January, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (1), 101—107 (1975) 101

Polymerizationn of Vinyl Compounds by Dihydridotetrakis(triphenylphosphine)ruthenium(II)

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(Received July 18, 1974)

Dihydridotetrakis(triphenylphosphine)ruthenium(II) **1** initiates the polymerization of α-substituted olefins of high *e*-values such as acrylonitrile and forms unstable complexes with olefins of low *e*-values. Molecular weight of the polymer obtained by the polymerization of acrylonitrile with **1** was independent of polymerization time and increased linearly with the monomer concentration. The rate of polymerization was measured by a dilatometry and compared with the rate of decomposition of **1** in the presence of acrylonitrile followed by a spectroscopic method. The rate of decomposition of **1** was found to be equivalent to the rate of initiation of polymerization and can be expressed by the following equations:

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Ru}] = k[\mathrm{Ru}], \quad \frac{1}{k} = A + \{B + C[\mathrm{PPh_3}]\}/[\mathrm{monomer}]$$

On the basis of the kinetic results and the independence of molecular weight of the polymer on time, a mechanism involving a slow initiation step followed by rapid propagation and termination steps is proposed.

Recent developments in the study of olefin polymerization by isolated transition metal allyl,[1] benzyl,[2] and alkyl[3] complexes have shed some light on the mechanism of coordination polymerization by Ziegler type catalysts. The polymerization mechanism with these isolated monometallic complexes has been accounted for as combination of elementary steps comprising the coordination of a monomer to the transition metal complex with a metal-carbon bond, the succeeding monomer insertion into the metal-carbon bond activated by coordination of the monomer and the spontaneous termination. A similar polymerization activity is expected for a transition metal hydride complex, and in fact some transition metal hydrides[4] are known to initiate the vinyl polymerization.

No detailed study, however, has been made to our knowledge on the vinyl polymerization by an isolated transition metal hydride except for the study by cobalt hydride.[5] Dihydridotetrakis(triphenylphosphine)ruthenium **1**,[6] which is a stable hydride complex easy to handle, catalyzes a variety of reactions of olefins, such as hydrogenation, H–D exchange, isomerization and polymerization, and serves as an appropriate model compound for studying the mechanisms of the olefin catalysis. This paper is mainly concerned with the kinetics of polymerization of acrylonitrile (AN) by **1**. Other ruthenium dihydride complexes with different substituted phosphine ligands have been examined as catalysts for vinyl polymerization and compared with **1**.

Results and Discussion

Polymerization of Vinyl Compounds by Ruthenium Hydride Complexes. The ruthenium hydride complex **1** reacts with a variety of olefins, substituted and unsubstituted. Table 1 summarizes the results of the reactions of **1**. The olefins in Table 1 are arranged in the decreasing order of Alfley Price's *e*-value[7] which parallels the electronegativity of the olefin. The most electronegative α,β-substituted olefins such as tetracyanoethylene and maleic anhydride give stable olefin-coordinated π-complexes and the α-substituted oefins of medium *e*-values are polymerized by **1**, whereas less electronegative olefins such as styrene and ethylene form unstable olefin-coordinated π-complexes. We have

Table 1. Reactions of $\mathrm{RuH_2(PPh_3)_4}$ with olefins

Monomer	*e*-Value[a]	Time	Temp.	Polymer yield (MW)	Complex isolated
Tetracyanoethylene (TCNE)			r. t.	—	$\mathrm{Ru(TCNE)_3(PPh_3)_2}$
Maleic anhydride (MAnh)	2.25	6 days	r. t.	—	$\mathrm{Ru(MAnh)}_n\mathrm{(PPh_3)}_{5-n}$
Acrylonitrile (AN)	1.20	5 min	r. t.	57% (8.1×10^4)	
Methacrylonitrile (MAN)	0.81	3 days	r. t.	23% (1.71×10^4)	
Acrolein (AC)	0.73	1 hr	r. t.	32%	
Methyl vinyl ketone (MVK)	0.69	5–6 days	r. t.	(low MW)	
Methyl acrylate (MA)	0.60	5–6 days	r. t.	90%	
Methyl methacrylate (MMA)	0.40	9 days	0 °C	0.1%	$\mathrm{Ru(MMA)(PPh_3)_3}$[b]
Ethyl methacrylate (EMA)	0.17	1 day	r. t.	—	$\mathrm{Ru(EMA)(PPh_3)_3}$[b]
Vinyl acetate (VAc)	−0.22	1 day	r. t.	—	$\mathrm{RuH(OAc)(PPh_3)_3}$[c]
Styrene (St)	−0.80	1 day	0 °C	—	$\mathrm{Ru(St)(PPh_3)_3}$
α-Methyl styrene (α-MeSt)		1 day	r. t.	—	Complex
Ethylene (E)		1 day	r. t.	—	$\mathrm{Ru(E)(PPh_3)_3}$

a) *e*-Values were taken from Ref. 7. b) The structures of these complexes will be reported separately.
c) See Ref. 18.

