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Ceric Ion Initiated Graft Polymerization onto Poly(vinyl Alcohol)

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Ceric Ion Initiated Graft Polymerization onto Poly(vinyl Alcohol)

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SUMMARY

This paper describes the kinetics of the ceric ion-initiated graft copolymerization of vinyl acetate-acrylonitrile to poly(vinyl alcohol). The graft copolymerization rate R_p was found to be first order with respect to the total concentration of the comonomer mixture [M], the concentration of vinyl alcohol repeating units [PVA], and the mole fraction of vinyl acetate in the comonomer feed mixture. R_p was independent of cerous ion. The grafting rate was independent of ceric ion above a ceric concentration of 0.0020 M but first order in ceric ion below that concentration. R_p initially increased rapidly with $[H^+]$ to a maximum and then decreased and levelled off at higher $[H^+]$. The rate of ceric ion disappearance was first order in [PVA], independent of [M], and increased with increasing $[H^+]$ with a leveling off at high $[H^+]$. A reaction mechanism

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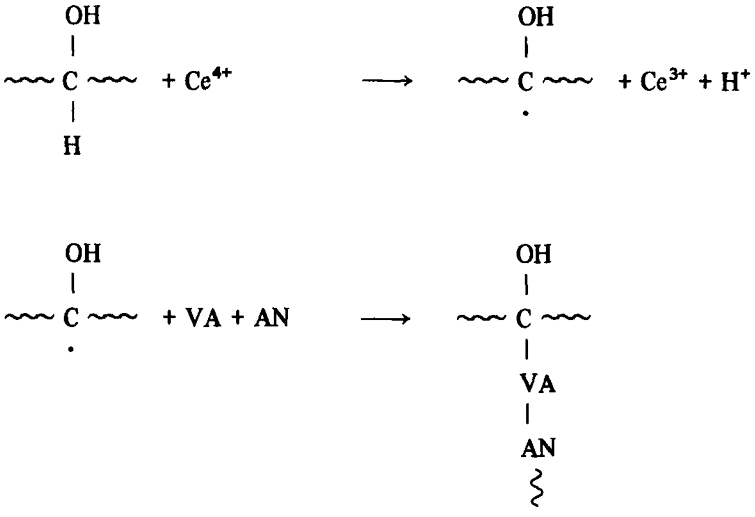
involving a termination which is first order in radicals is proposed to fit the kinetic data. The mechanism is consistent with all of the experimental concentration dependencies.

INTRODUCTION

This paper describes the kinetics of the ceric ion-initiated graft copolymerization of vinyl acetate (VA) and acrylonitrile (AN) onto poly(vinyl alcohol) (PVA)



$$\sim\sim\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\sim\sim + \mathrm{Ce}^{4+} \longrightarrow \sim\sim\overset{\mathrm{OH}}{\underset{\bullet}{\mathrm{C}}}\sim\sim + \mathrm{Ce}^{3+} + \mathrm{H}^{+}$$

$$\sim\sim\overset{\mathrm{OH}}{\underset{\bullet}{\mathrm{C}}}\sim\sim + \mathrm{VA} + \mathrm{AN} \longrightarrow \sim\sim\overset{\mathrm{OH}}{\underset{\underset{\underset{\wr}{\mathrm{AN}}}{\mathrm{VA}}}{\mathrm{C}}}\sim\sim$$

EXPERIMENTAL

Materials

Additives and low molecular weight polymer fractions were removed from PVA (Dupont Elvanol 73-125, $\overline{M}_n = 100{,}000$) by dissolution in distilled water (1% solution) at 90°C and precipitation with a 4-fold volume of acetone at 25°C. The procedure was repeated three times. Vinyl acetate was distilled at atmospheric pressure. Acrylonitrile was washed successively with equal volumes of 10% sodium hydroxide, 10% phosphoric acid and water, distilled at atmospheric pressure, and the distillate dried. Reagent grade inorganic chemicals were employed.

