Grafting Vinyl Monomers onto Silk Fibers: Graft Copolymerization of Vinyl Monomers onto Silk Using the Vanadyl Acetylacetonate Complex

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ABSTRACT

The graft copolymerization of methyl methacrylate (MMA) onto mulberry silk fibers was studied in aqueous solution using the acetylacetonate oxovanadium(IV) complex. The rate of grafting was investigated by varying the concentration of the monomer and the complex, the acidity of the medium, the solvent composition of the reaction medium, the surfactants, and the inhibitors. The graft yield increases with increasing concentration of the initiator up to 8.75×10^{-5} mol/L, of the monomer up to 0.5634 mol/L, and thereafter it decreases. Among the various vinyl monomers studied,

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MMA was found to be most suitable for grafting. Grafting increases with increasing concentration of $HClO_4$ and with increasing temperature. Inhibitors like picryl chloride and hydroquinone significantly decrease the extent of grafting. Alcoholic solvents at a solvent/water ratio of 10:90 seem to constitute the most favorable medium for grafting. A suitable reaction scheme has been proposed, and the activation energy calculated from the Arrhenius plots.

INTRODUCTION

The use of chelate complexes for initiating vinyl polymerization has attracted attention in recent years [1-7]. Arnett and Mendelsohn [3] observed that metal chelates, upon heating, decompose to generate free radical species by homolysis of the M–O bond with the reduction of the metal to a lower valency state. Kasting et al. [1, 8] reported that the acetylacetonates of Mn(III) and Co(III) are the most active initiators for vinyl polymerization. Bamford and Lind [6] and Otsu et al. [5, 7] reported the polymerization of vinyl monomers using a number of acetylacetonates. However, the use of metal acetylacetonates as excellent initiators for graft copolymerization was recognized only recently. Many workers reported grafting of vinyl monomers onto wool [9, 10], silk [11], nylon [12], and cellulose [13] using simple acetylacetonates. We have reported the graft copolymerization of a number of vinyl monomers onto wool and chemically modified wool using several metal acetylacetonates [10, 14, 15].

The present work describes the kinetics and mechanism of graft copolymerization of methyl methacrylate (MMA) and other vinyl monomers onto mulberry silk fiber using $VO(acac)_2$ as the initiator.

EXPERIMENTAL

Purification of silk, monomers, solvents, methods of rate measurement, and calculation of percentage of graft yield has been reported in our previous communications [13, 14].

DISCUSSION

Effect of Initiator Concentration

The rate of grafting was investigated by varying the $VO(acac)_2$ concentration within the range $3.75-18.75 \times 10^{-5}$ mol/L (Fig. 1). The data indicate that within the range, the graft yield increases up to 8.75×10^{-5} mol/L, decreasing thereafter.
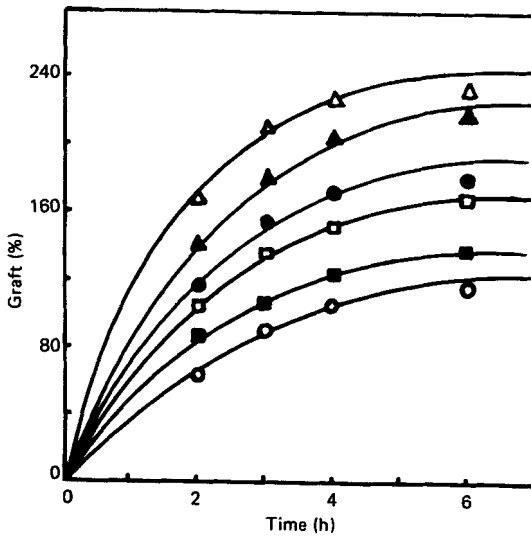
FIG. 1. Effect of $[VO(acac)_2]$ on graft yield: $[MMA]$ = 0.4694 mol/L, $[HClO_4]$ = 5×10^{-3} mol/L, [ethanol] = 1.71 mol/L, M:L = 1:100, 50°C. $[VO(acac)_2]$ values (in mol/L): (o) 3.75×10^{-5}, (•) 6.25×10^{-5}, (△) 8.75×10^{-5}, (▲) 12.5×10^{-5}, (□) 15.0×10^{-5}, (■) 18.75×10^{-5}.

