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Niroda C. Mohanty[a]; Nrusingha C. Pati[a]; Padma L. Nayak[a]
[a] Laboratory of Polymers and Fibers Department of Chemistry, Ravenshaw College, Cuttack, Orissa, India

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Vinyl Polymerization Initiated by Metal Chelates. III. Polymerization of Methyl Methacrylate Initiated by Vanadium(IV) Acetylacetonate Chelates

NIRODA C. MOHANTY, NRUSINGHA C. PATI, and PADMA L. NAYAK

Laboratory of Polymers and Fibers
Department of Chemistry
Ravenshaw College
Cuttack 753003, Orissa, India

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ABSTRACT

The polymerization of methyl methacrylate initiated by the vanadium acetylacetonate complex was investigated under a nitrogen atmosphere at 50°C. The effect of concentration of monomer, complex, acid, dioxane, inhibitor, and the effect of temperature on the rate of polymerization were studied. The rate of polymerization was found to increase upon increasing the concentrations of the monomer, the initiator, and the acid. The overall activation energy has been computed from the Arrhenius plot and a suitable kinetic scheme has been proposed.

INTRODUCTION

Vinyl polymerization initiated by metal chelates has been extensively studied by several workers [1-16]. Arnett and Mendelsohn [17] have reported that certain metal chelates with O,O donor atoms in the ligand molecules yield free radicals on thermal decomposition. The initiating

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particles are believed to be the ligand radicals formed by the homolytic scission of the metal-oxygen bond of metal acetylacetonate. At the same time, the formal valency of the metal is reduced by one, and this has been confirmed by spectral and ESR measurements [18-21].

Nayak and co-workers have reported the use of the metal chelates of V^{4+}, Mn^{3+}, Co^{3+}, and Fe^{3+} for initiating the graft copolymerization of vinyl monomers onto several fibers [22-25]. Very recently they have also reported vinyl polymerization initiated by Mn(III)-acetylacetonate chelate [26]. This communication presents the results of polymerization of methyl methacrylate initiated by vanadium-acetylacetonate chelate.

EXPERIMENTAL

Methyl methacrylate was washed with 5% NaOH, then with water, and dried over anhydrous $CaCl_2$. Vanadium acetylacetonate was prepared by the literature method [27]. Other reagents such as sulfuric acid, dioxane, hydroquinone, and picryl chloride, were of AnalaR grade.

Polymerization was carried out in Pyrex tubes (20.3 × 2.5 cm) fitted with B_{24} sockets closed by B_{24} cones equipped with gas inlet and outlet tubes. Desired quantities of water, monomer, acid, and dioxane were taken in the reaction vessel and deaerated for 20 to 30 min under nitrogen atmosphere. Polymerization was initiated by adding known amounts of the chelate. The reaction was carried out for different time intervals after which it was stopped by the addition of hydroquinone. The precipitated polymer was filtered, washed repeatedly with water, and dried to constant weight at 60°C in a vacuum oven. The rate of polymerization was calculated from the weight of the polymer obtained.

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RESULTS AND DISCUSSION

Effect of Monomer Concentration

The effect of monomer concentration on the rate of polymerization of methyl methacrylate initiated by vanadium(IV) acetylacetonate was investigated at several monomer concentrations ranging from 4.69×10^{-2} to 32.83×10^{-2} $\underline{M}$. The rate of polymerization was found to increase progressively with an increase of monomer concentration (Fig. 1). As the concentration of monomer is increased, the free radicals propagate at a faster rate, thus increasing the rate of polymerization.

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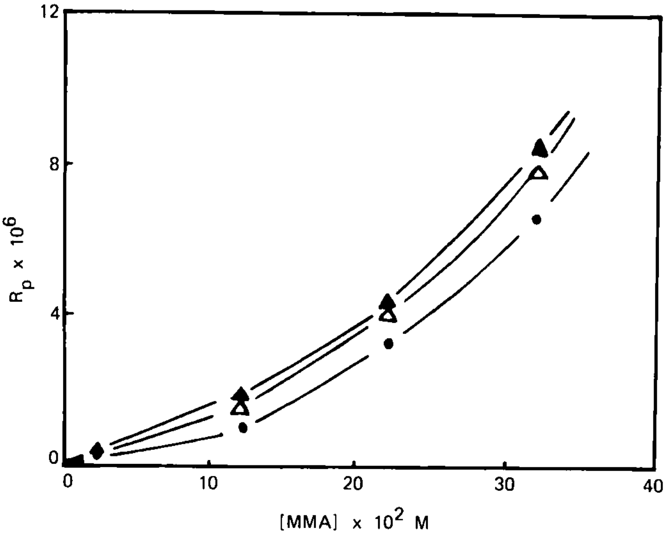