Table 2. Polymerization of vinyl compounds by ruthenium-hydride complexes coordinated with various phosphine ligands

Mono-mer	*e*-Value	RuH_2-$(PPh_3)_4$	RuH_2-$(PPh_2H)_4$	RuH_2-$(PPh_2Me)_4$	RuH_2-$(PPhMe_2)_4$
AN[a]	1.20	(57%)	(10%)	(19%)	(100%)
MAN[a]	0.81	(23%)	(94%)	X	X
MMA[b]	0.40	(0.1%)+C	X	X	X
St[b]	−0.80	C	X	X	X

The numbers in the parentheses show the polymer yields. X: No reaction was observed. C: Complex was formed. a) Room temperature. b) 0 °C.

briefly reported on the formation of the ruthenium complexes with ethylene and styrene.[8)]

Kinetics of Polymerization by **1**. Complex **1** is suitable for studying the kinetics of the vinyl polymerization as well as other isolated iron alkyl[3)] and cobalt hydride[5)] complexes, because the change of the complex can be conveniently followed by a spectroscopic method and compared with the kinetics of polymerization followed by a dilatometry.

When **1** is dissolved in dimethylformamide (DMF) and acrylonitrile is added to the solution, the visible spectrum of **1** changes with time showing an isosbestic point at 455 nm. By observing the decrease of the absorbance at 470 nm, the rate of decomposition of **1** in the presence of acrylonitrile can be followed. The decomposition rate can be expressed by the following equation, where [Ru] represents the total concentration of the dihydridoruthenium complex in solution and k_s denotes the pseudo-first-order rate constant observed by the spectroscopic method:

$$-\mathrm{d}[\mathrm{Ru}]/\mathrm{d}t = k_s[\mathrm{Ru}] \tag{1}$$

The rate of polymerization of acrylonitrile by **1** in DMF was followed by dilatometry and Fig. 1 demonstrates a typical time-yield curve. The polymerization is initiated without induction period and the yield levels off with time and approaches a constant value depending on the concentration of the catalyst. The dilatometric and spectroscopic experiments were carried out under the conditions that the change of the monomer concentration is negligible.

The plot of the logarithms of $(Y_\infty—Y_t)$ where Y_∞ is the yield at infinite polymerization time and Y_t is the yield at time t in Fig. 2 *versus* time gives a straight line (Fig. 2) indicating the following relationship:

$$\log(Y_\infty - Y_t) = -kt + \mathrm{const} \tag{2}$$

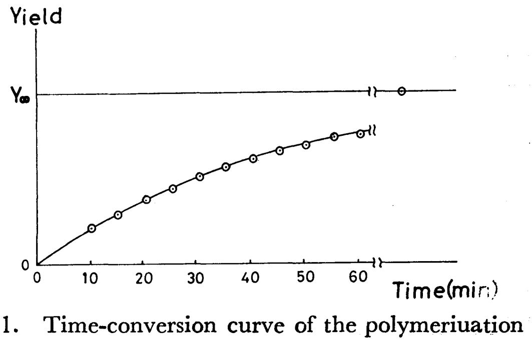


Fig. 1. Time-conversion curve of the polymeriuation of acrylonitrile by $RuH_2(PPh_3)_4$ in dimethylformamide 25 °C. [AN]=2.69 mol/l; $[PPh_3]$=0.109 mol/l.

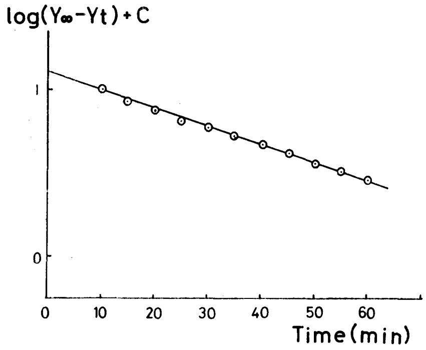


Fig. 2. The plot of logarithms of $(Y_\infty - Y_t)$ in Fig. 1 against time.