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Rate of Graft Copolymerization

One gram of purified PVA was dissolved in 90 ml of water at 90°C, the solution cooled to 25°C, and then flushed with nitrogen for 20 min to remove oxygen. Two milliliters of vinyl acetate-acrylonitrile comonomer mixture and 10 ml of ceric ammonium nitrate (CAN) in nitric acid were successively added, and the grafting reaction was allowed to proceed for various time periods.

Unless otherwise stated, the following molar concentrations of the various reactants were employed:

$$[M] = 0.254 \quad [Ce^{4+}] = [CAN] = 0.00200 \quad f_{VA} = 0.415$$
$$[PVA] = 0.220 \quad [H^+] = [HNO_3] = 0.0200$$

where [M] is the total concentration of monomers (i.e., the moles VA plus moles AN per liter), [PVA] is the molar concentration of vinyl alcohol (CH_2CHOH) repeating units, and f_{VA} is the mole fraction of vinyl acetate in the comonomer mixture.

The grafting experiments were carried out to relatively low conversions (<10-15%). The reaction was stopped by adding 10 ml of 5% aqueous hydroquinone solution and the mixture poured into 900 ml of acetone to precipitate the graft copolymer plus ungrafted PVA. After digesting for 24 hr, the precipitated polymer was filtered, dissolved in hot water, reprecipitated with acetone, filtered, vacuum dried at 50°C, and weighed. The amount of grafted copolymer was calculated as the weight increase relative to the starting PVA. Separate experiments showed that the loss of ungrafted or grafted PVA in this procedure is less than 0.2%. It was also ascertained that the amount of nongraft copolymer (i.e., homocopolymer) formed is small (<5% of the amount of the grafted copolymer). (The homocopolymer is not precipitated by the addition of acetone. Precipitation of homocopolymer is accomplished by the addition of nitric acid.)

In a separate study [1], the composition of the graft copolymer was analyzed by infrared spectroscopy using the carbonyl and nitrile bands at 5.75 and 4.45 μ, respectively. The monomer reactivity ratios were calculated as 4.97 and 0.07 for acrylonitrile and vinyl acetate, respectively. These values were in excellent agreement with those (4.83 and 0.10, respectively) obtained for nongraft copolymerization of the monomers.

Disappearance of Ceric Ion

Ceric ion and PVA form a complex which can be analyzed by its

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absorption at 400 mμ. (The yellow color of ceric changes to the brown of the complex when PVA and ceric ion are mixed.) The absorbance A at 400 mμ is related to the PVA and ceric concentration by

$$A = [Ce^{4+}] (a + b [PVA])$$

where a and b are empirical constants. The constants a and b were determined as 120 liter/mole and 820 $(liter/mole)^2$, respectively, from calibration experiments using solutions with known PVA and ceric ion concentrations. The rate of ceric ion disappearance in the grafting experiments was obtained by using the absorbance at 400 mμ and the above equation.

RESULTS

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The rates of graft copolymerization R_p and ceric ion disappearance were studied as a function of various parameters:

Rate of Graft Copolymerization

1. **Total Monomer Concentration, [M].** Figure 1 shows the increase of the weight of grafted copolymer with time for various initial total monomer concentrations. [M] values greater than 0.318 M could not be studied because of the limited solubility of the monomers in the PVA solution. The leveling-off effect with time is due to depletion of ceric ion. The grafting rates were calculated from the initial slopes of the data in Fig. 1. These were converted to the molar grafting rates (i.e., R_p in mole/liter-hr). There is a linear relationship between R_p and the total monomer concentration (Fig. 2).

2. **PVA Concentration, [PVA].** The effect of [PVA] on R_p was studied for solutions with [PVA] values to 0.33 M. This [PVA] corresponded to a weight concentration of polymer of about 1.5% and was the upper limit of solubility for the 100,000 molecular weight PVA used. Plots of the weight of grafted copolymer versus time were similar to those in Fig. 1. The R_p values were calculated from the initial slopes and plotted vs [PVA] in Fig. 3. R_p is linear with [PVA].