FIG. 1. Effect of monomer concentration: $[H_2SO_4] = 15 \times 10^{-2}$ M, [dioxane] = 5% v/v, 50°C, 2.5 h. (●) [complex] = 0.75×10^{-4} M, (△) [complex] = 1.25×10^{-4} M, (▲) [complex] = 1.75×10^{-4} M.

Effect of Initiator Concentration

The polymerization reaction was studied at several concentrations of the chelate at a fixed concentration of the monomer, acid, and dioxane. The rate of polymerization was evaluated by varying the concentration of the chelate from 2.5×10^{-5} to 25.00×10^{-5} M. The rate of polymerization was found to increase steadily with the chelate concentration from 2.5×10^{-5} to 17.5×10^{-5} M, after which it decreased (Fig. 2). The initial increase in the rate of polymerization with the chelate concentration might be due to the formation of a large number of free radicals ($R^•$, Eq. 1) which interact with the monomer molecules and thus propagate at a faster rate. But the decrease in the rate of polymerization beyond 17.5×10^{-5} M of the initiator concentration might be due to the termination of the growing radicals by the chelate or by the combination with other radicals. Similar observations have been reported by Nayak et al. in the case of the polymerization of MMA initiated by manganese-acetylacetonate chelate [26].

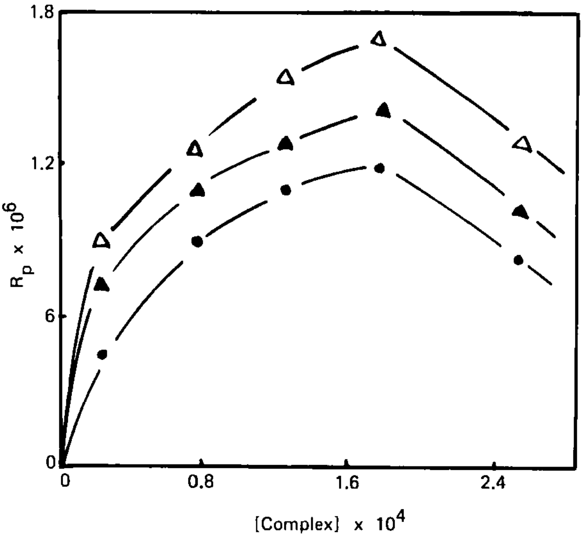

FIG. 2. Effect of the initiator concentration: $[H_2SO_4] = 15 \times 10^{-2}$ M, [dioxane] = 5% v/v, 50°C, 2.5 h, (●) [MMA] = 18.76×10^{-2} M, (▲) [MMA] = 28.14×10^{-2} M, (△) [MMA] = 46.94×10^{-2} M.

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Effect of Acid Concentration

Since the initiating efficiency of vanadium chelate is highly influenced by the acid concentration, it is necessary to study the effect of sulfuric acid concentration on the rate of polymerization. The rate of polymerization was evaluated at several concentrations of sulfuric acid ranging from 3.0×10^{-2} to 18.0×10^{-2} M while keeping the concentration of all other reagents constant. There is a progressive enhancement of the rate of polymerization with increasing acid concentration (Fig. 3).

Effect of Temperature

The effect of temperature on the rate of polymerization was studied by varying the temperature from 40 to 60°C. The rate of polymerization was found to increase with an increase of the temperature (Fig. 4). This might be due to an increase in the activation energy. Again, as the temperature is increased, the solubility of the monomer and its rate of diffusion into the active sites and growing radicals of the polymer chain are increased, as a result of which the rate of polymerization is increased.