Examination of the molecular weights of the polymers obtained after different intervals revealed that the molecular weight of the polymer was independent of the polymerization time. Since the concentration of the catalyst changes with time as expressed by Eq. (1), it can be concluded that the molecular weight is independent of the catalyst concentration.

Since the molecular weights of the polymers obtained at different conversions are almost constant, the yield of the polymer can be regarded as proportional to the number of the polymer chains produced. This suggests that the polymerization process of the vinyl monomer by **1** consists of a slow initiation step followed by rapid propagation and termination steps as in the polymerization by dialkylbis(dipyridyl)iron.[3)] If we assume that the ruthenium complex initiates the polymerization with an initiator efficiency f by insertion of one monomer into the Ru–H bond followed by insertion of monomers into the Ru–C bonds, and that the growth of the polymers is terminated spontaneously after reaching a certain degree of polymerization $\overline{DP}$, which is constant, the polymerization rate can be expressed as follows:

$$R_\mathrm{p} = \frac{\mathrm{d}[\mathrm{Y}]}{\mathrm{d}t} = f \times \overline{DP} \times \left(-\frac{\mathrm{d}[\mathrm{cat}]}{\mathrm{d}t}\right) \tag{3}$$

where [Y] is the yield expressed in mol of the monomer unit polymerized and [cat] is the molar concentration of the catalyst.

From Eqs. (1) and (3) the following equation can be derived:

$$\log(Y_\infty - Y_t) = -k_s t + \log(f \times \overline{DP} \times [\mathrm{cat}]_0) \tag{4}$$

where $[\mathrm{cat}]_0$ represents the initial concentration of the catalyst. Equation (4) is equivalent to Eq. (2). Thus if our assumptions are valid, it can be expected that the rate constant k measured from the dilatometry is equal to k_s, the rate constant obtained spectroscopically for the decomposition of the ruthenium complex **1**. Figure 3 demonstates the dependences of k and k_s on the monomer concentration. Both rate constants increase and level off with increasing monomer concentration and a satisfactory agreement is observed between k and k_s.

The plot of the reciprocal values of k in Fig. 3 against the reciprocal of the olefin concentration gives straight

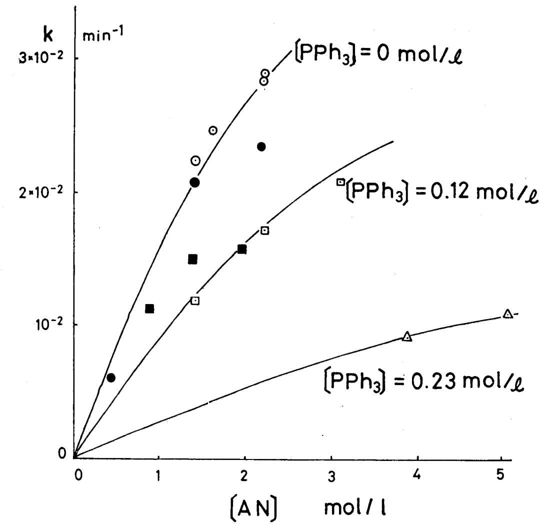


Fig. 3. Plot of the pseudo-first-order rate constants, k (observed by dilatometry ⊙, ⊡, △) and k_s (determined by spectrophotometry ●, ■).

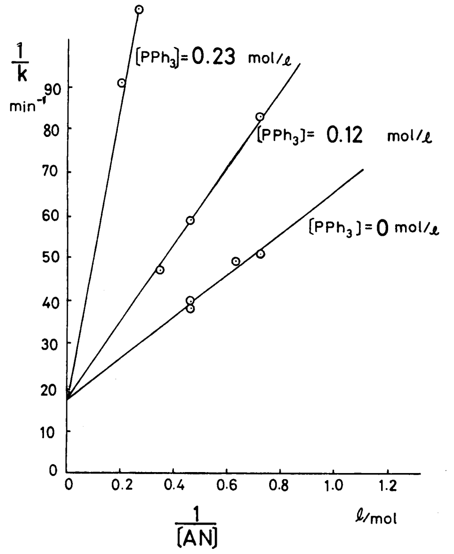


Fig. 4. Plot of the reciprocal of k *vs.* the reciprocal of [AN] at 37.1 °C.

