Vinyl Polymerization with Transition Metal Alkyls and Hydrides

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ABSTRACT

Transition metal alkyls and hydrides isolated from Ziegler-type catalyst mixtures serve as appropriate models for coordination polymerization. These transition metal complexes initiate the polymerization of some vinyl compounds and aldehydes. In some cases the monomer-coordinated complexes may be isolated and the interaction of the monomer with the transition metal complexes may be studied. Comparison of the polymerization kinetics of the vinyl compounds with the decay kinetics of the initial transition metal complexes on interaction with the monomer provided important information with respect to the mechanism of coordination polymerization by these complexes. The effect of organoaluminum compounds on the reactivity of the transition metal complexes has been also studied. These transition metal alkyls initiate the polymerization of acetaldehyde to give a polyether-type polymer at $-78°C$ and a polymer with OH groups at room temperature.

Ziegler-type catalysts represent one of the most versatile and excellent catalyst systems and have attracted, over two decades, the interest of very many polymer chemists. Nevertheless, their complexity and heterogeneity have hindered a clear understanding of the reaction mechanism, and some unsolved problems still remain concerning the details of the polymerization mechanism. It has been generally accepted, however, that an organotransition metal complex constitutes the active center, and the polymerization proceeds by coordination of monomers and their ensuing insertion into the transition metal-carbon or metal-hydrogen bond.

An approach to understanding the mechanism of the coordination polymerization is to isolate aluminum-free transition metal complexes with the metal-carbon or metal-hydrogen bond and study their behavior toward monomers [1, 2]. We have found that the transition metal alkyls and hydrides can be isolated from Ziegler-type reaction mixtures containing transition metal compounds and alkylaluminum compounds under appropriate conditions. Some of the isolated complexes show polymerization activities, and others form coordination compounds with some olefins. Table 1 summarizes the transition metal alkyls and hydrides which have been isolated and characterized, and also which of their polymerization activities have been examined in our group [2]. Tertiary phosphines and 2,2'-bipyridyl (bipy) proved to be particularly useful in stabilizing alkyl and hydrido complexes of later transition metals, whereas their stabilization effect was less pronounced in early transition metal complexes. Alkyls or hydrides of Ti [3], Cr [4], and Mn [5] have been prepared by the reactions of these transition metal halides with alkylaluminum compounds whereas the rest of the complexes shown in Table 1 have been prepared from transition metal acetylacetonates. Hydride complexes are considered to be formed by β-elimination reaction of unstable intermediate alkyl transition metal complexes.

Most of the alkyls and hydrides of Group VIII transition metals and copper reacted with various olefins and converted many vinyl monomers to high polymers, whereas some of the alkyls of early transition metals, initiated cationic polymerization. Detailed studies have been made on the reactions of $R_2Ni(bipy)$ [6-9], $R_2Fe(bipy)_2$ [10-16], $HCo(N_2)(PPH_3)_3$ [17-20], and $H_2Ru(PPh_3)_4$ [21-24] with various vinyl compounds, and we describe here an outline of the results.

$R_2Ni(bipy)$ (I) behaves somewhat differently from the other three complexes mentioned. It reacts with a variety of olefins but no polymerization is initiated in the complete absence of oxygen, and as such it serves as a good model compound for studying the interaction of a transition metal complex with olefins. The reaction

TABLE 1. Transition Metal Alkyls and Hydride Isolated from
Ziegler-Type Catalyst Systems