3. **Ceric Concentration, $[Ce^{4+}]$.** Figure 4 shows the dependence of R_p on $[Ce^{4+}]$. The grafting rate is independent of ceric ion above a ceric ion concentration of 0.0020 M.

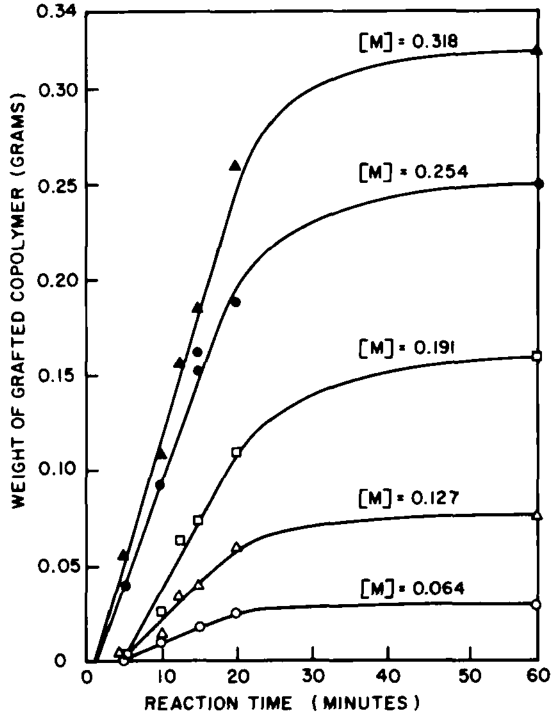

Fig. 1. Amount of grafted copolymer vs reaction time for different total monomer concentrations.

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4. **Comonomer Composition, f_{VA}.** The graft copolymerization rate was studied for various comonomer mixtures from pure vinyl acetate to pure acrylonitrile (f_{VA} values of 1 and 0, respectively). Figure 5 shows the linear dependence of R_p on f_{VA}.

5. **Acid Concentration, $[H^+]$.** The effect of $[H^+]$ on R_p was studied for two different ceric concentrations by varying the nitric acid concentration. Figure 6 shows that R_p initially increases rapidly with $[H^+]$ and then decreases and levels off at higher $[H^+]$.

6. **Cerous Concentration, $[Ce^{3+}]$.** Cerous concentrations (from cerous nitrate) in the range 0.002–0.1 M did not have any effect on the rate of graft copolymerization.

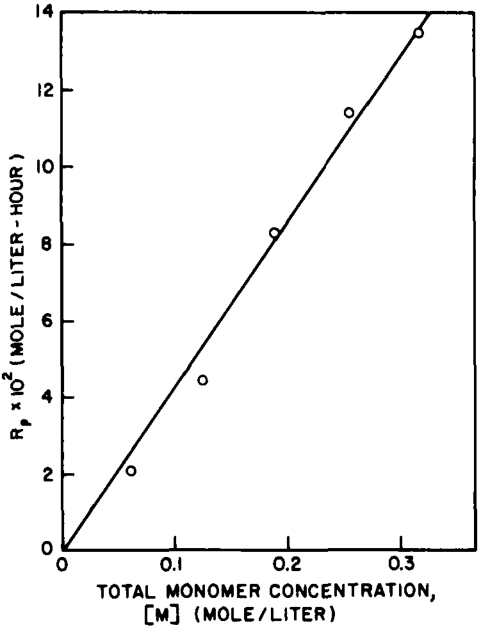

Fig. 2. Graft copolymerization rate vs total monomer concentration.

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Rate of Ceric Ion Disappearance

In a similar manner, the rate of ceric ion disappearance was found to depend on [PVA] and [H^+] as shown in Figs. 7 and 8. The ceric ion disappearance rate was independent of the total monomer concentration.