In the initial stages a charge transfer complex is probably formed between the pendant groups on the silk backbone with the chelate and the monomer. Hence the concentration of the chelate and monomer is increased in the vicinity of the fiber matrix. This assists the homolysis of the metal-oxygen bond forming acetylacetonate free radical $(R^\cdot)$.
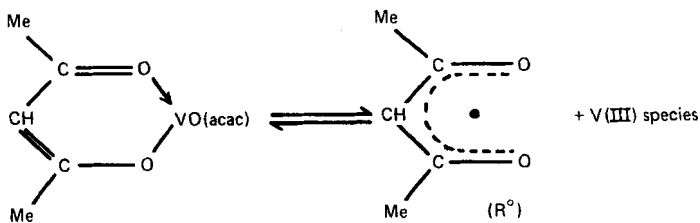

It is observed that $VO(acac)_2 Py$ (II) is a better initiator for graft copolymerization than $VO(acac)_2$ (I). The pentacoordinate complex,

$VO(acac)_2$, is known to take up a sixth ligand quite readily, becoming octahedral, with donors such as pyridine (Py) or triphenyl phosphine [17]. Such donors increase the electron density on the metal, and the homolytic cleavage of M–O bond presumably becomes easier.

I   II
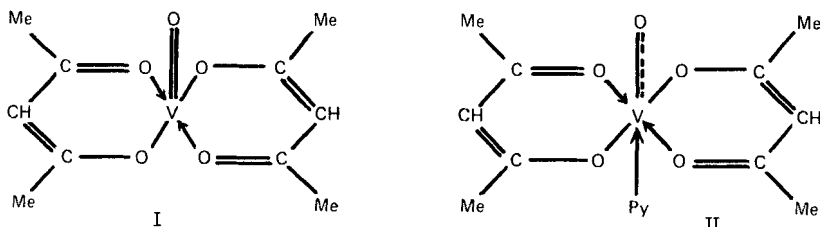
The formation of acetylacetonate free radical is assisted by the solvent [2], the acidity of the medium [2], and the monomer [16]. The solvent molecules and the monomer through the π-electrons seem to coordinate the metal, and the solvent presumably forms a hydrogen bond with oxygen. These factors weaken the M–O bond, facilitating the formation of radical in combination with the monomer:

$$VO(acac)_2 + CH_2=C(Me)COOMe \rightleftharpoons$$

(M)

III

$$\rightleftharpoons (acac)M^\cdot + V(III) \text{ species}$$

($R^\cdot$)
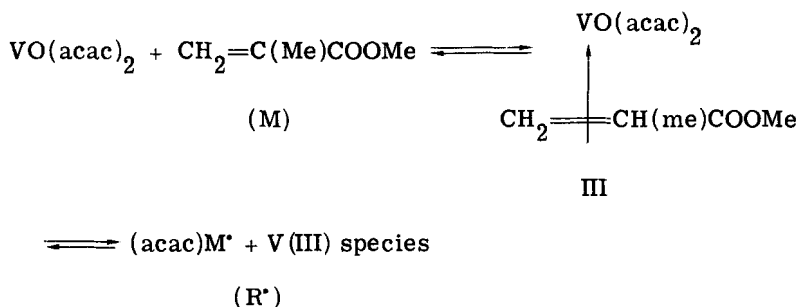
The free radicals formed interact with the active sites on the silk matrix to form silk macroradical. Monomer molecules form propagating chains at such radical sites to form grafted silk.

At higher concentrations of the complex, the free radicals produced on silk might be oxidized, thus terminating reactive sites. In addition, the complex might interact with growing PMMA radicals to produce homopolymers.