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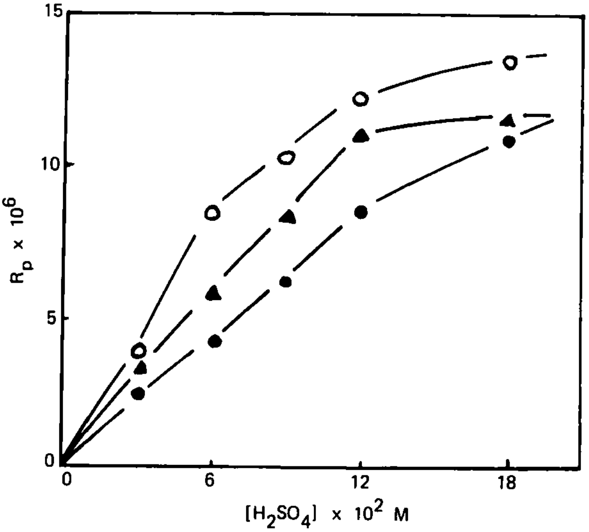

FIG. 3. Effect of acid concentration: [MMA] = 23.45 × 10^{-2} M, [dioxane] = 5% v/v, 50° C, 2.5 h, (●) [complex] = 0.75 × 10^{-4} M, (▲) [complex] = 1.25 × 10^{-4} M, (○) [complex] = 1.75 × 10^{-4} M.

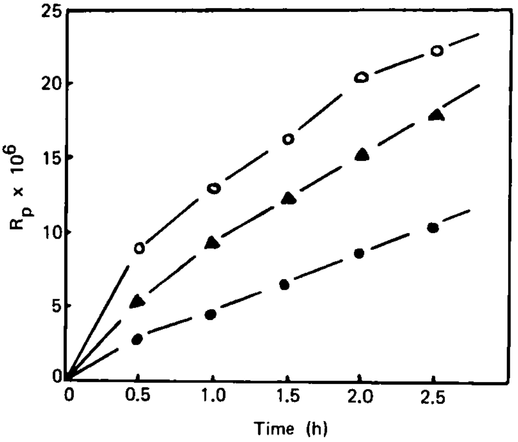

FIG. 4. Effect of temperature: [MMA] = 28.16 × 10^{-2} M, [complex] = 1.00 × 10^{-4} M, $[H_2SO_4]$ = 21 × 10^{-2} M, [dioxane] 5% v/v, (●) 40°C, (▲) 50°C, (○) 60°C.

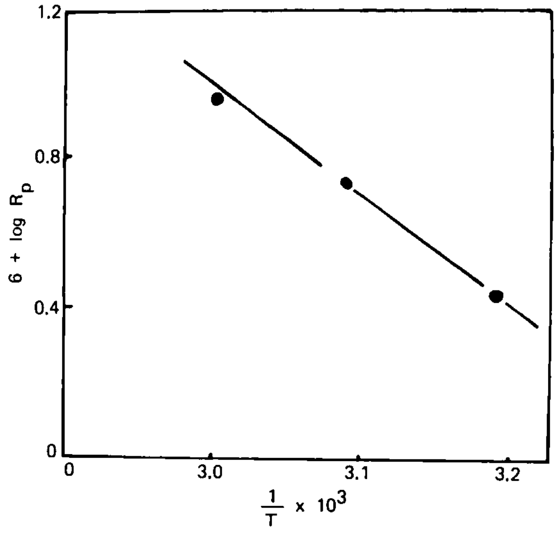

FIG. 5. Arrhenius plot of log R_p vs 1/T.

From an Arrhenius plot of log R_p vs 1/T (Fig. 5) the overall activation energy was computed to be 6.7 kcal/mol. Using the value of $E_p - {}^1/_2 E_t = 4 \sim 5$ kcal/mol given by Tobolsky [28], where E_p and E_t are the energies of propagation and termination, respectively, the energy of initiation, E_d, can be calculated as

$$E_d = 2E_a - (2E_p - E_t)$$

where E_a is the overall activation energy. The value of E_d computed for V^{4+} chelate was found to be 4.4 kcal/mol.