Group IV	$MeTiCl_3$, $MeTiCl_3 \cdot L$ (L = Py, THF, bipy, PPh_3)
VI	$RCrCl_2 \cdot L_3$ (R = Me, Et, Pr, i-Bu; L = THF, Py, α,β,γ-picolines, $PrNH_2$, $BuNH_2$) $MoH(acac)(dpe)_2$ dpe = 1,2-bis(diphenylphosphino)ethane
VII	$MnHI(THF)_{1,5}$
VIIIa	$R_2Fe(bipy)_2$ (R = Me, Et, Pr), $Me_2Fe(dpe)_2$, $H_2Fe(dpe)_2$, $Me_2Fe(PPh_3)_3$, $EtFe(acac)(PPh_3)_3$, H_2RuL_4 (L = PPh_3, Ph_2Me, PPh_2H)
VIIIb	$RCo(bipy)_2$ (R = Me, Et), $MeCo(dpe)_2$, $HCo(N_2)(PPh_3)_3$, $MeCo(PPh_3)_3$, $HRh(PPh_3)_4$
VIIIc	$R_2Ni(bipy)$ (R = Me, Et, Pr, i-Bu), $R_2Ni(dpe)$ (R = Me, Et), $MeNi(acac)(PPh_3)_2$, $EtNi(acac)(PPh_3)$, R_2NiL_2 (L = PEt_3, PBu_3)
IB	$MeCu$, $MeCu(bipy)$, $MeCuL_n$ (R = Me, Et, Pr, i-Bu; L = PPh_3, PCy_3, PPh_2Me, PPh_2Et, $PPhMe_2$, PBu_3, PEt_3), $(RCu)_2(dpe)_3$ (R = Me, Et, Pr, i-Bu)

proceeds through intermediate formation of an olefin-coordinated
dialykyl(bipyridyl)nickel complex (II) [6, 8, 9]:

$$\tag{1}$$
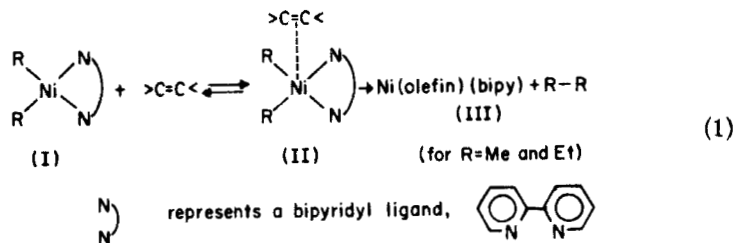
The intermediate olefin-coordinated alkylnickel complex (II) can be
isolated in the cases of acrylonitrile and acrolein at low temperatures.
The coordination of olefin to the alkylnickel complex leads to the
activation of the metal-carbon bonds, and the splitting of the M— C

bonds yields a zero-valent nickel complex coordinated with the olefin. The strength of interaction between the olefin and the zero-valent bipyridyl-nickel complex has been determined spectrophotometrically by examining the dissociation equilibrium of the zero-valent olefin-coordinated complexes (III) in solution. The study revealed that the olefin which interacts with nickel the more strongly activates the M–C bond in $R_2Ni(bipy)$ to the greater extent [9]. This finding has formed the basis for further study of the mechanism of the coordination polymerization of the vinyl monomers with iron, cobalt, and ruthenium complexes.

Examination of the reactions of $R_2Fe(bipy)_2$, $HCo(N_2)(PPh_3)_3$, and $H_2Ru(PPh_3)_4$ with various olefins and comparison of the kinetics of the decay of these complexes in the presence of olefins with those of the polymerization of vinyl compounds by these complexes revealed some common features in the reactions of the alkyl and hydrido transition metal complexes with olefins.

The behavior of $HCo(N_2)(PPh_3)_3$ (IV) is illustrative in demonstrating the characteristic reactions and will be described here [18-20].

BEHAVIOR OF $HCo(N_2)(PPh_3)_3$ TOWARD OLEFINS

Complex IV reacts with a very electronegative olefin such as tetracyanoethylene (TCNE) to yield an olefin-coordinated complex $CoH(TCNE)_2(PPh_3)_2$. Olefins of medium Alfrey-Price's e-values such as acrylonitrile, methacrylonitrile, acrolein, and methyl methacrylate are polymerized by IV. Olefins of lower e-values such as styrene form olefin-coordinated complexes and liberate 1 mole equivalent of the hydrogenated olefin, i.e., ethylbenzene from styrene:

$$HCo(N_2)(PPh_3)_3 + 2CH_2=CH \longrightarrow CH_2=CH-Ph + N_2 + PhEt$$
$$Ph \quad (Ph_2P)_2 Co-PPh_2$$

(2)

