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Polymerization of Vinyl Compounds with Hydridodinitrogentris(triphenylphosphine)cobalt(I)

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The kinetics of polymerization of vinyl compounds (acrylonitrile, methacrylonitrile, and methyl methacrylate) with hydridodinitrogentris(triphenylphosphine)cobalt(I), $CoH(N_2)(PPh_3)_3$ **1** (PPh_3: triphenylphosphine) was studied. By comparison with previous studies on the decomposition of **1** in the presence of vinyl compound a polymerization mechanism involving slow initiation followed by rapid propagation and unimolecular termination was proposed. The effects of concentration of monomer and of added triphenylphosphine on the molecular weight of the polymer were studied. The result of copolymerization was explained by the competitive coordination between the monomers involved. Poly(methyl methacrylate)s obtained by **1** in bulk and the solvent were all rich syndiotactic fraction.

Many investigations on the mechanisms of coordination polymerization by Ziegler type mixed catalysts have been made. However, a clear understanding of the polymerization mechanism by kinetic approaches[1] has been hindered by the complexity and instability of the mixed catalyst systems. By studying the polymerization kinetics with an isolated transition metal complex capable of initiating the polymerization, more information on the mechanism with Ziegler type catalysts might be expected. Employment of isolated transition metal complexes will make it possible to discover new catalysts so far unavailable with the mixed systems, where the reaction of the monomer with a catalyst component often invalidates the catalyst system. Examples of successful polymerization of vinyl monomers with Ziegler type catalysts, previously considered unpolymerizable, are increasing.[2] Recently some isolated transition metal allyls[3] and alkyls[4] have been reported to initiate the vinyl polymerization, detailed kinetic studies being made. Transition metal hydrides are also expected to initiate it, but few studies using the isolated transition metal hydrides have been made so far. We have continued our studies[5] on the reactions of hydridodinitrogentris(triphenylphosphine)cobalt(I) $CoH(N_2)(PPh_3)_3$[6] and $CoH(CO)(PPh_3)_3$ with olefins, and report in this paper the vinyl polymerization with $CoH(N_2)(PPh_3)_3$ together with information obtained on the polymerization kinetics.

Results and Discussion

Kinetics of Polymerization. The polymerization conditions, polymer yields, and molecular weights of polymers obtained with $CoH(N_2)(PPh_3)_3$ are summarized in Table 1. For cases where the olefins were not polymerized and olefin-coordinated complexes were obtained, the compositions of the complexes are included in the table. The synthesis and characterization of the olefin-coordinated cobalt complexes have been reported.[7] It was confirmed that triphenylphosphine alone does not initiate the polymerization. Nitrogen was released from $CoH(N_2)(PPh_3)_3$ with the polymerization of the vinyl monomers, but no hydrogen was evolved.

Figure 1 shows a typical time-conversion curve in the polymerization of methacrylonitrile by $CoH(N_2)(PPh_3)_3$. Polymerization starts after an induction period of about 2 minutes and the conversion approaches a certain maximum value with time. The induction period does not change with the concentra-

Table 1. Reactivities and polymerization activities of $CoH(N_2)(PPh_3)_3$ toward substituted olefins

Monomer	*e* value	Time	Polymer Yield	Mol. wt.	Complex Isolated
Tetracyanoethylene		1 hr	0	—	$CoH(TCNE)_3(PPh_3)_2$
Maleic anhydride	2.25	2 hr	0	—	$CoH(MAh)_x(PPh_3)_y$
Acryl amide	1.30	2 hr	0	—	$CoH(AcAm)_3$
Methacryl amide		6 hr	0	—	$CoH(MeAcAm)_3$
Acrylonitrile	1.20	3 days	11%	2.00×10^4	
Methacrylonitrile	0.81	5 min	59%	3.63×10^{5}[a)]	
Acrolein	0.73	1 hr	70%	—	
Methyl vinyl ketone	0.69	1 day	a few %	low mol. wt	
Methyl acrylate	0.60	2 hr	0	—	oily product
Methyl methacrylate	0.40	23 hr	20%	6.68×10^4	
Vinyl acetate	−0.22	3 hr	0	—	$CoH(VAc)_2$
Styrene	−0.80	3 hr	0	—	$Co(St)[P(C_6H_4)(C_6H_5)_2](PPh_3)_2$
Isobutyl vinyl ether	−1.77	2 days	0	—	$CoH(IBVE)_2$

Reaction temp: room temperature; −20°C for acrolein and methyl vinyl ketone. a) Poly(methacrylonitrile) produced by $CoH(N_2)(PPh_3)_3$ was soluble in acetone.

