The Mechanism of Vinyl Polymerization by Dialkylbis(dipyridyl)iron(II)

Takakazu Yamamoto, Akio Yamamoto, and Sakuji Ikeda
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo

(Received May 19, 1971)

Kinetics of polymerization of vinyl compounds (acrylonitrile, methacrylonitrile, acrolein, methyl vinyl ketone, methyl acrylate, alkyl methacrylates, and 2-vinylpyridine) with dialkylbis(dipyridyl)iron(II), $FeR_2(dipy)_2$ **1** (R= CH_3, C_2H_5, n-C_3H_7), was studied. By comparison with previous kinetic results in which the decomposition of **1** was followed spectroscopically, a polymerization mechanism including a slow initiation process followed by rapid propagation and unimolecular termination processes was proposed. The effects of the concentration of monomer, the addition of dipyridyl and the coordinating ability of solvent on the molecular weight of the polymer were explained by competitive coordination to the iron complex having a growing polymer chain. Results of copolymerization experiments were explained in terms of competitive coordination and insertion reactions between the monomers involved. A linear relationship was found between $\log(1/r_1)$ values and the logarithms of stability constants of nickel–olefin π-complexes with methacrylonitrile as the reference (M_1). From the formation of C_2H_5D in the polymerization of β-*cis*-d_1-methyl methacrylate with $Fe(C_2H_5)_2(dipy)_2$ a unimolecular termination process involving abstraction of β-hydrogens of the growing chain by the alkyl group or the iron complex was proposed.

Although great efforts have been made to unravel the mechanism of coordination polymerization by Ziegler type catalysts, the inherent complexity and instability of the mixed catalyst systems prepared *in situ* have hindered the drawing of a clear-cut conclusion on the kinetic results.[1]. Recently kinetic studies have been carried out successfully on the polymerization mechanisms of vinyl monomers[2] and butadiene[3] using isolated π-allyl-transition metal complexes. We have been studying the properties of isolated alkyl-nickel, cobalt, and iron complexes[4] which are thermally stable and appropriate for studies[5] on catalytic reactions of unsaturated conpounds. Our attention was focused on the activation mechanism of alkyl-iron bonds by interaction of dialkylbis(dipyridyl)-iron(II) with various olefins.[6] In this paper we deal mostly with the propagation and termination mechanisms. Vinyl polymerization by alkyl-iron and cobalt complexes has been communicated briefly.[7] NMR studies on the propagation mechanism have also been reported.[8]

Results and Discussion

Kinetics of Polymerization. The results of polymerization of various monomers with $FeR_2(dipy)_2$ are summarized in Table 1 where R=CH_3, C_2H_5, and n-C_3H_7. The monomers are arranged in decreasing order of Afrey-Price "*e*-value"[9]. The Table indicates a general trend, except for 2-vinylpyridine[6], for monomers with higher *e*-values to polymerize readily, monomers with medium *e*-values to polymerize slowly, and the polymerization of monomers with low or negative *e*-values to proceed either slowly or not take place. These monomers are not polymerized with dipyridyl alone; dipyridyl-iron complexes without R–Fe bonds such as $Fe(dipy)_2$[4], $Fe(dipy)_3$[4] and Fe(dipy)(vinyl acetate)$_2$[6] do not initiate polymerization. Methacrylic esters present an interesting intermediate case. Methyl methacrylate (*e*-value= 0.40) can be polymerized by $FeR_2(dipy)_2$ (R=CH_3, C_2H_5, C_3H_7), whereas less electronegative ethyl methacrylate (*e*-value=0.17) can be polymerized by $Fe(n\text{-}C_3H_7)_2(dipy)_2$ but not by the methyl and ethyl homologs (a negligible amount of polymer was obtained with $Fe(CH_3)_2(dipy)_2$). The results clearly indicate the important role of the alkyl-iron bond in the initiation process. In accordance with observation on the activation of alkyl-nickel bonds by interaction with olefins[5], the propyl-iron bond seems to be more easily activated than methyl- and ethyl-iron bonds. Once the polymerization is initiated by activation of the alkyl-iron bond through interaction with a monomer having a more electronegative substituent, a monomer with a less electronegative substituent can be taken into the copolymer; thus, ethyl methacrylate and methacrylonitrile were copolymerized with $Fe(C_2H_5)_2(dipy)_2$, but not ethyl methacrylate.

