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Vinyl Polymerization Initiated by Metal Chelates. II. Polymerization of Methyl Methacrylate Initiated by Acetylacetonato Complexes of Manganese(III), Cobalt(III), and Iron(III)

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ABSTRACT

The polymerization of methyl methacrylate was studied using $Mn(acac)_3$, $Co(acac)_3$, and $Fe(acac)_3$ complexes. The rate of polymerization at various complex and monomer concentrations were investigated and it was observed that the plots of R_p versus $[M]^2$ and R_p versus 1/[complex] were linear. The reactions were studied at different temperatures and the overall activation energies were computed to be 4.70, 5.50, and 6.40 kcal/mol for Mn^{3+}, Co^{3+}, and Fe^{3+} complexes, respectively. The effect of inhibitor on the polymerization rate was studied. Using the well-known Tüdös equation, the Tüdös inhibitor constant was computed to be 10. A suitable kinetic scheme for the polymerization has been pictured.

INTRODUCTION

Nayak and co-workers [1-15] have used a large number of metal ions in their higher valency states alone or coupled with easily reducible organic substrates for initiating vinyl polymerization. In recent years the use of metal chelates for initiating vinyl polymerization has attracted the attention of many research workers [16-31]. It was observed that certain metal chelates with O,O donor atoms in the ligand molecules yield free radicals on thermal decomposition [32]. Among the metal chelates studied, the acetylacetonate complexes of certain transitional metals have been used for vinyl polymerization. Initiating particles are believed to be the ligand radicals formed under the homolytic scission of the metal-oxygen bond of metal acetylacetonates. At the same time, the formal valency of the metal ion is reduced by one. The reduction of the metal ion during the process of polymerization has been confirmed by the spectral and ESR measurements [33-36]. Further, it has been observed that during the process of polymerization of vinyl monomers, the rate can be increased by the addition of various compounds, mainly halogen atoms containing compounds [16, 19-21] or compounds of electron-donating [22-24] or electron-accepting properties [28]. In the majority of cases studied so far, the polymerization proceeded as a typical free radical mechanism. However, in some cases, a significant specificity of metal chelates toward different monomers was observed. Thus manganese(III) trifluoroacetylacetonate, while extremely reactive toward methyl methacrylate and acrylonitrile, fails to initiate the polymerization of styrene and, comparatively, is a very weak initiator for vinyl acetate [26]. There are also several other examples of selective initiation of polymerization of vinyl and diene monomers by metal chelates [27-30]. The reaction mechanism of polymerization in certain cases is not exclusively radical, but involves participation of ion and ion-radical particles.

The ability of certain metal chelates to produce free radicals was first noted by Arnett and Mendelsohn [32] in the course of investigations on the oxidation of these compounds. Kastning et al. [16] reported that, of simple acetylacetonates, those of Mn^{3+} and Co^{3+} are the most active initiators. According to these authors, the chelates can be activated by preirradiation with γ-rays or ultraviolet light or by addition of a wide range of compounds, notably organic halogen compounds. Kastning et al. [16] observed a proportionality between the rate of polymerization of styrene at 110°C and the square of the concentration of the chelates both in the presence and absence of carbon tetrachloride and noted that their result was consistent with a free radical mechanism. Bamford and Lind [26] reported the polymerization of a number of vinyl monomers using acetylacetonate complexes of certain metal ions. With $Mn(acac)_3$ the initiation process is essentially scission of the ligand to produce a free radical with the reduction of the metal to the manganese(II) state. Otsu and co-workers

[27] studied the polymerization of styrene, methyl methacrylate, acrylonitrile, vinyl acetate, and vinyl chloride initiated by a multitude of metal acetylacetonates. Nayak and co-workers used $Mn(acac)_3$ complex as the initiator for polymerizing acrylonitrile [15].

This communication presents the results of the polymerization of methyl methacrylate using $Mn(acac)_3$, $Co(acac)_3$, and $Fe(acac)_3$ complexes as the initiators.