Effect of Monomer Concentration

The effect of various monomers on graft yield has been investigated. Among the various vinyl monomers, methyl methacrylate was found to
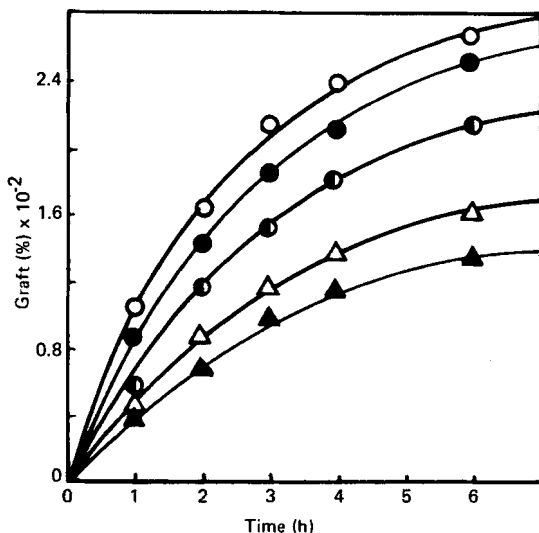
FIG. 2.   Effect of vinyl monomers on graft yield: $[VO(acac)_2]$ = 7.5×10^{-5} mol/L, $[HClO_4]$ = 7.5×10^{-3} mol/L, [ethanol] = 1.71 mol/L, M:L = 1:100, 50°C. Monomer = 0.3 mol/L: (o) MMA, (•) MA, (◐) EA, (△) BA, (▲) AA.

be the most active, the order of reactivity being methyl methacrylate > methyl acrylate (MA) > ethyl acrylate (EA) > n-butyl acrylate (BA) > acrylic acid (AA) (Fig. 2). This trend suggests that the formation of initiating radical is monomer assisted since the charge transfer complex III would be formed with maximum ease in the case of MMA. It is because of the increased π-electron density arising out of the +I effect of the substituted –Me group that MMA can coordinate better with the metal. In AA the –COOH group significantly decreases the π-electron density, making it least reactive. The decreasing order of graft yield from MA to BA is largely due to steric hindrance. The approach of the monomer to form charge transfer complexes with the active groups on silk matrix and with the initiator is sterically hindered.

Silk was graft copolymerized within the range from 0.1878 to 0.8449 mol/L of MMA concentration. It was observed that the graft yield increases up to 0.5634 mol/L, decreasing thereafter (Fig. 3). The initial increasing trend can be ascribed to 1) complexation of silk with monomer, 2) ease of formation of charge transfer such complexes as III, and 3) the gel effect.

At higher concentrations of the monomer, the rate of combination and disproportionation of PMMA macroradicals is increased faster than the rate of their combination with silk [18]. Besides, the rate of mono-
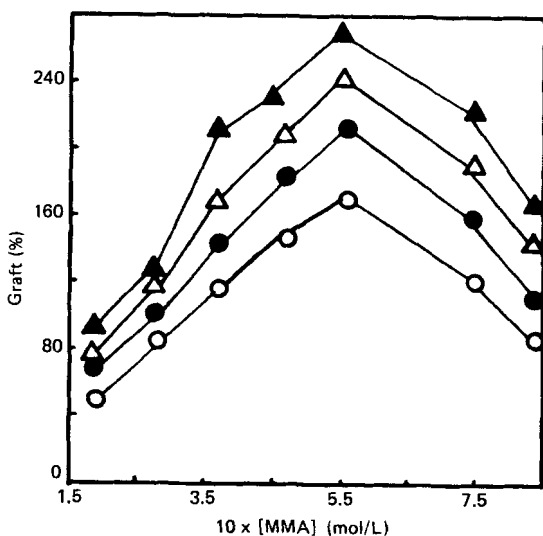
FIG. 3. Effect of MMA on graft yield: $[VO(acac)_2]$ = 7.5 × 10^{-5} mol/L, $[HClO_4]$ = 5 × 10^{-3} mol/L, [ethanol] = 1.71 mol/L, M:L = 1:100, 50°C. Time (in h): (○) 2, (●) 3, (△) 4, (▲) 6.

mer diffusion is bound to be progressively affected by the polymer deposit formed, and this effect is more pronounced at higher concentrations of the monomer [19].