DISCUSSION

The following reaction mechanism is proposed to fit the observed experimental data:

Initiation

$$Ce^{4+} + PVA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \tag{1}$$

$$B \xrightarrow{k_d} Ce^{3+} + H^+ + PVA \tag{2}$$

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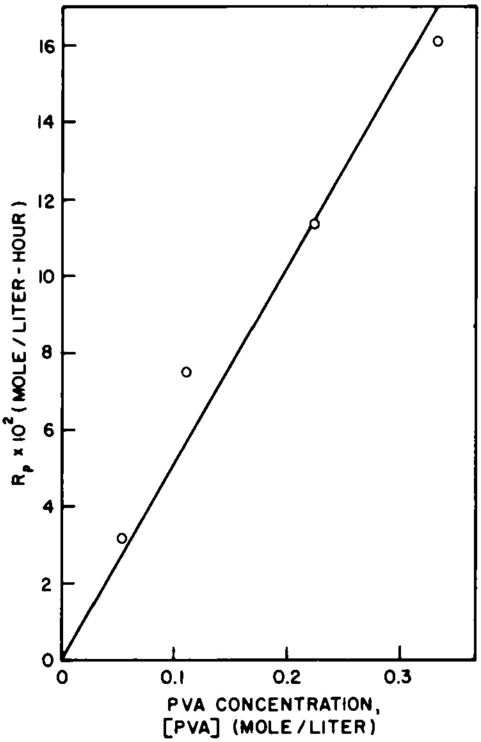

Fig. 3. Graft copolymerization rate vs PVA concentration.

$$\text{PVA}\cdot + \text{M}_1 \longrightarrow \text{PVAM}_1\cdot \qquad (3)$$

$$\text{PVA}\cdot + \text{M}_2 \longrightarrow \text{PVAM}_2\cdot \qquad (4)$$

Propagation

$$\text{PVAM}_1\cdot + \text{M}_1 \xrightarrow{k_{11}} \text{PVAM}_1\cdot \qquad (5)$$

$$\text{PVAM}_1\cdot + \text{M}_2 \xrightarrow{k_{12}} \text{PVAM}_2\cdot \qquad (6)$$

$$\text{PVAM}_2\cdot + \text{M}_1 \xrightarrow{k_{21}} \text{PVAM}_1\cdot \qquad (7)$$

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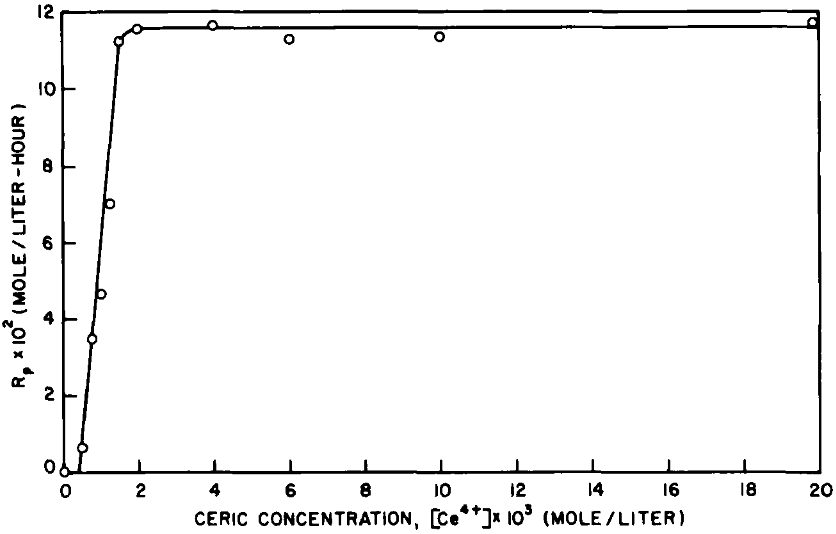

Fig. 4. Graft copolymerization rate vs ceric ammonium nitrate concentration.