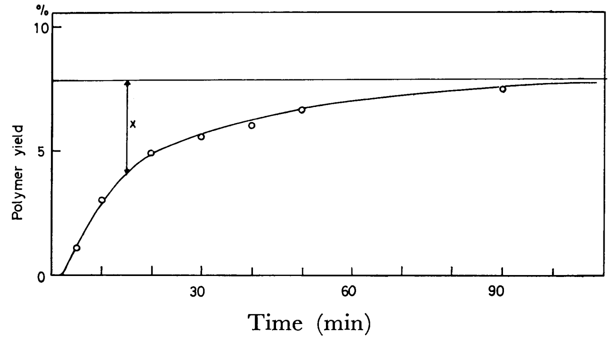


Fig. 1. Time-conversion curve of the polymerization of methacrylonitrile with $\mathrm{CoH(N_2)(PPh_3)_3}$ at 25 °C. Yield against time. Methacrylonitrile, 10 ml; toluene, 20 ml; $\mathrm{CoH(N_2)(PPh_3)_3}$, 2.28×10^{-3} mol/l.

tions of free triphenylphosphine and of $\mathrm{CoH(N_2)(PPh_3)_3}$. The reason for the presence of the induction period remains unexplained. Since the polymer yield is low, concentration of methacrylonitrile can be regarded as constant during the course of polymerization.

The molecular weight of the polymer is independent of time and conversion having a value of 1.5×10^5. The reactions of $\mathrm{CoH(N_2)(PPh_3)_3}$ with olefins are of first order in the concentration of $\mathrm{CoH(N_2)(PPh_3)_3}$ under the conditions where the olefin concentrations can be regarded invariant,[5] and can be expressed as follows.

$$R_{\mathrm{N_2}} = -\mathrm{d[CoH(N_2)(PPh_3)_3]}/\mathrm{d}t = k_{\mathrm{N_2}}\mathrm{[CoH(N_2)(PPh_3)_3]} \tag{1}$$

where $R_{\mathrm{N_2}}$ denotes the rate of change of $\mathrm{CoH(N_2)(PPh_3)_3}$ under nitrogen. Thus, the concentration of $\mathrm{CoH(N_2)(PPh_3)_3}$ decreases with time in the presence of an olefin and should markedly decrease in the time scale shown in Fig. 1. It can be concluded that the molecular weight of the polymer is independent also of the concentration of $\mathrm{CoH(N_2)(PPh_3)_3}$. This is supported by experimental results showing the invariance of the molecular weights of the polymers with varying initiator concentrations over a three-fold range. 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 polymer chains produced. This suggests that the polymerization process of the vinyl monomer consists of a slow initiation step followed by rapid propagation and termination steps as in the polymerization with dialkylbis(dipyridyl)iron[4] or dihydridotetrakis(triphenylphosphine)ruthenium.[8] Features common to the polymerization by the transition metal complexes are the strong inhibition effects of ligands. As was done previously[4] the logarithm of the value x(=the maximum yield (Y_∞)—the yield at time $t(Y_t)$) is plotted against time. Except for the induction period the straight lines having the slope $\bar{k}$ are obtained indicating the relationship

$$\log(Y_\infty - Y_t) = -\bar{k}t + \text{const.} \tag{2}$$

The change of slope $\bar{k}$ against the methacrylonitrile concentration is plotted in Fig. 2. The value $\bar{k}$ increases with the increase in methacrylonitrile concentration, approaching a limiting value of $1.60 \times 10^{-3}\,\mathrm{s^{-1}}$. We proposed the following mechanism of the decomposition of the cobalt complex.[5]

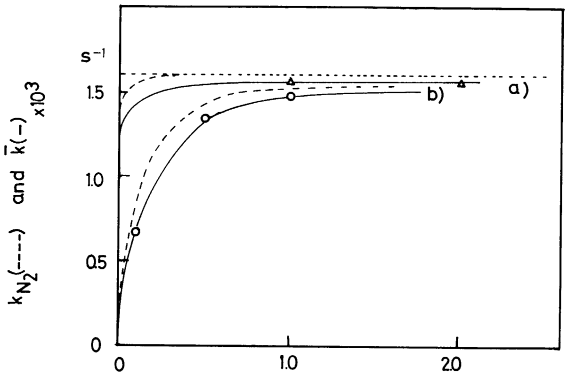


Fig. 2. Plots of pseudo-first-order rate constants, $k_{\mathrm{N_2}}$ and $\bar{k}$, against the concentration of methacrylonitrile, a) in the absence of triphenylphosphine; b) Concentration of triphenylphosphine, 8.50×10^{-2} mol/l. Solvent: toluene; $\mathrm{CoH(H_2)(PPh_3)_3}$, 3.40×10^{-3} mol/l. Polymerization temperature: 25 °C.