(V)
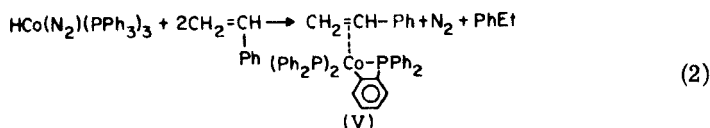
Ethylbenzene is considered to be formed by insertion of styrene into the Co–H bond followed by abstraction of hydrogen at the ortho-position of one of the coordinated triphenylphosphines. On the other hand, a less electronegative olefin, isobutyl vinyl ether (IBVE), displaced all the triphenylphosphine ligands from IV to give $CoH(IBVE)_2$. Vinyl acetate showed an unique reactivity to give cobalt acetate with evolution of ethylene [24].

The corresponding methylcobalt complex showed similar reactivities toward various olefins [18].

The course of the reactions of $HCo(N_2)(PPh_3)_3$ with various olefins can be conveniently followed by observing the spectral change of the complex in solution. The electronic spectrum of complex IV with a peak at 390 nm decays in the presence of olefins following the first-order kinetics with respect to the concentration of IV:

$$-\frac{d}{dt}\left[HCo(N_2)(PPh_3)_3\right] = k[HCo(N_2)(PPh_3)_3] \tag{3}$$

The pseudo-first-order rate constant k increases with an increase in olefin concentration and approaches a constant value k_1 of 1.6×10^{-3} sec^{-1} at 25°C which is independent of the kind of olefin. Analysis of the dependence of the pseudo-first-order rate constant on the olefin concentration and the examination of the inhibition effects of the addition of triphenylphosphine and of nitrogen pressure revealed that k can be expressed by

$$\frac{1}{k} = \frac{1}{k_1} + A\{B + C[N_2]\}\frac{[PPh_3]}{[M]} \tag{4}$$

where $[M]$ is the olefin concentration and A, B, and C are constants. The kinetic results expressed by Eqs. (3) and (4) are compatible with the mechanism

$$HCo(N_2)(PPh_3)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCo(N_2)(PPh_3)_2 + PPh_3$$
$$[C_1] \qquad\qquad\qquad [C_2]$$

$$[C_2] + olefin \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HCo(olefin)(N_2)(PPh_3)_2$$
$$[C_3]$$

$$[C_3] \underset{k_{-3}}{\overset{k_3,\ -N_2}{\rightleftharpoons}} HCo(olefin)(PPh_3)_2 \overset{k_4}{\longrightarrow} \text{irreversible reaction} \tag{5}$$
$$[C_4] \qquad\qquad\qquad \text{(polymerization)}$$

$CoH(N_2)(PPh_3)_3$ is a coordinatively saturated species and it slowly liberates one of the triphenylphosphine ligands in solution to

accommodate a coordination site for the incoming olefin. The coordi-
nation of olefin leads to the activation of the Co–H bond and
of the coordinated N_2, and the olefin may be inserted into the Co–H
bond, thus liberating N_2. This process is considered as the rate-
determining step. The insertion of the olefin may be followed by
ensuing insertions of monomers into the Co—C bond to yield a
polymer attached to cobalt which is spontaneously and irreversibly
terminated. Assumptions of the above mechanism and of steady-state
concentrations for $[C_2]$, $[C_3]$, and $[C_4]$ lead to the first-order
kinetics of Eq. (3), and the pseudo-first-order rate constant k ex-
pressed as

$$\frac{1}{k} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2 k_3}\frac{[PPh_3]}{[M]}\left\{(k_{-2}+k_{-3}) + \frac{k_{-2}k_{-3}}{k_4}[N_2]\right\} \qquad (6)$$

Equation (6) is in agreement with the experimental results expressed
by Eq. (4).

Examination of the ^{31}P NMR spectrum of $CoH(N_2)(PPh_3)_3$ in toluene
supports the slow dissociation of triphenylphosphine. The proton-
decoupled ^{31}P NMR spectrum of IV in the absence of added triphenyl-
phosphine shows no peak of free triphenylphosphine. In the presence
of an equivalent amount of added triphenylphosphine, the ^{31}P NMR
spectrum shows very sharp peaks of the coordinated triphenylphosphine
and free triphenylphosphine in a peak ratio of 3:1 at -80°C, and these
peaks approach each other accompanied by broadening with an increase
of the temperature. These results show that the dissociation of tri-
phenylphosphine from IV is negligible at room temperature but the
added triphenylphosphine does exchange with the coordinated triphenyl-
phosphine, suggesting that a slow $S_N 1$ type dissociation of triphenyl-

phosphine from $CoH(N_2)(PPh_3)_3$ is taking place.