EXPERIMENTAL

The complexes of $Mn(acac)_3$, $Co(acac)_3$, and $Fe(acac)_3$ were prepared according to the literature procedure [37]. Methyl methacrylate was washed according to the standard procedure. All other reagents were of Analytical grade. The method of rate measurement and calculation of rate parameters were similar to our previous publications [1-15].

RESULTS AND DISCUSSION

Methyl methacrylate was polymerized in aqueous solutions at 40-60°C and in the presence of acetylacetonate complexes of Mn^{3+}, Co^{3+}, and Fe^{3+} as the initiator. A typical set of time-conversion curves at 50°C is shown in Fig. 1. The rate of polymerization increases with increasing reaction time.

Effect of Monomer Concentration

The rate of polymerization has been investigated by varying the monomer concentration within the 0.0469-0.4694 M range at different complex concentrations. The rate of polymerization increases with increasing monomer concentration. Plots of R_p versus $[M]^2$ are linear and pass through the origin (Fig. 2), and hence the order with respect to monomer is two. Comparing the R_p values of the three metal chelates, the order of reactivity is $Mn^{3+} > Co^{3+} > Fe^{3+}$.

The abnormally high initiating ability of $Mn(acac)_3$ might be based on the structural strain as has been stated by Morosin and Brathrode [38], but the exact reason is not clear.

Effect of Initiator Concentration

The rate of polymerization was studied at various concentrations at different monomer concentrations. The initiator concentration was varied from 7.5 to 17.5×10^{-3} M in the case of the $Mn(acac)_3$ complex

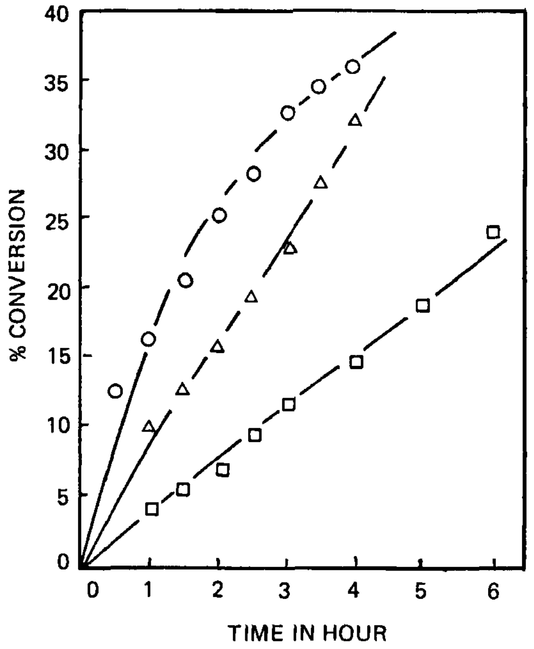


FIG. 1. Percentage conversion: [MMA] = 0.938 M, [H_2SO_4] = 15×10^{-2} M, dioxane = 5% (v/v), temperature 50° C. (○) [$Mn(acac)_3$] = 7.5×10^{-3} M. (△) [$Mn(acac)_3$] = 2.5×10^{-4} M. (□) [$Fe(acac)_3$] = 2.5×10^{-4} M.

and 0.25×10^{-4} to 2.50×10^{-4} M in the case of both $Co(acac)_3$ and $Fe(acac)_3$ complexes. In the case of the $Fe(acac)_3$ complex, the rate of polymerization increases with increasing chelate concentration, but in both the cases of Mn^{3+} and Co^{3+} the rate of polymerization in the lower concentration range of the initiator increases and in the higher concentration range the rate decreases. This might be due to termination by the metal chelates at higher chelate concentrations. Plots of R_p versus 1/[complex] were linear (Fig. 3).

Effect of Temperature

The effect of temperature on the rate of polymerization in the case of all the systems was also investigated. The rate of bulk polymerization was obtained in the temperature range between 40 and 60° C. From the plots (Fig. 4) the apparent activation energies for overall polymerization were computed to be 4.70, 5.50, and 6.40 kcal/mol for $Mn(acac)_3$, $Co(acac)_3$, and $Fe(acac)_3$, respectively.