Effect of Temperature

Graft copolymerization was studied at 40, 45, 50, and 55°C. Results indicate that with increasing temperature, the graft yield increases. This can be ascribed to 1) greater ease of acetylacetonate free radical formation, 2) increased solubility, and 3) enhanced diffusion rate of the monomer.

From the slopes of the Arrhenius plot of R_p versus 1/T (Fig. 4), the overall energy of activation was found to be 57.9 kJ/mol for initiation by $VO(acac)_2$ and 41.9 kJ/mol by $VO(acac)_2Py$. The overall energy of activation (E_a) accounts for 1) energy of activation for the decomposition of the catalyst (E_d), 2) energy of activation for the growing radical to chain transfer with the backbone to form silk macroradical (E_{tr}), 3)
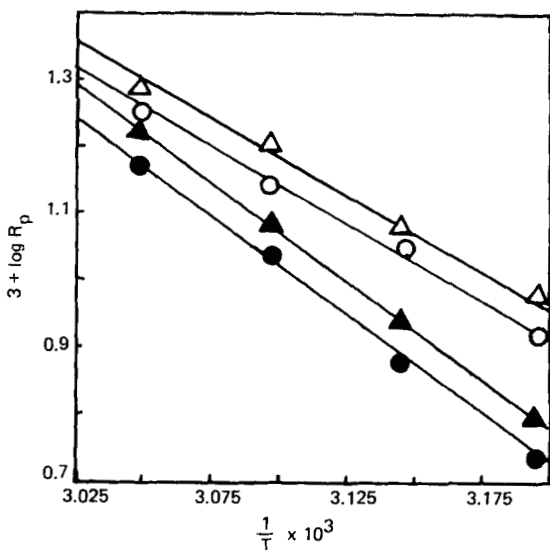
FIG. 4. Arrhenius plots of log R_p vs 1/T. VO(acac)$_2$: (▲) 2 h, (●) 4 h. VO(acac)$_2$Py: (△) 2 h, (○) 4 h.

activation energy for propagation (E_p), and 4) activation energy for termination (E_t). These terms are related to E_a by the expression

$$E_a = \tfrac{1}{2} E_d + \tfrac{1}{2} E_{tr} + E_p - \tfrac{1}{2} E_t$$

Using the value of $E_p - \tfrac{1}{2} E_t = 18.9$ kJ/mol given by Tobolsky [20], the sum $\tfrac{1}{2}(E_d + E_{tr})$ for VO(acac)$_2$ was computed to be 39.0 kJ/mol and that for VO(acac)$_2$Py to be 23.0 kJ/mol. Since E_{tr} would be the same for both initiators, the lower value for VO(acac)$_2$Py indicates that the activation energy of decomposition for VO(acac)$_2$Py is lower than that of VO(acac)$_2$. This further substantiates the observation that VO(acac)$_2$Py is a more efficient initiator than VO(acac)$_2$.

Effect of Acid Concentration and Polymerization Medium

Graft copolymerization was studied within the range of 2.5 to 12.5 × 10^{-3} mol/L of $HClO_4$. Acid presumably assists the decomposition of the complex and, at higher concentrations, more initiating radicals are formed.

The effect of different types of solvents on graft yield has been investigated. Alcoholic solvents at a solvent/water ratio of 10:90 follow the order of reactivity: MeOH > EtOH > n-PrOH > n-Butyl-OH > Amyl-OH. This ratio seems to be most favorable for all the alcohols except for amyl alcohol which provides a suitable medium at a solvent/water ratio of 5:95. Some of the chain transfer solvents, solvents acting as solubilizers of the monomer at a solvent/water ratio of 5:95, follow the order of reactivity: $CHCl_3 > CCl_4 >$ EtSH (yield ~ 1%) and MeCOOH > HCOOH > dioxane > MeCOMe > DMF. Regardless of the solvent used, an increase in the amount of solvent in the reaction mixture tends to decrease the graft yield [14].