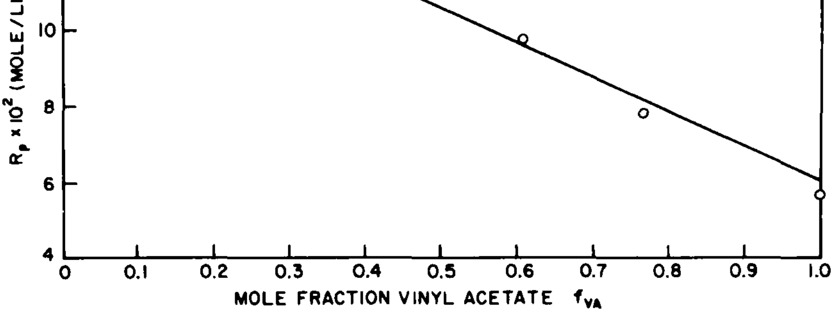

Fig. 5. Graft copolymerization rate vs mole fraction vinyl acetate in comonomer mixture.

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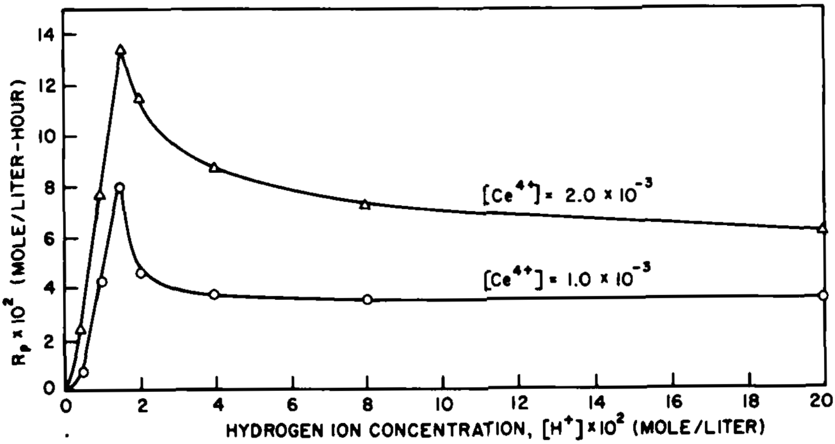

Fig. 6. Graft copolymerization rate vs hydrogen ion concentration for different ceric ion concentrations.

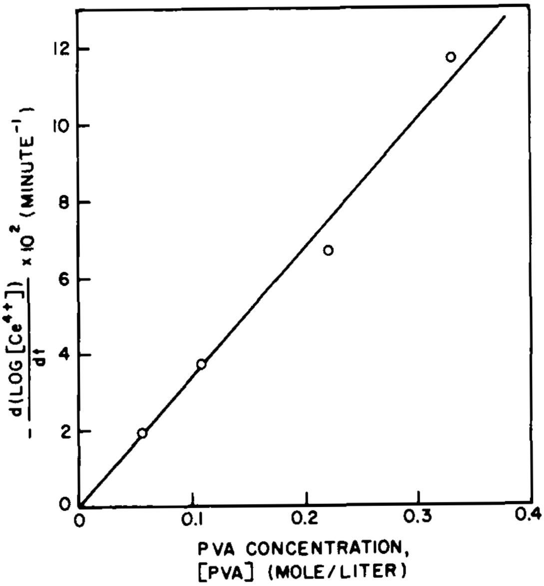

Fig. 7. $-d(\log [Ce^{4+}])dt$ vs PVA concentration.