Effect of Solvents

The rate of polymerization was investigated by increasing the proportion of dioxane from 2.5 to 12.50% v/v in the reaction medium (Fig. 6). It has been observed that the rate of polymerization increased with an increase in the proportion of dioxane. This could be explained by proposing the following mechanism for the decomposition of the complex where the solvent plays a major role.

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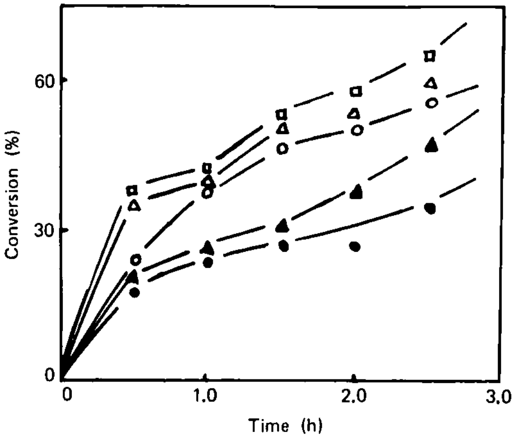
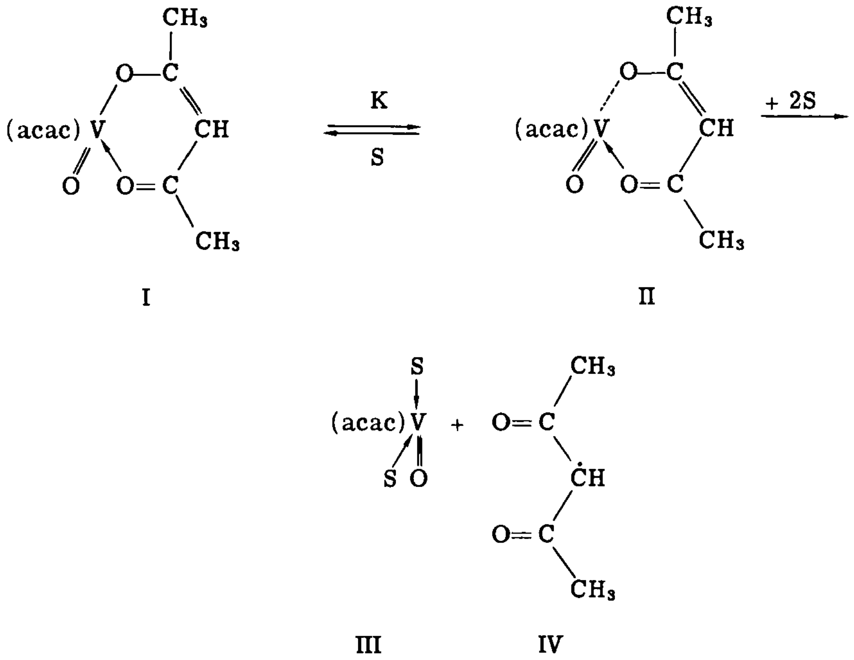


FIG. 6. Effect of solvent: [complex] = 1.25×10^{-4} $\underline{M}$, [MMA] = 23.47×10^{-2} $\underline{M}$, $[H_2SO_4] = 7.5 \times 10^{-2}$ $\underline{M}$, 50°C, (●) [dioxane] = 2.5% v/v, (▲) [dioxane] = 5.0% v/v, (○) [dioxane] = 7.5% v/v, (△) [dioxane] = 10.0% v/v, (□) [dioxane] = 12.5% v/v.



where S = dioxane.

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In the first stage, there is an equilibrium between the activated complex (II) and the chelate (I). The activated complex represents the species having a weakened metal-oxygen 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 the diacetyl methyl radical (IV) for which the rate of polymerization is enhanced by increasing the proportion of dioxane.

Effect of Inhibitors

The inhibition of polymerization initiated by the vanadium-acetylacetonate chelate has been investigated by using picryl chloride and hydroquinone as the potential inhibitors. The rate of polymerization dramatically decreased with an increase in the concentration of the inhibitors.