Effect of Surfactants and Initiators

Graft copolymerization was studied in the presence of an anionic surfactant, sodium lauryl sulfate (NaLS), and cationic micelles of cetyl trimethyl ammonium bromide (CTABr) at the critical micellar concentration (CMC) (Fig. 5). It is observed that addition of NaLS increases the graft yield whereas CTABr decreases it. At CMC, the micelles formed are roughly spherical in size. In the case of micelles of NaLs, the sulfate ions form the Gouy-Chapman double layer [21]. The entanglement of these micelles with the silk fibers facilitates the formation of a charge transfer complex with the initiator [22]. The concentration of $VO(acac)_2$ increases in the vicinity of the fiber, which enhances free radical formation on the silk backbone, resulting in an increase in graft yield. In the case of CTABr, the ammonium ions form the Gouy-Chapman double layer. The entanglement of the micelles with silk fiber presumably results in a decreased tendency of the initiator to form a charge transfer complex with the fiber.

The effect of such inhibitors as picryl chloride and hydroquinone on graft yield has been studied (Fig. 6). The graft yield is greatly suppressed in the presence of either inhibitor, picryl chloride being a more efficient inhibitor than hydroquinone. The extent of inhibition increases with increasing inhibitor concentration. At higher concentrations it traps more and more free radicals, reducing the molecular size of the graft and hence decreasing the graft yield.
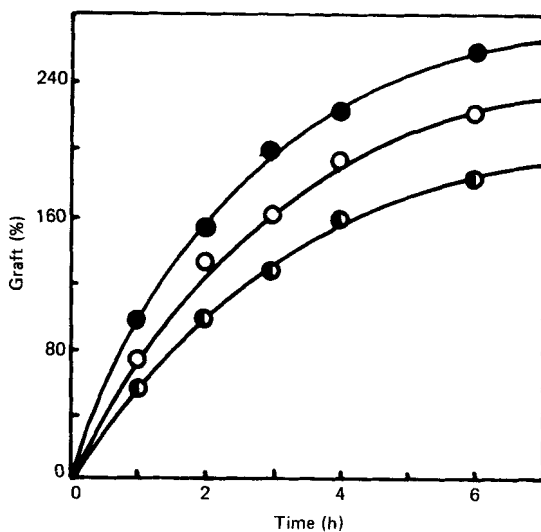
FIG. 5. Effect of surfactants on graft yield: $[CO(acac)_2]$ = 7.5 × 10^{-5} mol/L, [MMA] = 0.3756 mol/L, $[HClO_4]$ = 6.5 × 10^{-3} mol/L, [ethanol] = 1.71 mol/L, M:L = 1:100, 50°C. Surfactants at CMC: (•) NaLS, (⊕) CTABr, (○) control.

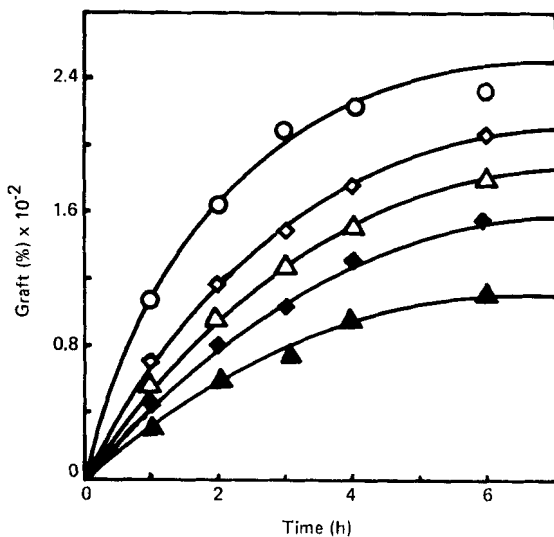FIG. 6. Effect of inhibitors on graft yield: $[VO(acac)_2]$ = 8.75 × 10^{-5} mol/L, [MMA] = 0.4694 mol/L, $[HClO_4]$ = 5 × 10^{-3} mol/L, [ethanol] = 1.71 mol/L, M:L = 1:100, 50°C. [Picryl chloride] (in mol/L): (△) 10 × 10^{-5}, (▲) 20 × 10^{-5}. [Hydroquinone] (in mol/L): (◇) 10 × 10^{-5}, (◆) 20 × 10^{-5}, (○) control.