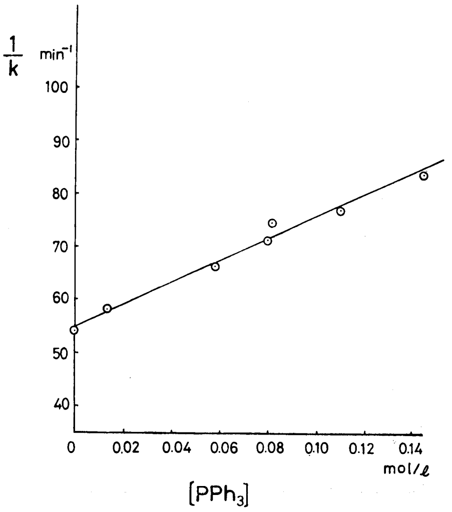


Fig. 5. Plot of the reciprocal of k *vs.* $[PPh_3]$ at 31.7 °C. AN=5 ml DMF=30 ml

lines converging to a constant (Fig. 4).

The addition of triphenylphosphine to the system has an inhibition effect on the polymerization and the linear dependence of the reciprocal of k on the concentration of the added triphenylphosphine is shown in Fig. 5.

These kinetic results are summarized by Eq. (5):

$$\frac{1}{k} = A + \{B + C[\mathrm{PPh_3}]\}/[\mathrm{monomer}] \qquad (5)$$

These results are consistent with the mechanism shown below:

$$\mathrm{RuH_2(PPh_3)_4} + \mathrm{DMF} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{RuH_2(PPh_3)_3(DMF)} + \mathrm{PPh_3} \qquad (6)$$

$$\mathrm{RuH_2(PPh_3)_3(DMF)} + \mathrm{AN} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{RuH_2(AN)(PPh_3)_3} + \mathrm{DMF} \qquad (7)$$

$$\mathrm{RuH_2(AN)(PPh_3)_3} \xrightarrow{k_3} \text{insertion} \qquad (8)$$

$$\downarrow n\mathrm{AN}$$

propagation

$$\downarrow$$

termination
(catalyst inactivation)

In the mechanism proposed here, we assume the predissociation of a triphenylphosphine ligand from $RuH_2(PPh_3)_4$ in solution (DMF) to give a solvent-coordinated species, $RuH_2(PPh_3)_3(DMF)$. Coordination of a monomer molecule (AN) displacing the coordinated solvent to give the monomer-coordinated species leads to activation of the Ru–H bonds and to insertion of the coordinated monomer into one of the Ru–H bonds. The first insertion is reagrded as the rate-determining step which is followed by rapid monomer insertions (propagation step). When the polymer reaches a certain length the polymer bonded with the complex may be spontaneously split from the complex which becomes thus inactive (termination step).

The kinetic result is in agreement with the scheme shown in Eqs. (6)—(8). By assuming the equilibrium for Eqs. (6) and (7) and the rate-determining step for Eq. (8), the following equations may be derived.

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Ru}] = k[\mathrm{Ru}]$$

$$= \frac{k_1k_2k_3[\mathrm{AN}][\mathrm{Ru}]}{k_1k_{-2}[\mathrm{DMF}] + k_1k_2[\mathrm{AN}] + k_{-1}k_{-2}[\mathrm{PPh_3}]} \qquad (9)$$

$$\frac{1}{k} = \frac{1}{k_3} + \frac{1}{K_1K_2k_3}\cdot\frac{[\mathrm{PPh_3}]}{[\mathrm{AN}]} + \frac{1}{K_2k_3}\cdot\frac{[\mathrm{DMF}]}{[\mathrm{AN}]} \qquad (10)$$

$$\text{where } K_1 = \frac{k_1}{k_{-1}}, \quad K_2 = \frac{k_1}{k_{-2}}$$

Equation (10) is in agreement with the experimental result shown by Eq. (5). The intercept to which the straight lines in Fig. 4 converge corresponds to $1/k_3$, the reciprocal of the rate constant for the insertion of acrylonitrile into the ruthenium-hydrogen bond. In the previous studies using $R_2Fe(dipy)_2$ and $CoH(N_2)$-

$(PPh_3)_3$ the dissociation of the ligand was rate-determining at high concentration of the monomer and the similar intercept as shown in Fig. 4 corresponded to the reciprocal of the dissociation rate of the ligand from the complex. On the other hand the kinetic decomposition behavior of $RuH_2(PPh_3)_4$ differs from those of $R_2Fe(dipy)_2$ and $CoH(N_2)(PPh_3)_3$ in that the dissociation of **1** in solution is extensive and the rate of insertion into the Ru–H bond constitutes the rate-determining step over the whole olefin concentration range. Estimation of the activation energy for the insertion of acrylonitrile into Ru–H bond based on the temperature dependence of k_3 at 25.0, 31.5, and 37.1 °C gave the value of *ca.* 20 kcal/mol.