$k_{\mathrm{N_2}}$ (······): pseudo-first-order rate constants obtained by a spectroscopic method.[5]

$\bar{k}$ (——): pseudo-first-order rate constants obtained from the time-conversion curve.

$$\begin{tikzcd}
\mathrm{CoH(N_2)(PPh_3)_3} \arrow[r, shift left, "k_1"] & \mathrm{CoH(N_2)(PPh_3)_2 + PPh_3} \arrow[l, shift left, "k_{-1}"] \arrow[d, shift left, "k_2 + \text{olefin}"] \\
& \mathrm{CoH(N_2)(olefin)(PPh_3)_2} \arrow[u, shift left, "k_{-2}"] \arrow[d, shift left, "k_3"] \\
& \mathrm{CoH(olefin)(PPh_3)_3 + N_2} \arrow[u, shift left, "k_{-3}"] \arrow[d, "k_4"] \\
& \text{decompsition}
\end{tikzcd} \tag{3}$$

The pseudo-first-order rate constant $k_{\mathrm{N_2}}$ in Eq. (1) can be expressed as follows.

$$\frac{1}{k_{\mathrm{N_2}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2 k_3}\frac{[\mathrm{PPh_3}]}{[\mathrm{olefin}]}\left\{(k_{-2}+k_{-3}) + \frac{k_{-2}k_{-3}}{k_4}[\mathrm{N_2}]\right\} \tag{4}$$

The limiting value of $\bar{k}$, $1.60 \times 10^{-3}\,\mathrm{s^{-1}}$ in Fig. 2 is in agreement with the k_1 value corresponding to the rate constant for the dissociation of a triphenylphosphine ligand from the cobalt complex. The whole feature of the curves (Fig. 2) obtained from the time-conversion curves agrees with the decomposition pattern of $\mathrm{CoH(N_2)(PPh_3)_3}$. The results suggest a relationship between the decomposition rate of the cobalt complex and the polymerization rate. If we assume that the cobalt complex initiates the polymerization with initiator effeciency f by insertion of one monomer into the Co–H bond followed by insertion of monomers into the Co–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:

$$R_p = \frac{d[Y]}{dt} = f\cdot\overline{DP}\cdot\left\{-\frac{d[CoH(N_2)(PPh_3)_3]}{dt}\right\} \tag{5}$$

Substituting Eq. (1) into Eq. (5), we have

$$\log(Y_\infty - Y_t) = -k_{N_2}t + \log\{f\cdot\overline{DP}\cdot[CoH(N_2)(PPh_3)_3]_0\} \tag{6}$$

where $[CoH(N_2)(PPh_3)_3]_0$ is the initial concentration of the cobalt complex. Equation (6) is identical in form with Eq. (2). There is a reasonable agreement between $\bar{k}$ derived from the time-conversion curve, and k_{N_2} rate constant of the decomposition of $CoH(N_2)(PPh_3)_3$ measured by the spectroscopic method (Fig. 2). The results support our assumption that the initiation process, which probably proceeds *via* the insertion of the monomer into the Co–H bond, is the rate-determining step followed by rapid propagation and termination process by which the complex is eventually destroyed.

TABLE 2. EFFECTS OF CONCENTRATION OF ADDED TRIPHENYLPHOSPHINE ON THE MOLECULAR WEIGHT OF POLY(METHACRYLONITRILE)

$[PPh_3]$ mmol	Yield %	Mol. wt.
0	60	5.71×10^5
1.29	50	2.65×10^5
6.85	30	5.79×10^4
43.8	0	—

Polymerization time, 1 day; Temp., 25°C
[MAN]: 2.00 mol/l; $[CoH(N_2)(PPh_3)_3]$: 0.34 mmol/l