Determination of Average Molecular Weight ($\overline{M}$)

Several samples of silk were subjected to grafting under identical reaction conditions. Grafted samples were removed after regular time intervals and Soxhlet-extracted. Separation and purification of grafted polymer were carried out by 1) digesting in 5 M HCl, 2) extracting with 0.96 mol/L diethyl ether in methanol, and 3) dissolving in ethyl acetate and reprecipitating by cold methanol. The average molecular weight of the regenerated PMMA was determined viscometrically by employing the relationship [23, 24]

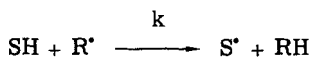$$[\eta] = 9.6 \times 10^{-5} \ (\overline{M})^{0.69}$$

The results suggest that with an increase in graft yield, $\overline{M}$ of PMMA decreases. Since the initial monomer concentration for each sample of silk was the same, with increasing reaction time, i.e., with an increase in graft percentage, the concentration of the monomer decreases in the vicinity of the base polymer, as a result of which the frequency of chain transfer increases. This will evidently decrease $\overline{M}$ [14].

In another set of experiments, several samples of silk were graft copolymerized by varying the initial concentration of the monomer within the range from 0.1878 to 0.5634 mol/L. After a definite time interval, the samples were removed, purified, and the grafted PMMA was regenerated. The average molecular weight of PMMA was found to increase with increasing graft percentage. It is already known that within the range of study, the higher the initial monomer concentration, the higher is the graft yield. The average molecular weight is thus linearly related to the initial concentration of the monomer; i.e., a plot of $1/\overline{M}$ versus $1/[MMA]$ (Fig. 7) is a straight line. This is expected, based on the observed kinetic behavior of the system where the termination step is mutual.
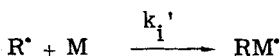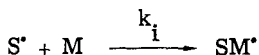
Reaction Mechanism and Rate Equation

All the observations can be suitably explained by the following mechanism:
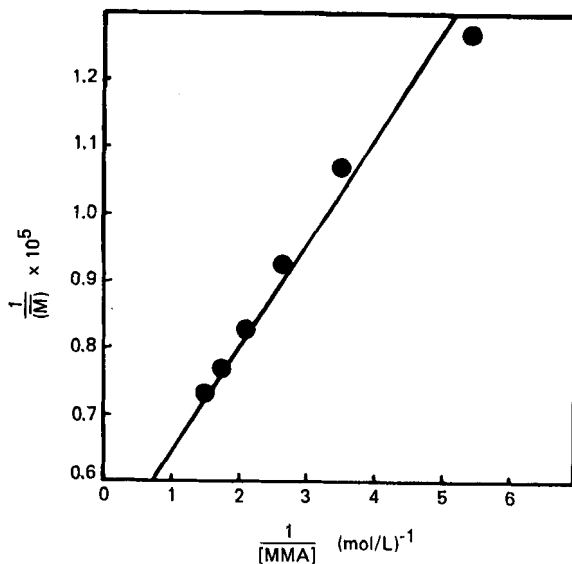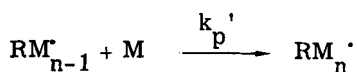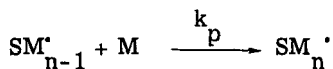
Production of free radical on silk backbone:

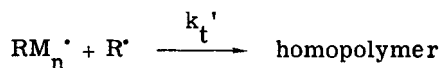$$SH + R^\bullet \xrightarrow{\ \ k\ \ } S^\bullet + RH$$

Initiation:

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

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

FIG. 7. Plot of $1/(\overline{M})$ versus $1/[M]$.