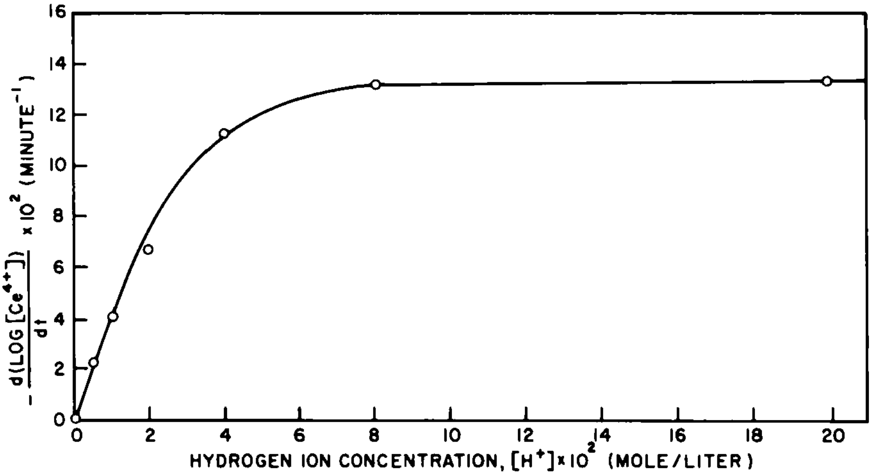

Fig. 8. $-d(\log [Ce^{4+}])/dt$ vs hydrogen ion concentration.

$$PVAM_2\cdot + M_2 \xrightarrow{k_{22}} PVAM_2\cdot \tag{8}$$

Termination

$$PVAM_1\cdot + Ce^{4+} \xrightarrow{k_{t1}} PVAM_1\cdot + Ce^{3+} + H^+ \tag{9}$$

$$PVAM_2\cdot + Ce^{4+} \xrightarrow{k_{t2}} PVAM_2\cdot + Ce^{3+} + H^+ \tag{10}$$

Ceric ion reacts reversibly with PVA to form the brown colored complex B which decomposes slowly to form a PVA polymeric radical. Similar mechanisms have been proposed for reactions between the ceric ion and low molecular weight alcohols such as methanol [2-4]. The ceric ion is reduced to cerous ion as a hydrogen atom is abstracted from PVA and oxidized to form a hydrogen ion. The polymeric radicals react with both type of monomers to form two different types of radicals. Propagation takes place in the usual manner. Termination involves abstraction of a hydrogen atom from a polymeric radical by ceric ion to yield a grafted copolymer chain with a double bond at its end. This unimolecular mode of termination (one polymer radical consumed per each termination) is quite different from the usual mode of bimolecular termination in radical polymerizations.

Consider now the derivation of expressions for the rates of grafting and ceric ion disappearance. The rate of graft copolymerization R_p is given by the sum of the rates of Reactions 5-8

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$$R_p = k_{11}[\mathrm{PVAM_1}\cdot][M_1] + k_{12}[\mathrm{PVAM_1}\cdot][M_2] + k_{21}[\mathrm{PVAM_2}\cdot][M_1] + k_{22}[\mathrm{PVAM_2}\cdot][M_2] \tag{11}$$

Two different types of steady-state assumptions are made. The first assumes a steady-state in the total radical concentration, i.e., the rate of Reaction 2 is equal to the sum of the rates of Reactions 9 and 10

$$[B]k_d = k_{t1}[\mathrm{Ce^{4+}}][\mathrm{PVAM_1}\cdot] + k_{t2}[\mathrm{Ce^{4+}}][\mathrm{PVAM_2}\cdot] \tag{12}$$

One also assumes a steady-state concentration for each type of radical, i.e., the rate of Reaction 6 is equal to the rate of Reaction 7

$$k_{12}[\mathrm{PVAM_1}\cdot][M_2] = k_{21}[\mathrm{PVAM_2}\cdot][M_1] \tag{13}$$