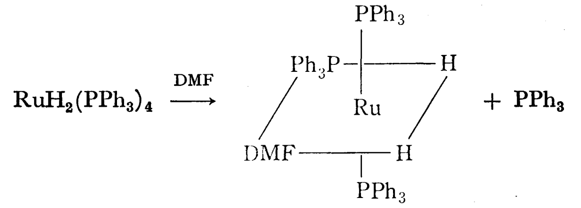
Analysis of Fig. 4 allows the estimation of K_1 and K_2 for the equilibria of Eqs. (6) and (7). In the absence of added triphenylphosphine $1/k$ can be expressed as follows:

$$\frac{1}{k} = \frac{1}{k_3} + \frac{[\mathrm{DMF}]}{k_3K_2}\,\frac{1}{[\mathrm{AN}]}$$

Using the value of k_3, estimated from the intercept of Fig. 4 as 1/18 min^{-1}, and the concentration of DMF computed as 12 mol/l, K_2 at 37.1 °C was estimated as 4.5 from the slope of Fig. 4 where $[PPh_3]=0$. The value of K_1 at 37.1 °C was evaluated as 0.011 from the slope of Fig. 4 at PPh_3 concentration of 0.12 mol/l and using Eq. (10) with k_3 and K_2 values. Estimation of the degree of dissociation at $[Ru]=1.33$ mol/l using the values of 0.011 and 12 mol/l for K_1 and [DMF] indicates that over 98% of $RuH_2(PPh_3)_4$ is dissociated in DMF liberating triphenylphosphine.

The validity of this mechanism is supported by the following evidence.

(1) ^1H NMR spectrum of **1** in DMF shows two sets of hydridic protons at τ 18.2 (triplets of a doublet) and τ 16.3 (quartet) indicating the *cis* dihydride configuration[9] as shown below.



^{31}P NMR spectrum of **1** also supports the above configuration in which a triphenylphosphine ligand is completely dissociated in solution. The olefin will most probably displace the solvent molecule and coordinate to ruthenium occupying the site where the solvent was previously coordinated.

(2) The formation of such an intermediate monomer-coordinated hydride complex at 0 °C[10] was confirmed in the case of methacrylonitrile, although in the case of acrylonitrile the direct evidence for the formation of the acrylonitrile-coordinated complex could not be obtained because of the high polymerization activity of **1** toward acrylonitrile. Under the conditions that the polymerization of methacrylonitrile with **1** does not take place, the methacrylonitrile-coordinated complex was separated as a yellow solid which showed a ν(Ru–H) band at 1900 cm^{-1} and ν(C≡N) band at 2182 cm^{-1} which is shifted to lower frequency from the frequency of the uncoordinated methacrylonitrile by 40 cm^{-1}, the fact indicating the coordination of methacrylonitrile to ruthenium probably through the double bond.[11]

Copolymerization of Vinyl Monomers with 1. For obtaining further information concerning the mechanism of vinyl polymerization by **1**, copolymerizations of some sets of monomer combinations have been examined. Copolymerization of acrylonitrile with methyl methacrylate in a 1 : 1 monomer ratio by **1** gave only an acrylonitrile homopolymer and the copolymerization of methacrylonitrile with methyl acrylate in the same ratio gave a methacrylonitrile homopolymer, whereas acrylonitrile and methyl acrylate gave a copolymer.