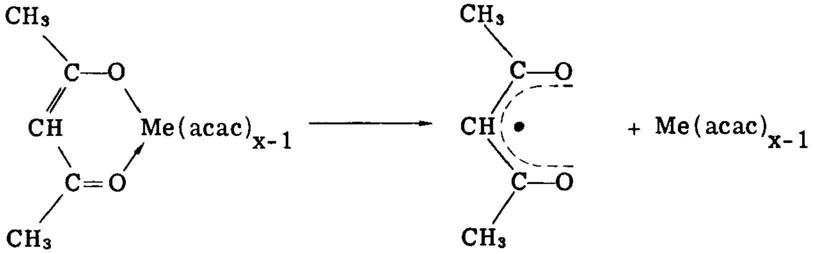
The inhibition kinetics of vinyl polymerization have been extensively studied by Ostromyslensky [29], Foord [30], and Schulz [31]. Various mechanisms have been suggested for the inhibition of polymerization by nitro compounds and by hydroquinone. One of the most convincing mechanisms has been suggested by Tüdős and co-workers [32, 33]. The well-known Tüdős equation for inhibition is

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

where I = inhibitor concentration and K_H = Tüdős inhibitor constant. From a linear plot of log R_p versus log [I] (Fig. 7), the Tüdős inhibitor constant K_H was computed to be 18.197.

Reaction Mechanism and Rate Law

Arnett and Mendelsohn [17] have reported that the initiation mechanism by $Me(acac)_x$ is considered to occur through the homolysis of their metal-oxygen bonds:



where Me = metal.

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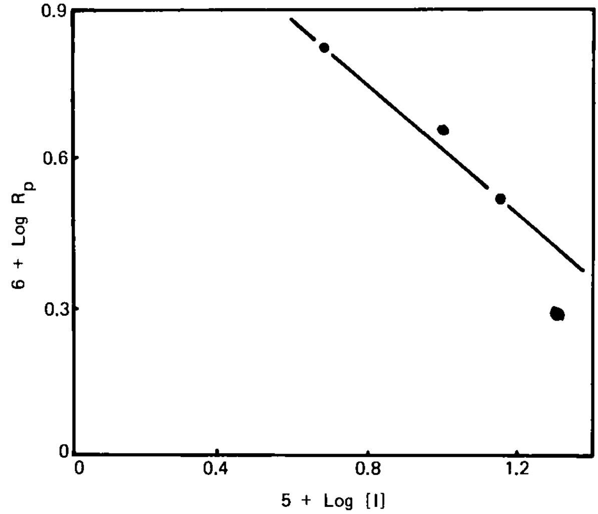

FIG. 7. Plot of log R_p vs log [I].

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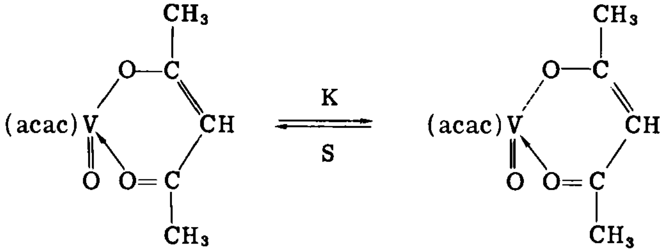
This mechanism was supported by Bamford and Lind [11] from the observed rate expression, $R_p = k'$ [MMA]. Thus, according to the above mechanism, the acetylacetonate radical must be produced as an initiating radical and at the same time the central metal ion of Me(acac)$_x$ must be reduced [33]. However, Izawa et al. [34] have pointed out that the radical formation of Me(acac)$_x$ is not observed in nonpolar solvents. This results in a 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 close to two. This suggests that the monomer molecule participates in the homolysis of Me(acac)$_x$, i.e., in the initiating radical production step.

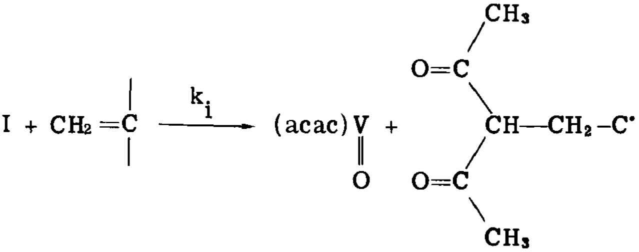
Therefore, the first step is the formation of an activated complex (I) in equilibrium with VO(acac)$_2$. This reaction with monomer yields the radicals which initiate polymerization. From the proportionalities obtained between measurable parameters and variables, a reaction scheme is suggested.