Propagation:

$$SM^{\bullet}_{n-1} + M \xrightarrow{k_p} SM^{\bullet}_n$$

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

Termination:

$$SM^{\bullet}_n + SM^{\bullet}_n \xrightarrow{k_t} \text{grafted silk}$$

$$RM^{\bullet}_n + R^{\bullet} \xrightarrow{k_t'} \text{homopolymer}$$

Oxidation:

$$S^{\bullet} + VO(acac)_2 \longrightarrow \text{oxidation products} + V(III) \text{ species}$$
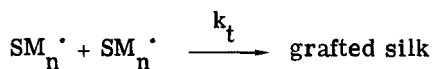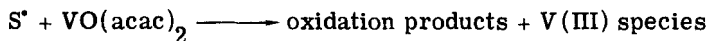
where SH is silk fiber, M is monomer, and $S^{\bullet}$ and $M^{\bullet}$ are the corresponding radicals.
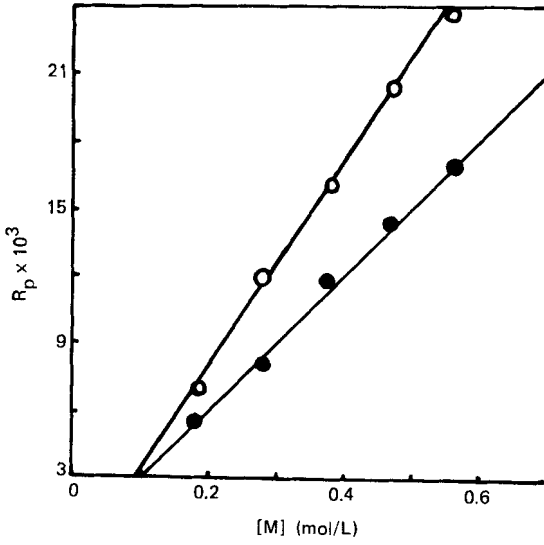
FIG. 8. Plot of R_p vs $[M]$: (○) 2 h, (●) 4 h.
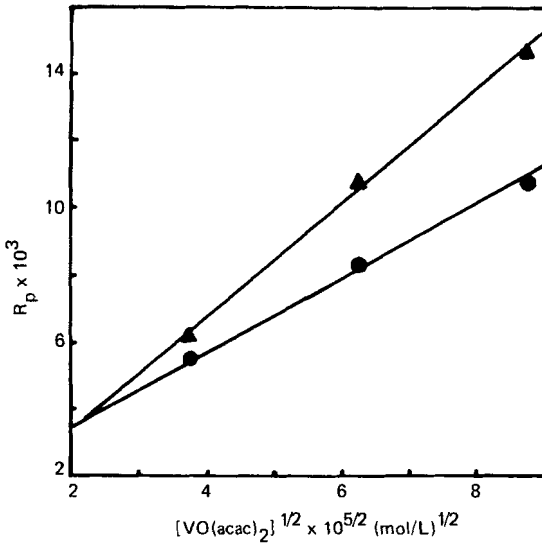

FIG. 9. Plot of R_p vs $[complex]^{1/2}$: (▲) 3 h, (●) 6 h.

Taking into account mutual termination and assuming the steady-state principle, the rate of grafting was derived [14]:

$$R_p = k_p \left[\frac{k}{k_t}\right]^{1/2} [SH]^{1/2} [VO(acac)_2]^{1/2} [M]$$

The plots of R_p versus $[M]$ (Fig. 8) and R_p versus $[VO(acac)_2]^{1/2}$ (Fig. 9) are linear, confirming the validity of the above reaction scheme.

ACKNOWLEDGMENT

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