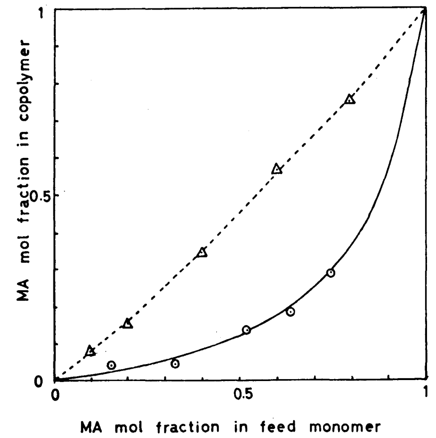


Fig. 6. Copolymerization of acrylonitrile with methyl acrylate by $RuH_2(PPh_3)_4$ catalyst. $[RuH_2(PPh_3)_4]$, 2.07 mol/l.
Solvent: toluene; solvent/monomer=1; temperature: 25 °C
—— experimental points; ------ radical polymerization.[17]

Figure 6 shows the copolymerization curve of acrylonitrile with methyl acrylate by **1**. The copolymerization curve is obviously different from that by a free-radical initiator. The monomer reactivity ratios estimated by a Fineman-Ross method[12] were as follows:

$$r_{AN} = 4.8 \pm 0.1, \qquad r_{MA} = 0.1 \pm 0.05$$

Our previous study[3] on the copolymerization of vinyl monomers with an alkyl iron complex coordinated with dipyridyl ligands has shown the tendency that an electronegative monomer can be introduced in preference to the less-electronegative monomer into the copolymer, in such a way that acrylonitrile had a higher monomer reactivity ratio than methacrylonitrile and methyl acrylate higher than methacrylonitrile. The present result with **1** is somewhat different from the result with the alkyliron complex in that **1** showed a higher polymerization activity toward methacrylonitrile rather than acrylonitrile.

Termination. In order to obtain further insight into the mechanism of propagation and termination the dependences of the molecular weights of polymers on various factors were examined. As mentioned earlier, the molecular weight of the polymer was found

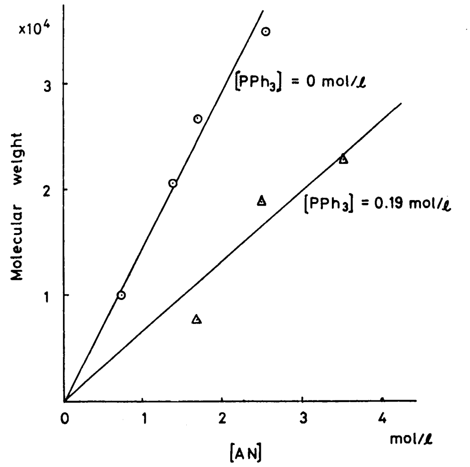


Fig. 7. The effect of the concentration of acrylonitrile on the molecular weight of polyacrylonitrile at 25 °C in DMF.

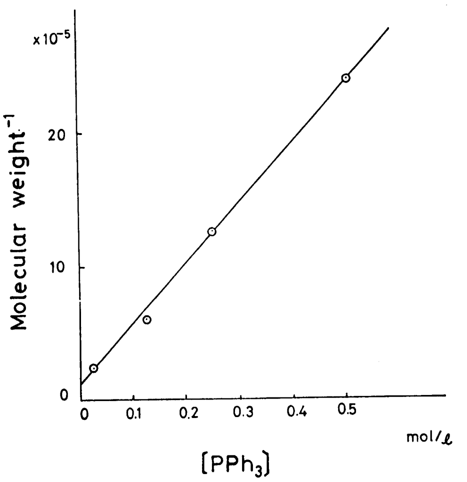


Fig. 8. The effect of the concentration of the added triphenylphosphine on the molecular weight of polyacrylonitrile at 25 °C in benzene.

to be independent of the polymerization time, the conversion, and the initiator concentration. Figure 7 demonstrates that the molecular weight of the polymer is proportional to the monomer concentration. Examination of the effect of the added triphenylphosphine concentration on the polymer weight revealed the relationship as shown in Fig. 8. The result indicates that triphenylphosphine competes with the monomer in the propagation and the coordination of triphenylphosphine to the complex having growing polymer chain leads to termination.

As we have noted in our previous paper concerning the vinyl polymerization with the alkyliron complex, the solvent may also compete with the monomer in the propagation step leading to the termination of the growing polymer chain. Thus the degree of polymerization ($\overline{DP}$) may be expressed by the following equations:

$$\overline{DP} = \frac{R_p}{R_t} = \frac{k_p[\text{Cat*}][\text{M}]}{k_t[\text{Cat*}][\text{PPh}_3]+k_t'[\text{Cat*}][\text{solv}]} \tag{11}$$