Formation of activated complex:

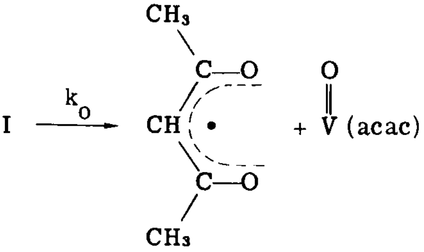


I

Initiation:



(R•)



(R•)

(1)

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

Propagation:

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

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

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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 $RM_n^{\bullet}$, making the usual assumption that radical activity is independent of radical size, and assuming initiation by the primary radical $[R^{\bullet}]$ and termination by the complex and mutual type, we get

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

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

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

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

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

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

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

At higher complex concentrations, neglecting the second term, we get

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

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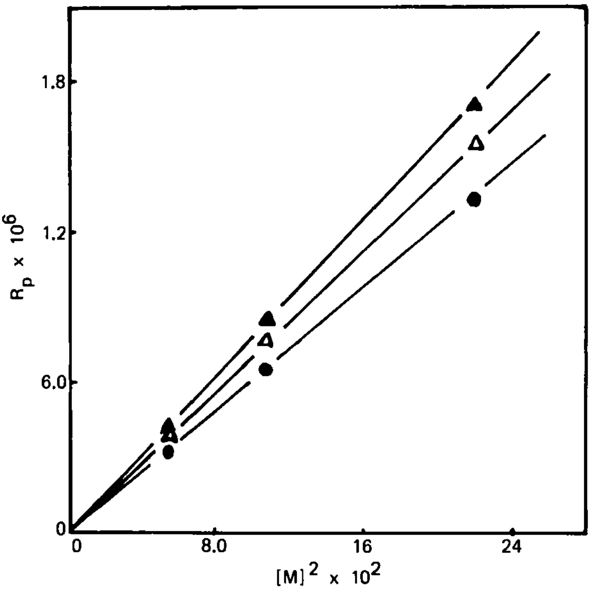

FIG. 8. Plot of R_p vs $[M]^2$: (●) [complex] = 0.75 × 10^{-4} M, (△) [complex] = 1.25 × 10^{-4} M, (▲) [complex] = 1.75 × 10^{-4} M.

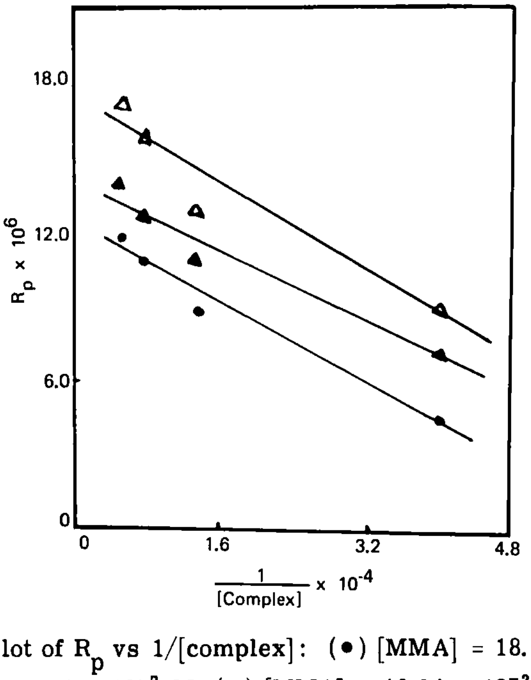

FIG. 9. Plot of R_p vs 1/[complex]: (●) [MMA] = 18.76 × 10^{-2} M, (▲) [MMA] = 28.14 × 10^{-2} M, (△) [MMA] = 46.94 × 10^{-2} M.

The dependence of R_p on $[M]^2$ (Fig. 8) and 1/[complex] (Fig. 9) satisfies the above reaction mechanism.

CONCLUSION

The acetylacetonate complex of vanadium(IV) is a very good initiator for the aqueous polymerization of vinyl monomers. This method could be used as a suitable initiator for grafting vinyl monomers onto natural and synthetic polymers.

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