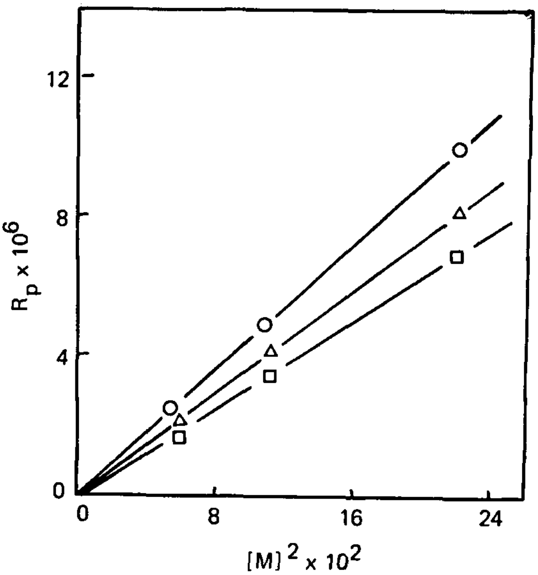


FIG. 2. Plot of R_p versus $[M]^2$. $[H_2SO_4] = 15 \times 10^{-2}$ M, dioxane = 5% (v/v), temperature 50°C, time 6 h. (○) $[Mn(acac)_3] = 10 \times 10^{-3}$ M. (△) $[Co(acac)_3] = 0.75 \times 10^{-4}$ M. (□) $[Fe(acac)_3] = 0.75 \times 10^{-4}$ M.

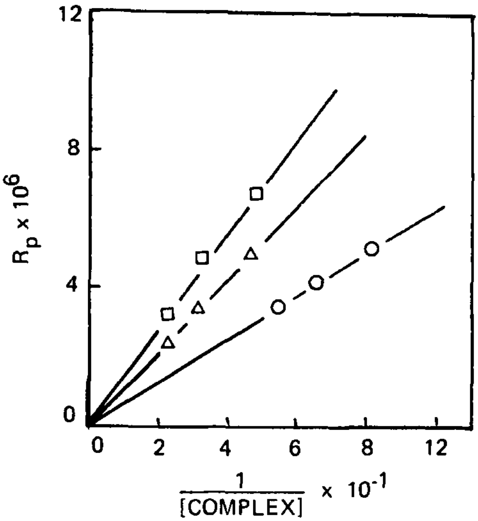


FIG. 3. Plot of R_p versus $[\text{complex}]^{-1}$: $[MMA] = 0.1876$ M, $[H_2SO_4] = 15 \times 10^{-3}$ M, dioxane = 5% (v/v), time 3 h. (○) $[Mn(acac)_3]$. (△) $[Co(acac)_3]$. (□) $[Fe(acac)_3]$.

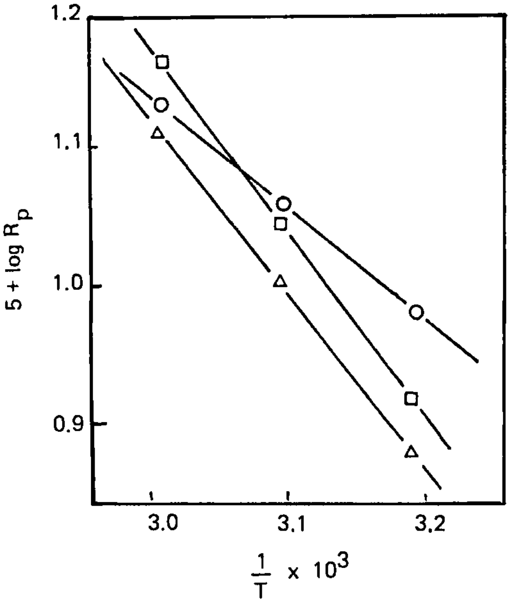
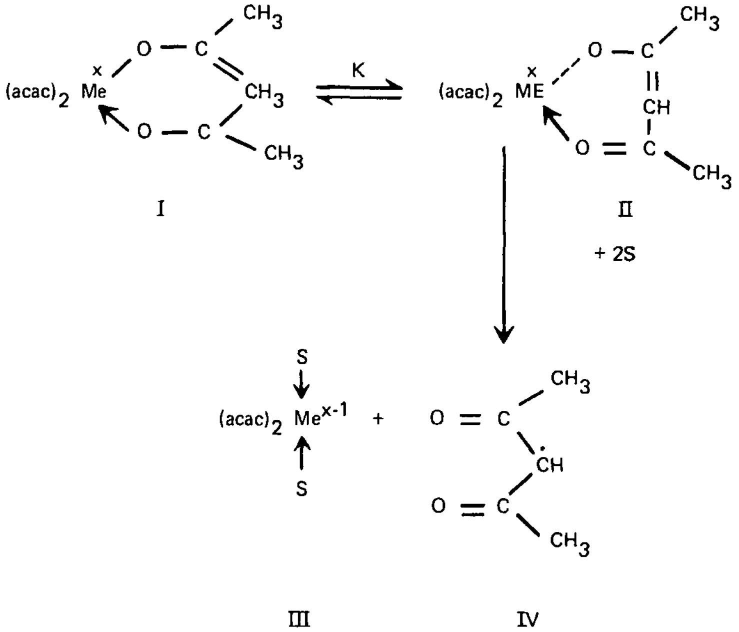