Combination of Eqs. 12 and 13 with

$$K = k_1/k_2 = [B]/[\mathrm{Ce^{4+}}][\mathrm{PVA}] \tag{14}$$

yields the concentrations of the two types of radicals as

$$[\mathrm{PVAM_1}\cdot] = \frac{Kk_d[\mathrm{PVA}]}{k_{t1} + k_{t2}\dfrac{[M_2]k_{12}}{[M_1]k_{21}}} \qquad [\mathrm{PVAM_2}\cdot] = \frac{Kk_d[\mathrm{PVA}]}{k_{t2} + k_{t1}\dfrac{[M_1]k_{21}}{[M_2]k_{12}}} \tag{15,16}$$

Combining Eqs. 11, 15, and 16 yields R_p as

$$R_p = Kk_d[\mathrm{PVA}][M]\left\{\frac{(\delta_1\delta_2)(f_1^2 r_1 + 2f_1f_2 + f_2^2 r_2)}{(f_1r_1\delta_2 + f_2r_2\delta_1)}\right\} \tag{17}$$

where f_1 and f_2 are the mole fractions of the two monomers, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, $\delta_1 = k_{11}/k_{t1}$, and $\delta_2 = k_{22}/k_{t2}$

For the vinyl acetate (M_1)-acrylonitrile (M_2) system, Eq. 17 takes a simpler form. The $f_1^2 r_1$ term can be neglected since r_1 is very small compared to r_2. Further, the ratio of the rates of grafting of pure VA and pure AN is given by

$$\frac{R_p(f_1 = 1)}{R_p(f_2 = 0)} = \frac{Kk_d[\mathrm{PVA}][M]\delta_1}{Kk_d[\mathrm{PVA}][M]\delta_2} = \frac{\delta_1}{\delta_2} \tag{18}$$

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$R_p(f_1 = 1)$ and $R_p(f_1 = 0)$ were experimentally found as 0.057 and 0.153 mole/liter-hr, respectively. Thus, δ_1 and δ_2 are of the same order of magnitude and the term $f_1 r_1 \delta_2$ can be neglected compared to $f_2 r_2 \delta_1$. Equation 17 becomes

$$R_p = Kk_d\,[PVA]\,[M]\left\{\frac{f_1\delta_2(2 - r_2)}{r_2} + \delta_2\right\} \tag{19}$$

The rate of ceric ion disappearance is given by

$$-d[Ce^{4+}]/dt = k_1\,[Ce^{4+}]\,[PVA] - [B]k_2 + k_{t1}[Ce^{4+}]\,[PVAM_1\cdot]$$

$$+ k_{t2}\,[Ce^{4+}]\,[PVAM_2\cdot] \tag{20}$$

The assumption of a steady-state for the concentration of B yields

$$[B] = \frac{k_1\,[Ce^{4+}]\,[PVA]}{k_2 + k_d} \tag{21}$$

Substituting Eq. 21 into Eq. 20, the first two terms on the right side of Eq. 20 become

$$k_1\,[Ce^{4+}]\,[PVA]\,\frac{k_d}{k_2 + k_d} \tag{22}$$

which simplifies to $Kk_d[Ce^{4+}]\,[PVA]$ for $k_d << k_2$. Combination of this result with the substitution of Eqs. 15 and 16 for the third and fourth terms of the right side of Eq. 20 yields

$$-d[Ce^{4+}]/dt = 2\,Kk_d[Ce^{4+}]\,[PVA] \tag{23}$$

or

$$-d(\log[Ce^{4+}])/dt = 2\,Kk_d[PVA] \tag{24}$$

Equations 19 and 24 show the theoretical dependence of R_p and $d(\log Ce^{4+})/dt$ on various reaction parameters. The linear dependence of R_p on [PVA], [M], and f_{VA} corresponds to the experimental results shown in Figs. 2, 3, and 5. Further, R_p was found to be independent of

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cerous ion as required by Eq. 19. The dependence of d(log Ce^{4+})/dt on [PVA] and its independence of [M] corresponds to the data of Figs. 7 and 8.