$$= \frac{k_p[\text{solv}]}{k_t[\text{PPh}_3]+k_t'[\text{solv}]} \tag{12}$$

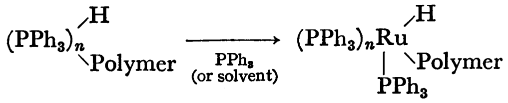
$$\frac{1}{\overline{DP}} = \frac{1}{[\text{M}]}\left\{\frac{k_t}{k_p}[\text{PPh}_3]+\frac{k_t'}{k_p}[\text{solv}]\right\} \tag{13}$$

where [M], [PPh_3], [solv], and [Cat*] denote the concentrations of the monomer, added triphenylphosphine, the solvent and propagating polymer chain attached to the catalyst, and k_p, k_t, and k_t' the rate constants for propagation, terminations caused by coordination of triphenylphosphine and the solvents, respectively. The results demonstrated in Figs. 7 and 8 are in agreement with Eqs. (12) and (13).

The fact that the straight lines in Fig. 7 pass through the origin indicates that the chain transfer reaction with monomer can be neglected.

From the slopes [PPh_3]=0 and 0.19 in Fig. 7 and utilizing Eq. (12) an approximate value of k_t/k_t' was computed as 90, indicating that the termination process involving the participation of triphenylphosphine is the predominant reaction and the contribution of the solvent to the termination is small.

Two possibilities are considered as the mechanism of termination. One is the β-hydrogen elemination from the growing polymer chain by ruthenium regenerating the ruthenium dihydride and the other is the hydrogen migration from the ruthenium hydride to the growing polymer chain as shown below:



$$(\mathrm{PPh_3})_n\begin{matrix}\diagup\mathrm{H}\\ \diagdown\mathrm{Polymer}\end{matrix} \xrightarrow[\text{(or solvent)}]{\mathrm{PPh_3}} (\mathrm{PPh_3})_n\mathrm{Ru}\begin{matrix}\diagup\mathrm{H}\\ \diagdown\mathrm{Polymer}\end{matrix}\atop{|\;\mathrm{PPh_3}}$$

$$\longrightarrow (\mathrm{PPh_3})_{n+1}\mathrm{Ru} + \text{H-Polymer}$$

The β-hydrogen elimination mechanism does not appear reasonable, because the ruthenium hydride thus reproduced should be still active for initiating the polymerization. On the other hand the hydrogen migration mechanism as shown above seems more probable since the zero-valent ruthenium complex thus produced may not be active any more. The hydrogen migration mechanism is further supported by the result that $RuH_2(PPh_3)_4$ reacts with ethylene and styrene giving Ru(ethylene)$(PPh_3)_3$ and Ru(styrene)$(PPh_3)_3$ accompanied by the formation of 1 mol each of ethane and ethylbenzene per complex **1**.[8] Ethane and ethylbenzene were probably formed by the insertion of ethylene and styrene into a Ru–H bond giving hydrido-alkyl ruthenium complexes, resembling the propagating species, from which the alkanes are reductively eliminated by the migration of hydrogen from the remaining Ru–H to the alkyl group.

Polymerization of Vinyl Monomers by Dihydrido-ruthenium(II) Complexes Having Various Phosphine Ligands. Some dihydrido-ruthenium complexes other than triphenylphosphine initiate the polymerization of a few vinyl monomers. Table 2 shows the polymerization activities of the dihydrido-tuthenium complexes of the type RuH_2L_4 where L=PPh_2H,[13] PPh_2Me,[9] $PPhMe_2$.[14] The results summarized in Tables 1 and 2 indicate that the triphenylphosphine-coordinated complex is most reactive toward the vinyl compounds examined and initiate the vinyl polymerization or forms π-complexes with a wide range of vinyl compounds whereas the other phosphine-coordinated complexes reacted only with acrylonitrile and methacrylonitrile.