The yield and molecular weight of the polymer are affected by the monomer concentration, the concentration of the added triphenylphosphine and the solvent. The polymer yields and the decrease in molecular weight by the increase of the concentration of the added triphenylphosphine are given in Table 2. If we assume the initiation process to be formulated in Eq. (3) involving the dissociation of triphenylphosphine from $CoH(N_2)(PPh_3)_3$, the inhibition effect of triphenylphosphine can be readily explained. The effects of monomer concentration and the added triphenylphosphine on the molecular weight of the polymer can be explained by assuming a competitive coordination between the monomer, the solvent and the ligand toward the growing polymer chain end with a cobalt-carbon bond as in the polymerization with the alkyl-iron complex.[4] When the growing polymer end is coordinated by a monomer molecule, the monomer can be inserted between the metal-carbon bond with a certain probability, whereas the coordination of the solvent and the triphenylphosphine may cause the termination of the polymer growth with different probabilities. The effect of solvent is particularly marked in the polymerization of a monomer, such as methyl methacrylate, having a weaker coordinating ability toward the complex. The polymerization of methyl methacrylate, given in Table 3, is retarded in solution, being severely hindered in solvents of stronger coordinating power, such as tetrahydrofuran and dimethylformamide.

TABLE 3. EFFECTS OF SOLVENTS ON THE YIELD OF POLY(METHYL METHACRYLATE)

MMA	Solvent	Time	Yield %
8 ml	none	1 day	17
5 ml	Toluene	7 days	5
5 ml	Benzene	7 days	0.2
5 ml	Tetrahydrofuran	7 days	trace
5 ml	Dimethylformamide	7 days	trace

$[CoH(N_2)(PPh_3)_3]$: 4—5 mmol/l 25°C

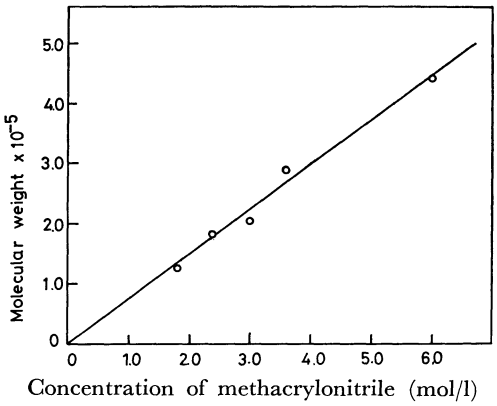


Fig. 3. The effect of concentration of methacrylonitrile on the molecular weight of poly(methacrylonitrile).

The molecular weight of poly(methacrylonitrile) increases linearly with increasing monomer concentration(Fig. 3). This supports our assumption that the coordination of the monomer to the complex with a growing polymer chain leads to the insertion of the monomer between the M–C bond. If we assume the following propagation and termination reactions

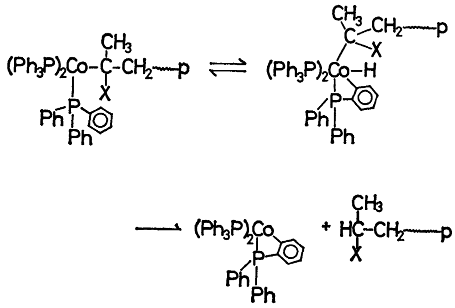
$$R_p = k_p[M][C^*]$$
$$R_t = k_t[C^*],$$

where $[C^*]$ represents the concentration of the catalyst with a growing polymer chain, the degree of polymerization of the polymer can be given by

$$\overline{DP} = (k_p/k_t)[M],$$

in agreement with the experimental result.

We showed that at least a part of the termination process takes place by hydrogen abstraction from the



X = CN for methacrylonitrile
COOCH₃ for methyl methacrylate
Termination mechanism
Scheme 1.

β-position of the polymer chain bonded to the metal with the polymer end bearing the substituents.[9] If a similar β-hydrogen abstraction takes place also in this case, it would regenerate an active cobalt hydride species to initiate the polymerization again. That the initiator efficiency is lower than unity is not compatible with such a chain transfer mechanism. A possible termination mechanism is the one which involves the participation of ortho hydrogens of the triphenylphosphine ligand (Scheme 1).

The formation of a cobalt complex Co(styrene)(C_6H_4-PPH_2)$(PPh_3)_2$,[8] in which cobalt is bonded with an *ortho* carbon of the triphenylphosphine ligand in the reaction of $CoH(N_2)(PPh_3)_3$ with styrene, supports the feasibility of the above mechanism.