A quite similar kinetic behavior is observed with $CoH(CO)(PPh_3)_3$
which can be prepared by displacement of N_2 with CO from IV [19].
The kinetic results are in agreement with the mechanism

$$CoH(CO)(PPh_3)_3 \underset{k_{-1}}{\overset{k_1'}{\rightleftharpoons}} CoH(CO(PPh_3)_2 + PPh_3$$

$$k_{-2}' \Updownarrow k_2'$$
$$+ \text{ olefin}$$

$$CoH(\text{olefin})(PPh_3)_2$$
$$\downarrow$$
irreversible reaction   (7)
(polymerization)

In the polymerization of vinyl monomers with IV, the polymerization starts after a short induction period of about 2 min and, with time, the polymer yield (Y_t) approaches a certain maximum value (Y_∞) which depends on the concentration of IV. The molecular weight of the polymer was independent of the polymer yield, polymerization time, and the initiator concentration, and increased linearly with the monomer concentration. Plotting of $\log(Y_\infty - Y_t)$ against polymerization time gave straight lines indicating the relationship.

$$\log(Y_\infty - Y_t) = -\bar{k}t + const \tag{8}$$

The $\bar{k}$ value increases with the monomer concentration, approaching a limiting value of 1.6×10^{-3} sec^{-1} at $25°C$.

On the basis of the spectroscopic study of the decay kinetics of $CoH(N_2)(PPh_3)_3$ in the presence of the monomer and on the assumption that a polymer molecule is produced from the complex with an initiator efficiency f, followed by further rapid insertion of monomers into the Co–C bond (propagation) and spontaneous termination after the polymer reached a certain degree of polymerization $\overline{DP}$, the rate of polymerization R_p can be expressed by

$$R_p = \frac{d[Y]}{dt} = f\overline{DP} \left\{ -\frac{d[CoH(N_2)(PPh_3)_3]}{dt} \right\} \tag{9}$$

Integration of Eq. (9) utilizing the relationship of Eq. (3) leads to

$$\log(Y_\infty - Y_t) = -kt + \log\{f\overline{DP}[CoH(N_2)(PPh_3)_3]_0\} \tag{10}$$

where $[CoH(N_2)(PPh_3)_3]_0$ represents the initial concentration of IV.

The form of Eq. (10) is identical with Eq. (8). The comparison of $\bar{k}$, obtained from polymerization kinetics, with k, observed by the spectroscopic method following the decay kinetics of IV, indicated a reasonable agreement, supporting the validity of our assumptions.

A linearity was observed between the molecular weight of the polymer and the monomer concentration. Addition of triphenylphosphine to the polymerization system caused a decrease in polymer yield as well as in the molecular weight. Employment of solvents of higher coordinating abilities also caused a decrease in the polymer yield.

These results suggest that coordination of monomer to the complex

with a growing polymer chain leads to insertion of the monomer be-
tween the cobalt-carbon bond whereas the coordination of triphenyl-
phosphine or the solvent molecule leads to spontaneous termination
with certain probabilities. These assumptions lead to the following
equation which is in agreement with the experimental results:

$$\overline{DP} = (k_p/k_t)\,[M] \tag{11}$$

The linearity between $\overline{DP}$ and $[M]$ passing through the origin indicates
the absence of a chain transfer with the monomer.