Two factors may be involved in determining the reactivity of the ruthenium complex toward the olefins. One is the dissociation of the phosphine ligand from the coordinatively saturated complex RuH_2L_4 for accomodating the incoming olefin to coordinate, and the other is the intrinsic reactivity of the coordinatively unsaturated RuH_2L_3 toward olefins. The fact that the triphenylphosphine-coordinated complex was most reactive may be largely due to the reason that the bulky triphenylphosphine ligand is extensively dissociated in solution as demonstrated by the NMR spectrum of **1** in DMF whereas the other phosphine-coordinated complexes are dissociated only to a minor extent as revealed by their NMR spectra.[9,13,14] The polymerization of acrylonitrile by phenyldimethylphosphine-coordinated complex might be caused, at least partially, by the free ligand itself which may be formed by dissociation from RuH_2L_4. The free tertiary phosphines are known to initiate the vinyl polymerization[15] and the polymerization activity of the phosphine ligand itself decreased in the order of $PPhMe_2 > PPh_2Me \sim PPh_2H > PPh_3$; free phenyldimethylphosphine initiated a quite rapid polymerization of acrylonitrile whereas the polymerization by free triphenylphosphine was quite sluggish and can be neglected in comparison with the rapid polymerization by the triphenylphosphine-coordinated complex. Methacrylonitrile was not polymerized by none of the free phosphines and the polymerization activities of $RuH_2(PPh_3)_4$ and $RuH_2(PPh_2H)_4$ must be associated with the intrinsic reactivities of the complexes. The most important factors in determining the intrinsic reactivity of the complex concerned may be the interaction of the complex with the olefin and the insertion of the olefin into the metal-hydrogen bond. Electronic as well as steric factors must be operative there and it is often difficult to predict the reactivity of the particular complex on the basis of our present knowledge. That the diphenylphosphine-coordinated complex was very reactive as the initiator for methacrylonitrile, moderately reactive for more electronegative acrylonitrile and inactive for methyl methacrylate and styrene suggests that an optimum activity may be developed by appropriate choice of the ligand which modifies the electron density of the dihydrido-ruthenium complex to interact with the particular olefin.

Experimental

Preparation of Materials. Dihydridotetrakis(triphenylphosphine)ruthenium(II) $RuH_2(PPh_3)_4$ was prepared as previously described.[6] It was found later that by the reflux of the system containing $RuCl_3$, PPh_3, and $AlEt_3$ in THF, the yield of the hydrido complex was increased. The addition of excess triphenylphosphine to the toluene solution of **1** caused easier recrystallization because of the prevention of the dissociation of triphenylphosphine. Dihydrido complexes containing various phosphine ligands were prepared by the method reported previously.[9,13,14] Monomers and solvents were purified by usual method and kept under nitrogen at −20 °C before use.

Chemical Reactions. The reactions were usually carried out in an ampoule in which **1**, an olefin and a solvent were transferred in a nitrogen atmosphere or by trap-to-trap distillation in a vacuum. After the set time of polymerization, the ampoule was opened and the content was poured into acidic methanol. The precipitate was filtered, washed with methanol and dried in a vacuum. Yields and molecular weights are listed in Table 1. In some cases complex formations were observed which will be reported separately.

Copolymerization by Complex 1. Copolymerization of vinyl monomers by **1** was performed in a sealed amoule in which **1** (2.07 mol/l), toluene and olefin were transferred under nitrogen or by a trap to trap distillation in a vacuum. The ampoule was kept in a thermostatted bath at 25 °C for a few hours. The content was poured into a large excess of methanol. The copolymer formed was filtered and washed with methanol a few times and dried in a vacuum. Composition of each monomer component in the copolymer was analyzed by elemental analysis performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2. The results are as follows.

MA mole fraction in monomers	N% in copolymer	yield	MA mole fraction in copolymer
0.745	16.00	0.2%	0.288
0.631	19.54	0.3	0.186
0.523	20.96	0.4	0.137
0.328	23.85	1.0	0.042
0.155	24.88	2.0	0.034

Dilatometry. Kinetic study of polymerization was carried out by dilatometry under nitrogen. Acrylonitrile was added into a DMF solution containing the catalystat. a constant temperature under vigorous stirring of the solution The solution was immediately transferred into a dilatometer in a thermostatted bath under nitrogen and the decrease of the volume of the solution was followed.

Molecular Weight. The molecular weight of the polymer was determined by a viscometry using an Ubbelode viscometer. Molecular weight-viscosity equation of $[\eta]=39.2\times10^{-5}\times MW^{0.75}$ (25 °C in DMF) was employed for determining the molecular weight of polyacrylonitrile.[16]

Estimation of Decomposition Rate Constants k_s of 1 in the Presence of Acrylonitrile. Decomposition rate of **1** was followed by observing the decrease of absorbance in the visible spectra at a constant temperature. The pseudo-first-order rate constant k_s was estimated from the slope of $\log(A_\infty - A_t)$ *vs* time, where A_∞ and A_t represent the absorbances at infinite time and at time t.

The authors thank Dr. T. Yamamoto for his helpful discussions and for the support of the work by Ministry of Education.

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