TABLE 4. STEREOREGULARITY OF POLY(METHYL METHACRYLATE)

No.	Solvent	Triad[a)] mm	mr	rr	Pm[b)]
1	—	10	25	65	0.23
2	Toluene	9	32	59	0.27
3	DMF	3	24	73	0.15

a) Triad tacticities: mm, isotactic; mr, heterotactic; rr, syndiotactic; peak areas determined by NMR spectra measured in nitromethane at 120°. b) Probability of *meso* placement; Average values calculated from triad are shown. Catalyst: $CoH(N_2)(PPh_3)_3$ at room temparature.

It was observed that the stereoregularity of poly(methyl methacrylate) obtained by the alkyl iron complex is affected by solvents, an acetone-soluble polymer rich in syndiotactic fraction, and an acetone-insoluble stereoblock type polymer being obtained.[10] The methyl methacrylate polymers obtained by the cobalt complex in toluene, dimethyl formamide and in the absence of solvent were soluble in acetone. The triad tacticities determined by NMR spectroscopy are given in Table 4. The polymers are all rich in syndiotactic fraction. The polymerization process appears to obey the Bernoulli trial with the probability of *meso* placement Pm[11] ranging from 0.15 to 0.27 depending on the solvent employed. The main factor in determining the stereoregularity of the polymer may be the mutual electrostatic and steric interactions between the substituents of the coordinating monomer and those of the polymer end attached to cobalt.

In order to obtain further information on the propagation mechanism, the copolymerization of methyl methacrylate (M_1) with methacrylonitrile (M_2) was studied. The results indicate that the copolymerization curve differs distinctly from that of free radical polymerization,[12] being somewhat similar to that of anionic polymerization.[13] The copolymer produced by the present catalyst, however, contains more methacrylonitrile units than those obtained by the conventional anionic initiators. The monomer reactivity ratios determined by an intersection method[14] for the copolymerization by $CoH(N_2)(PPh_3)_3$ were 0.20 ± 0.05 (r_1), 7.50 ± 0.40 (r_2), and $r_1\times r_2=1.5\pm0.5$. A preferential introduction of methacrylonitrile to methyl methacrylate into the copolymer may be caused by the stronger coordinating ability of methacrylonitrile than methyl methacrylate in the compeptitive coordination of the monomers toward the complex with the growing polymer chain.[4]

In conclusion, the overall feature of the polymerization of vinyl monomers with the cobalt hydride complex is quite similar to that with the alkyliron[4] and ruthenium hydride[8] complexes: (i) the rate-determining initiation process involves the dissociation of the ligand for making a coordination site available toward the incoming monomer which enters into the metal–hydrogen or metal–carbon bond; (ii) the compeptitive coordination process is important in regulating the molecular weight and copolymer composition; (iii) the termination process is probably a spontaneous unimolecular process without involving a chain transfer process.

Experimental

General. Hydridodinitrogentris(triphenylphosphine)-cobalt was prepared as reported.[6] Monomers and solvents were purified by the usual methods and stored under nitrogen.

Polymerization. Polymerization was mostly carried out in a sealed ampoule in which the catalyst, monomer and solvent were transferred in a nitrogen stream or by a trap-to-trap distillation *in vacuo*. The ampoule was opened after the set time of polymerization and the content was poured into acidic methanol. The polymer was filtered, washed with methanol and dried. Kinetic study was carried out with a Schlenk type flask in a thermostatted water bath, the monomer being added with a pipette into the Schlenk type flask containing the catalyst solution. The yield was measured by weighing the polymer obtained after a set interval.

Copolymerization Experiment. Compositions of the copolymers between methyl methacrylate and methacrylonitrile were determined from the microanalysis of carbon, hydrogen and nitrogen.

Molecular Weight. The molecular weights of polymers were measured by a viscocity method using the following equations: for poly(methyl methacrylate),[15] $[\eta]=3.80\times10^{-5}\,M^{0.79}$; for poly(acrylonitrile),[16] $[\eta]=1.66\times10^{-4}\,M^{0.8}$; for poly(methacrylonitrile),[17] $[\eta]=9.55\times10^{-4}\,M^{0.56}$.

NMR Spectra. Proton magnetic resonance spectra of poly(methyl methacrylate) were obtained at 100 °C with a JEOL PS-100 Spectrometer at 100 MHz by using the sample solutions in nitromethane (*ca.* 10% W/V) containing a few per cent of tetramethylsilane as an internal standard.

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