    In the polymerization of methyl methacrylate with $Et_2 Fe(bipy)_2$,
we have confirmed the formation of ethane-d_1 when cis-
$CHD{=}C(CH_3)CO_2 CH_3$ was used [15]. This fact was taken as evidence
indicating the participation of a termination mechanism involving the
hydrogen abstraction from the β-position of the polymer chain bonded
to iron. In the case of $HCo(N_2)(PPh_3)_3$ such a termination process is
unlikely since it would regenerate the active cobalt hydride species
to initiate the polymerization again. A possible termination mechan-
ism is the one which involves the participation of the ortho-hydrogen
of the triphenylphosphine ligand:

$$\tag{12}$$
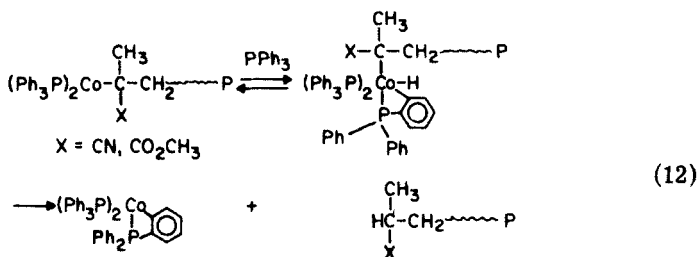
This scheme is in line with the formation of the previously described
ortho-metallated species, Eq. (2).

STEREOREGULARITIES OF POLYMERS PRODUCED
WITH TRANSITION METAL ALKYLS AND HYDRIDES

    Methyl methacrylate can be polymerized with $HCo(N_2)(PPh_3)_3$ and
$R_2 Fe(bipy)_2$, and the stereoregularity of the polymers was examined
by NMR spectroscopy. The polymers produced with $HCo(N_2)(PPh_3)_3$

were rich in syndiotactic fraction, and the polymerization process
appears to obey the Bernoulli statistics with the probability of meso-
placement p_m ranging from 0.15 to 0.27 depending on the solvent
employed. In contrast, $R_2 Fe(bipy)_2$ gave two types of poly(methyl
methacrylate): one was rich in syndiotactic fraction and the other
was a stereoblock-type polymer. The latter was prepared by polym-
erization of methyl methacrylate by $Et_2 Fe(bipy)_2$ in solvents of weak
coordinating abilities, and the polymerization process that gave this
type of polymer obeyed the first-order Markovian statistics with a
penultimate effect, whereas the former was obtained in strongly
coordinating solvents and the propagation process obeyed the Bernoulli
statistics. Based on these results, a possible mechanism of stereoregu-
lation involving the control of monomer coordination toward the complex
with the remaining alkyl group, bipyridyl, and the growing polymer
chain attached to iron has been discussed [14].

NMR examination of the mode of double bond opening in the polym-
erization of $cis\text{-}CHD{=}C(CH_3)CO_2 CH_3$ with $Et_2 Fe(bipy)_2$ revealed
trans-opening of the double bond, and mechanisms compatible with
the result have been discussed [16].

COPOLYMERIZATION

Some sets of vinyl monomers may be copolymerized with
$HCo(N_2)(PPh_3)_3$, $R_2 Fe(bipy)_2$, and $H_2 Ru(PPh_3)_4$. Examination of
the compositions of these copolymers indicated a trend of electro-
negative monomers with stronger coordinating abilities to transition
metal being introduced into the copolymer in preference to less elec-
tronegative monomers with weaker coordinating abilities (12-14, 20,
23].

CONCLUSIONS OF THE STUDY ON THE MECHANISM OF VINYL POLYMERIZATION WITH TRANSITION METAL ALKYLS AND HYDRIDES

1. Predissociation of a part of the ligands from the coordinatively
saturated transition metal complex is required to accommodate the
incoming monomer.

2. The coordination of the monomer to the transition metal com-
plex leads to the activation of the M–C or M–H bond, and the rate-
determining initiation step probably involves the insertion of the
monomer into the activated M–C or M–H bond. The slow initiation
step is followed by a rapid propagation step involving the successive

insertion of the monomers into the M–C bonds and the spontaneous termination process.

3. Coordination of the monomer with the transition metal complex constitutes the most important factor in controlling copolymerization and stereospecific polymerization.