The dependence of R_p on [Ce^{4+}] is more complex. Over a wide range of ceric concentrations above 0.002 M, R_p is independent of ceric ion. However, R_p is linearly dependent on ceric ion below that concentration. Apparently, at low ceric concentrations, termination of the propagating radicals does not involve ceric ion via Eqs. 9 and 10. Possible termination reactions include expulsion of a hydrogen radical (without the subsequent oxidation by Ce^{4+} to H^+) and chain transfer to water of impurities. These reactions would lead to a kinetic scheme with a first-order dependence of R_p on ceric ion since termination would be independent of ceric ion.

The derived expression for R_p (Eq. 19) shows no explicit relationship between R_p and the hydrogen ion concentration. However, Fig. 6 shows a complex relationship between the two. The observed phenomena can be explained in terms of the different forms in which ceric ion exists in aqueous solution [5, 6]. The following reversible equilibria exist:

$$Ce^{4+} + H_2O \rightleftharpoons (CeOH)^{3+} + H^+ \tag{25}$$

$$2(CeOH)^{3+} \rightleftharpoons (Ce{-}O{-}Ce)^{6+} + H_2O \tag{26}$$

Thus, ceric ion exists as Ce^{4+}, $(CeOH)^{3+}$, and $(Ce{-}O{-}Ce)^{6+}$ in relative amounts depending on [H^+]. The two equilibria shift to the right with decreasing [H^+]. The different species would be expected to have different activities in terms of the initiation and termination steps of the grafting reaction.

The observed zero grafting rate at zero nitric acid concentration (i.e., neutral conditions) indicates the inability of $(Ce{-}O{-}Ce)^{6+}$ to form a complex with PVA in the initiation step. The grafting rate increases as [H^+] increases due to an increase in the concentrations of $(CeOH)^{3+}$ and Ce^{4+} at the expense of $(Ce{-}O{-}Ce)^{6+}$. Ce^{4+} and $(CeOH)^{3+}$ are more reactive than $(Ce{-}O{-}Ce)^{6+}$ in forming a PVA complex due probably to their smaller size. This leads to an increase in Kk_d as [H^+] increases—resulting in increases in the steady-state radical concentrations according to Eqs. 15 and 16. The net over-all result is an increase in R_p.

As [H^+] increases further, R_p begins to decrease and then levels off. At high [H^+], the equilibria (Eqs. 25 and 26) shift progressively toward Ce^{4+} and $(CeOH)^{3+}$. The observed R_p data can be explained by assuming these two species to have higher k_{t1} and k_{t2} values than $(Ce{-}O{-}Ce)^{6+}$. This leads to an increase in the over-all k_{t1} and k_{t2} (i.e., the sum of the values for each of the three forms of ceric). The steady-state radical concentrations decrease—resulting in the observed decline in R_p. The leveling off of R_p probably corresponds to the point at which all of the ceric is in the Ce^{4+} form.

The equilibria in Eqs. 25 and 26 also explain the dependence of $-d(\log[Ce^{4+}])/dt$ on $[H^+]$ as shown in Fig. 8. The rate of ceric disappearance increases with $[H^+]$ as Kk_d increases. The rate reaches a maximum corresponding to the complete shifting of the equilibria to the left. (The effect of the changes in the over-all k_{t1} and k_{t2} are, of course, not noted in $-d(\log[Ce^{4+}])/dt$.)

The values of some of the various constants can be determined. Kk_d was calculated as 0.166 liter/mole-hr from the slope of the plot in Fig. 7. Based on Eq. 19, δ_2 was obtained as 15.4 from the slope of the plot in Fig. 5. The intercept of this plot at $f_{VA} = 0$ also gives δ_2. The value of δ_2 obtained in this manner is 16.2 which is in good agreement with that obtained from the slope. The intercept of the same plot at $f_{VA} = 1$ yields δ_1 as 6.32.

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