino alcohols and organic halogen compounds was also studied. It was found that if, instead of free AE, another amino alcohol is added to the system, the initiating ability of the system decreases and is dependent on the substitution of amino alcohol. The rate of polymerization of MMA and AN falls in the order aminoethanol > 1-amino-2-propanol > 2,2'-iminodiethanol ≈ 2-diethylaminoethanol ≥ ephedrine. The polymerization of styrene did not change on addition of any ligands. The addition of carbon tetrachloride to the Cumea/vinyl monomer leads to polymerization. In this case the reactivity of the monomers was found to be in the order St < MMA < AN.

Reaction Mechanism and Rate Law

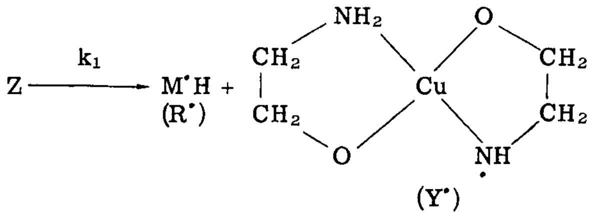
From the kinetic results obtained under variable conditions, it was proposed that Cumea can initiate free-radical polymerization in two ways.

(a) In the absence of reducing agents such as free amino alcohol and/or CCl_4, Cumea initiates only the polymerization of MMA, i.e., in this case Cumea acts as a selective initiator. The suggested mechanism may be qualitatively described as follows.

In the reaction between MMA (M) and Cumea (C), the first step involves the formation of an unstable complex (Z). The complex (Z) subsequently decomposes via hydrogen transfer from the amino group of the ligand to monomer to produce the initiating radical (R•), which initiates polymerization:

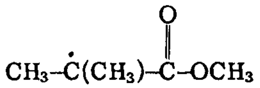


(3)



(4)

where $R^\bullet \cong M^\bullet H \cong$



$$CH_3\text{-}\dot{C}(CH_3)\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OCH_3$$

This assumption is corroborated by the fact that N-hydrogen atoms of amino alcohols bonded to Cu(II) ion are easily abstractable as can be judged from their reaction with the N:N-diphenylpicrylhydrazyl (DPPH) stable radical [91]. Radicals with an unpaired electron on the nitrogen atom prepared from Cu(II)-aminoalcoholates were identified by the Barton et al. in their papers [91, 92].

The monomer radical M•H initiates polymerization:

$$\underset{(R^\bullet)}{M^\bullet H} + M \xrightarrow{k_2} M_2{}^\bullet H\ (P^\bullet) \qquad (5)$$

$$P_n{}^\bullet + M \xrightarrow{k_3} P^\bullet_{n+1}$$

The polymeric radical (P•) decays in reaction with Cumea:

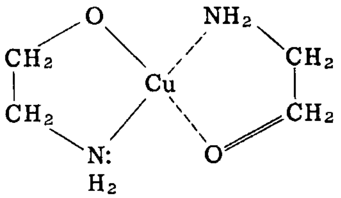
$$P^\bullet + C \xrightarrow{k_4} P_nH + Y^\bullet \qquad (6)$$

The complex radical Y• may decay by further reaction:

$$Y^\bullet \xrightarrow{k_5} (\text{reduced } Y + \text{oxidation products of ligand})$$

$$\longrightarrow \text{complex of } Cu^+ \qquad (7)$$

where the Cu^+ complex could be (2-aminoethanol-N,O)Cu(I)-2-aminoethanolate:



The complex radical $Y^\bullet$ may also decay in a bimolecular termination reaction:

$$Y^\bullet + Y^\bullet \xrightarrow{k_6} Y\text{–}Y \tag{8}$$

(b) In the presence of reducing agents the polymerization of MMA is initiated by the free-radicals arising from the reaction between Cumea (C) and the reducing complexing agent (L). The reaction between monomer and Cumea is then negligible because the monomer is a relatively weak complexing agent in comparison with L. The monomer does not take part in the formation of the initiating radical ($R^\bullet$), which is connected with a loss of selectivity of Cumea in the initiation of polymerization of vinyl monomers. In such a situation the mechanism of the polymerization reaction can be described as follows:

$$C + L \overset{K_Q}{\rightleftharpoons} Q \tag{9}$$

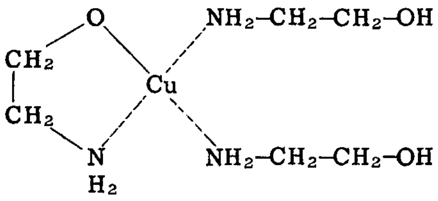
$$Q \xrightarrow{k_1'} R_1' + \text{reaction products} \tag{10}$$

$$R_1^\bullet + M \xrightarrow{k_2'} P^\bullet \tag{11}$$

$$P_n^\bullet + M \xrightarrow{k_3'} P_{n+1}^\bullet \tag{12}$$

$$P^\bullet + P^\bullet \xrightarrow{k_4^\bullet} P\text{–}P \tag{13}$$

The initiating radical formed by homolytic dissociation of the Cu–O band in the complex Q is the 2-aminoethoxyl radical ($^\bullet$O–CH$_2$–CH$_2$–NH$_2$) and its isomer the 2-hydroxyethylaminyl radical (HO–CH$_2$–CH$_2$–$\dot{N}$H). The reaction products containing Cu$^+$ is probably bis(2-aminoethanol)-Cu(I)-2-aminoethanolate:



On the basis of Eqs. (9)-(13), for a stationary concentration of radicals in the system the following relation was obtained:

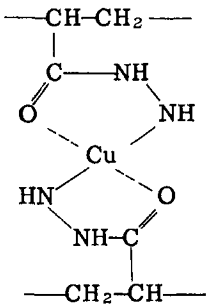
$$k_1'[Q] = k_2'[R_1^\bullet][M] = k_4'[P^\bullet]^2 \tag{A}$$

and after expressing the concentration of the complex (C) from Eq. (9) by using the approximation $[L - Q] = [L]$ if $K_Q \ll 1/[L]_0$, the rate of polymerization (R_p) can be expressed as

$$R_p = k_3 \left(\frac{k_1'K_Q}{k_4'}\right)^{0.5} [\text{Cumea}]_0^{0.5} [\text{AE}]_0^{0.5} [M] \tag{B}$$

This is in good agreement with the experimentally found order with respect to Cumea ($n_{\text{Cumea}} = 0.44 \pm 0.07$) and AE ($n_{\text{AE}} = 0.53 \pm 0.07$).

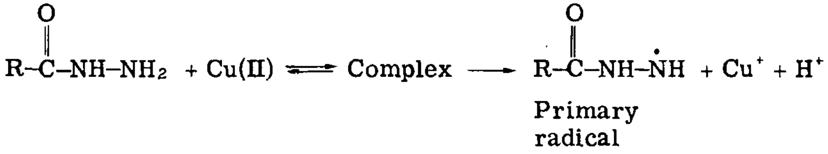
(8) Cu(II)-chelate of polyacrylic hydrazide. Recently there has been much interest in exploring the catalytic action of chelate polymers in connection with biological materials [93-95]. The use of the Cu(II)-chelate of polyacrylic hydrazide as the initiator of radical polymerization was reported by Machida et al. [96, 97]. One of the most interesting aspects of their report is that the polymerization of vinyl monomers can be carried out even at ordinary temperatures. The polymerization of a number of vinyl monomers was carried out in homogeneous medium, except those of butylacrylate and St. It was found that acrylate monomers are readily polymerized by the chelate, but acrylic acid, St, and 2-methyl-N-vinylimidazole were not polymerized. As corresponding monomeric models, the copper-chelates of acethydrazide, propiohydrazide, and benzhydrazide were also investigated for comparison. The polymeric chelate employed in the investigation has the structure (I). The influence of the concentration of the Cu(II) ion, the molecular weight of the polymer-ligand, the ionic strength, the hydrogen ion concentration, and the composition of the solvent on the polymerization were investigated. From the various kinetic aspects studied, the authors found that polyacrylic hydrazide behaves as a very weak acid, similar to polyvinyl alcohol [98], polyacrolein oxime [99], and polyacryl hydroxamic acid [100], under the



(I)

condition of the reaction studied. From the measurement of the dissociation constant it was found that the value of the dissociation constant of polyacrylic hydrazide is in the range of about 0.1 to 0.5 of the degree of ionization. From this they concluded that the hydrazide groups in the polymer chains are separately and randomly distributed under the conditions of the reaction.

No difference in the activity of the hydrazide groups for complexation with cupric ion exists between polyacrylic hydrazide and propiohydrazide. For the mechanism of the initiation of polymerization by the Cu(II)-chelate of hydrazide, the following type of decomposition of the complex to yield a radical is proposed:



$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}NH_2 + Cu(II) \rightleftharpoons \text{Complex} \longrightarrow \underset{\text{Primary radical}}{R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}\dot{N}H} + Cu^+ + H^+$$

The activity is transferred from the primary radical to the monomer to initiate polymerization. If, however, the polymer ligand radical initiates polymerization directly, a graft copolymerization is propagated. This has been observed by the authors. The rate of polymerization of MMA is considerably higher in the case of the Cu(II)-chelate of polyacrylic hydrazide than that of the Cu(II)-chelate of propiohydrazide, and raising the molecular weight of the ligand-polymer increases the rate of polymerization. The difference in the catalytic activity between the polymeric and monomeric chelates is attributed to the frequency factor rather than to the activation energy. It is believed that the monomer is adsorbed at the chelate-polyelectrolyte and initiates polymerization. Some free hydrazide groups in the chain seem to participate in the adsorption.

Although it is supposed that the vinyl monomer carrying electron-attracting group should readily polymerize because such a monomer is apt to be attracted to the chelate polymer by a hydrogen bond between a free hydrazide group in the polymer and the electron-attracting group in the monomer, acrylic acid and 2-methyl-N-vinyl imidazole are not polymerized. This may be due to the fact that acrylic acid causes the hydrazide groups to protonate and 2-methyl-N-vinylimidazole disturbs the formation of the complex and thus inhibits the initiation of polymerization. It is not well understood why St fails to polymerize. The unstability of the chelate caused by the conformation of the polymer-ligand might also relate to its easy decomposition. Yamamoto et al. [100] have reported that the interaction between ligand and metal is decreased by increasing the molecular weight of the ligand. In the author's report, however, the instability of the complex appeared to have less effect on the activity for the initiation of polymerization than the attraction of the monomer to the coiled polymer. The chemical structure of the monomer bears an important relation to the polymerizability of the system.

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