EFFECT OF ORGANOALUMINUM COMPOUNDS

While the main characteristics in the polymerization of vinyl monomers with transition metal alkyls and hydrides isolated from Ziegler-type mixed catalyst systems may be summarized by the above conclusions, the actual Ziegler catalysts prepared in situ from transition metal halides and alkylaluminum compounds are more complicated and the effect of the alkylaluminum component cannot be neglected. In order to study the role of the alkylaluminum component in Ziegler catalysts, the behavior of transition metal alkyls in the presence of alkylaluminum compounds were examined [25]. The aluminum-free alkyltransition metal complexes CH_3TiCl_3, $R_2Ni(bipy)$, $C_2H_5CrCl_2 \cdot Py_3$, $R_2Fe(bipy)_2$, and $CH_3Cu(PPh_3)_3 \cdot$(toluene) [26] are stable compounds but they are decomposed by the addition of alkylaluminum compounds, whereas $HMnI(THF)_{1.5}$ was somewhat stabilized [5]. Kinetic study of the decomposition of M–C bond in CH_3TiCl_3 and $R_2Ni(bipy)$ revealed that the decomposition reactions were first order in the concentrations of the transition metal alkyls. Comparison of the effect of different aluminum compounds showed that the destabilizing effect of the aluminum compound increased in the order of Lewis acidity, $AlR_2(OEt) < AlR_3 < AlCl_3$.

In explaining the role of the aluminum component in the actual Ziegler catalyst, some binary models, such as the one shown here, have been proposed [29-31]:
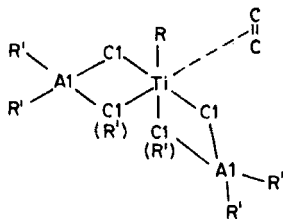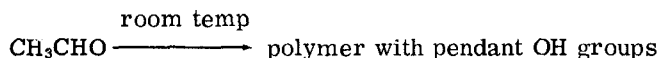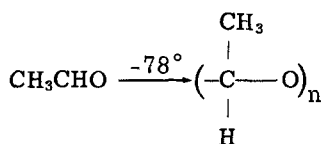
In this model the alkylaluminum components are bridged with titanium through chlorine or alkyl bridges and indirectly modify the activity of the active center–in this case, alkyltitanium complex. We consider that there are two main effects of the alkylaluminum component: 1) as a modifier of the stability of the transition metal-alkyl bond, and hence the activity toward insertion of the monomer into the M–R bond, and 2) as a modifier of the reactivity of the transition metal complex toward olefin. The striking destabilization of the transition metal alkyls by the addition of alkyl aluminum compounds suggests that the above binary model may be useful in accounting for the role of alkyl-aluminum compounds. The alkylaluminum compound complexed with an alkyltransition metal may be considered as acting as a Lewis acid by withdrawing electrons from the alkyl transition metal. Thus the situation may resemble that of the complexation of electronegative olefins, which may be regarded as π-acids, with R_2Ni(bipy) leading to the destabilization of R–Ni bonds.

POLYMERIZATION OF OTHER MONOMERS

In addition to vinyl monomers, other types of monomers may be polymerized with alkyltransition metal complexes [2]. Butadiene can be converted to its oligomers; cyclooctadiene, vinyl cyclohexene can be obtained with R_2Fe(bipy)$_2$ [10]; methyl heptatriene with RCo(bipy)$_2$ [27]; and cyclododecatriene with R_2Ni(bipy) [7]. Propylene can be rapidly converted to its dimers with R_2Ni(bipy) in the presence of AlEt$_2$Cl [28].

In this case the aluminum component appears to modify the nature of the catalytically active nickel species by complexation as discussed in the preceding section.

Polymerization of acetaldehyde gives two types of polymers. The polymerization with alkyl transition metals at -78°C gives a poly-ether-type polymer whereas polymerization above room temperature leads to viscous to powdery polymers of the "polyvinyl alcohol-type."

$$CH_3CHO \xrightarrow{-78°} (-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}{-\!-}O)_n$$

$$CH_3CHO \xrightarrow{room\ temp} polymer\ with\ pendant\ OH\ groups$$

The mechanism of polymerization for the latter polymer is not com-
pletely understood at the moment, but the polymerization seems to
proceed through the repetitive occurrence of aldol condensation
initiated by the alkyltransition metal complexes.

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