FIG. 4. Arrhenius plot of log R_p versus 1/T. (○) [$Mn(acac)_3$]. (△) [$Co(acac)_3$]. (□) [$Fe(acac)_3$].

Effect of Solvent

The rate of polymerization was investigated by increasing the proportion of dioxane from 2.5 to 15.0% (v/v) in the reaction medium. It has been observed that increasing the proportion of dioxane has a dramatic effect on the rate of polymerization. This could be fairly explained by proposing the following mechanism of the decomposition of the complex where the solvent plays a major role.

In the first stage there is an equilibrium between activated complex (II) and the chelate (I). The activated complex represents a species having a weakened M–O bond. If S is a polar solvent, it may encourage the decomposition of the activated complex (II) by chelation as represented in III. Since dioxane is a polar solvent, it encourages the chelation of the activated complex forming diacetylmethyl radical (IV) for which the rate of polymerization is enhanced by increasing the proportion of the dioxane.



where Me = metal = Mn^{3+}, Co^{3+}, and Fe^{3+}; S = dioxane.

Effect of Inhibitors

In 1925 Ostromyslensky [39] observed that the polymerization of styrene is inhibited by hydroquinone and aromatic nitro compounds. The effect of these compounds on the rate of polymerization was investigated more extensively by Foord [40] and later by Schulz [41]. It was stated that the retarding effect is enhanced by increasing the number of nitro groups. Various mechanisms have been suggested for the inhibition of polymerization by the nitro compounds and by hydroquinone. One of the most convincing mechanisms has been suggested by Tüdős and co-workers [42, 43].

In the present investigation the inhibition of polymerization initiated by the metal chelates has been examined by using picryl chloride and hydroquinone as the potential inhibitors.

The well-known Tüdős equation for inhibition has been used:

$$\log R_p = \log I + \log K_H$$

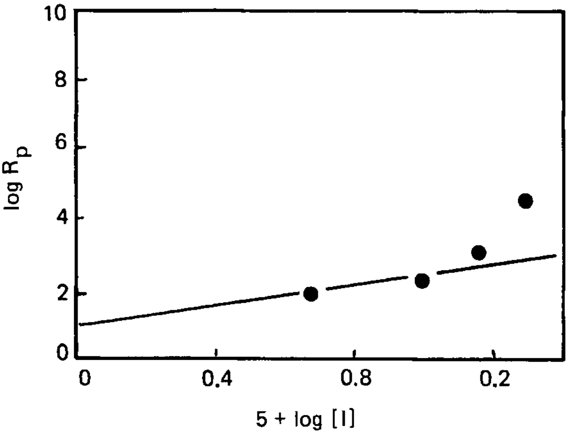


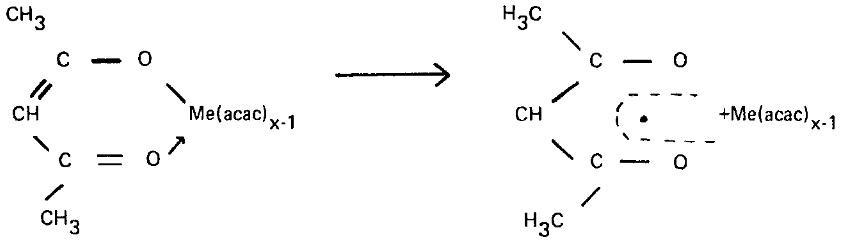
FIG. 5. Plot of log R_p versus log [I] for Mn[(acac)$_3$].

where I is the inhibitor concentration and K_H represents the Tüdős inhibitor constant. From the linear plot of log R_p versus log I (Fig. 5), K_H was computed to be 10.

Reaction Mechanism and Rate Law

The polymerization of vinyl monomers in aqueous media initiated by Me-acetylacetonate (Me = Mn^{3+}, Co^{3+}, and Fe^{3+}) shows characteristic features of heterogeneous polymerization.

As pointed out by Arnett and Mendelsohn [32], the initiation mechanism by Me(acac)$_x$ is considered to occur through the homolysis of their metal oxygen bonds:

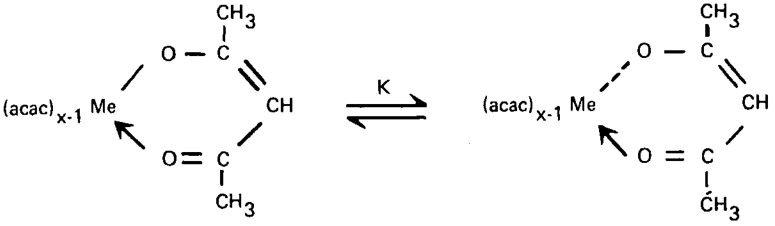


This mechanism was supported by Bamford and Lind [26] from the observed rate expression, i.e., $R_p = k'[MMA]$.

If this mechanism is correct, the acetylacetonate radical must be produced as an initiating radical, and at the same time, the central metal ion of Me(acac)$_x$ must be reduced. However, Izawa et al. [44] pointed out that the radical formation of Me(acac)$_x$ was not observed in nonpolar solvents. This result, in combination with our observations that the activation energy for the initiation of MMA by Me(acac)$_x$ was not very high and that the dependency of the monomer concentration on R_p was closed to two, may suggest that the monomer molecule must participate in the homolysis of Me(acac)$_x$, i.e., in the initiating radical production step.

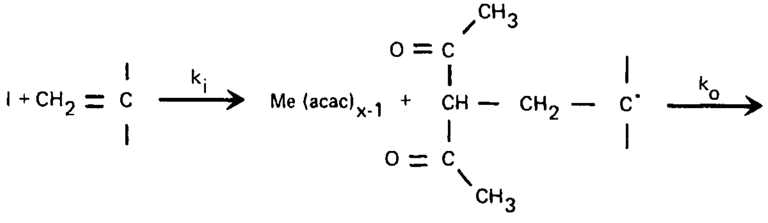
Therefore, the first step is the formation of an activated species (I) in equilibrium with Me(acac)$_x$. On reaction with monomer it yields the radicals which initiate polymerization. If a polar solvent is present, it might encourage the decomposition of the chelates to produce the free radical. From the proportionalities obtained between measurable parameters and variables, a reaction scheme is suggested as represented below.

Formation of activated complex:



I

Initiation:



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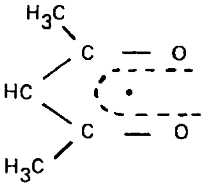

$$R^{\bullet} + M \xrightarrow{k_i'} RM_1^{\bullet}$$

Propagation:

$$RM_1^{\bullet} + M \xrightarrow{k_p} RM_2^{\bullet}$$

$$RM^{\bullet}_{n-1} + M \xrightarrow{k_p} RM_n^{\bullet}$$

Termination:

$$RM_n^{\bullet} + RM_m^{\bullet} \xrightarrow{k_t} \text{dead polymer}$$

$$RM_n^{\bullet} + \text{complex} \xrightarrow{k_t'} \text{dead polymer}$$

Applying the steady-state principle to the primary radical $R^{\bullet}$ as well as to the growing radical $RM_n^{\bullet}$, and making the usual assumption that radical reactivity is independent of radical size, and assuming initiation by the primary radical $[R^{\bullet}]$ and termination by the complex and mutual type, we obtain

$$R_p = \frac{k_p[M]^2}{k_t'[\text{complex}]}\left[\frac{Kk_ik_i'[\text{complex}]}{k_i[M] + k_0[\text{complex}]} + k_i'[\text{complex}]\right]$$

$$- \frac{k_p[M]^3k_t}{k_t'[\text{complex}]^3}\left[\frac{Kk_i'k_i[\text{complex}]}{k_i[M] + k_0[\text{complex}]} + k_i'[\text{complex}]\right]^2$$

Further, if $k_i' \ll k_i$, then

$$R_p = \frac{k_p[M]^2}{k_t{}^3[\text{complex}]} \cdot \left[\frac{k_iKk_i'[\text{complex}]}{k_i[M] + k_0[\text{complex}]}\right]$$

$$- \frac{k_p[M]^3k_t}{(k_t'[\text{complex}])^3}\left[\frac{k_ik_i'K[\text{complex}]}{k_i[M] + k_0[\text{complex}]}\right]^2$$

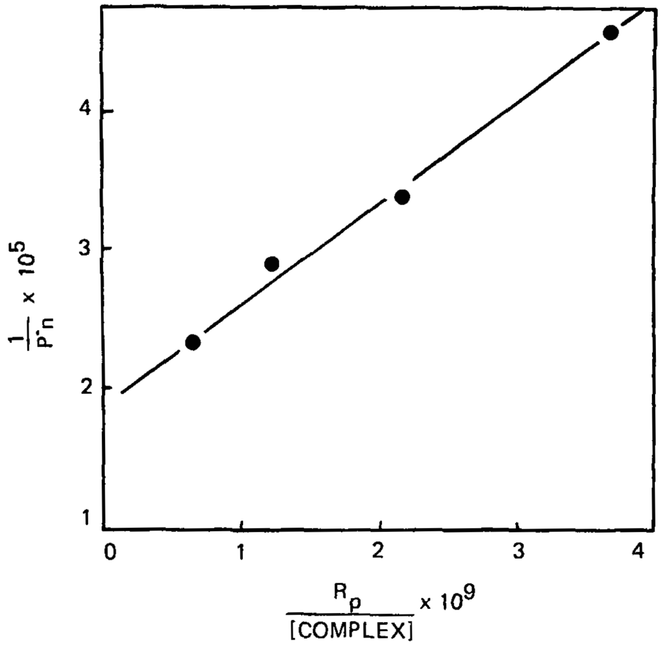

FIG. 6. Plot of $1/P_{\bar{n}}$ versus $R_p^2/[\text{complex}]$ for $\text{Mn}[(\text{acac})_3]$.

Again, if $k_0[\text{complex}] \gg k_i[M]$,

$$R_p = k_p \left(\frac{k_i K k_i'}{k_0}\right) \frac{[M]^2}{k_t'[\text{complex}]} - k_p \left(\frac{k_i K k_i'}{k_0}\right) \frac{[M]^3}{k_i'[\text{complex}]^3}$$

At higher complex concentrations, neglecting the second term,

$$R_p = k_p \left(\frac{k_i K k_i'}{k_t' k_0}\right) \frac{[M]^2}{[\text{complex}]}$$

The dependence of R_p on $[M]^2$ (Fig. 2) and $1/[\text{complex}]$ (Fig. 3) satisfies the above reaction mechanism.

The relationship between chain length and rate of polymerization, R_p, was derived to be

$$\frac{1}{P_{\bar{n}}} = \frac{k_t}{k_p{}^2Kk_i} \frac{R_p{}^2}{[\text{complex}]}$$

The plots of $1/P_{\bar{n}}$ versus $R_p{}^2/[\text{complex}]$ were linear (Fig. 6) which is further evidence in support of the mechanism.

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