Figure 1 shows a typical time-conversion curve of the polymerization of acrylonitrile with $Fe(C_2H_5)_2(dipy)_2$ and the dependence of molecular weight of the polymer on conversion. The polymerization was carried out in the presence of extra dipyridyl added in order to control the polymerization rate. Since the polymerization yield is low, the concentration of acrylo-

---

[1] L. Reich and A. Schindler, "Polymerization by Organometallic Compounds," Interscience Publishers, New York (1966).

[2] D. G. Ballard, W. H. Jones, and T. Medinger, *J. Chem. Soc., B*, **1968**, 1168, 1176.

[3] J. H. Harrod and L. R. Wallace, *Macromolecules*, **2**, 449 (1969).

[4] a) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Amer. Chem. Soc.*, **87**, 4652 (1965); b) *ibid.*, **90**, 1878 (1968); c) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Organometal. Chem.*, **6**, 572 (1966); *J. Amer. Chem. Soc.*, **88**, 5198 (1966).

[5] T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **93**, 3350, 3360 (1971).

[6] T. Yamamoto, A. Yamamoto, and S. Ikeda, This Bulletin, **45**, 1104 (1972).

[7] A. Yamamoto, T. Shimizu, and S. Ikeda, *Makromol. Chem.*, **136**, 297 (1970).

[8] A. Yamamoto, T. Shimizu, and S. Ikeda, *Polymer J.* (Japan), **1**, 171 (1970).

[9] J. Brandrup and E. H. Immergut, "Polymer Handbook," II-341, Interscience Publishers, New York, London, Sydney (1966).

TABLE 1. POLYMERIZATION OF VINYL MONOMERS BY $FeR_2(dipy)_2$

$FeR_2(dipy)_2$ (g)	Monomer (m*l*)		Temp. (°C)	Time	Yield (%)	Mol. wt. $\times 10^{-4}$
R = C_2H_5, 0.050	Acrylonitrile	5.0	30	9 min	30	1.05
C_2H_5, 0.020	Methacrylonitrile	10.0	room temp.	3 days	53	12.7
C_2H_5, 1.04	Acrolein	6.0	−30	2 days	70	
C_2H_5, 1.37	Methyl vinyl ketone	5.0	−20	10 days	77	
C_2H_5, 0.24	Methyl acrylate	6.0	room temp.	18 hr	64	
CH_3, 0.040	Methyl methacrylate	10.0	25	6 days	16	
C_2H_5, 0.13	Methyl methacrylate	10.0	31	3 days	5.6	12.6
n-C_3H_7, 0.38	Methyl methacrylate	8.0	30	2 days	33	
CH_3, 0.35	Ethyl methacrylate	10.0	room temp.	2 days	trace	
C_2H_5, 0.23	Ethyl methacrylate	10.0	room temp.	7 days	0	
n-C_3H_7, 0.20	Ethyl methacrylate	5.0	room temp.	9 days	3.6	
C_2H_5, 0.91	Vinyl acetate	5.5	room temp.	3 days	0	
n-C_3H_7, 0.50	Vinyl acetate	6.0	room temp.	17 days	0	
C_2H_5, 0.30	2-Vinylpyridine	4.0	20	3 days	45	
C_2H_5, 0.44	Styrene	5.0	room temp.	7 days	0	
n-C_3H_7, 0.43	Styrene	5.0	room temp.	15 days	0	
C_2H_5, 0.62	Isobutyl vinyl ether	5.0	50	20 hr	0	

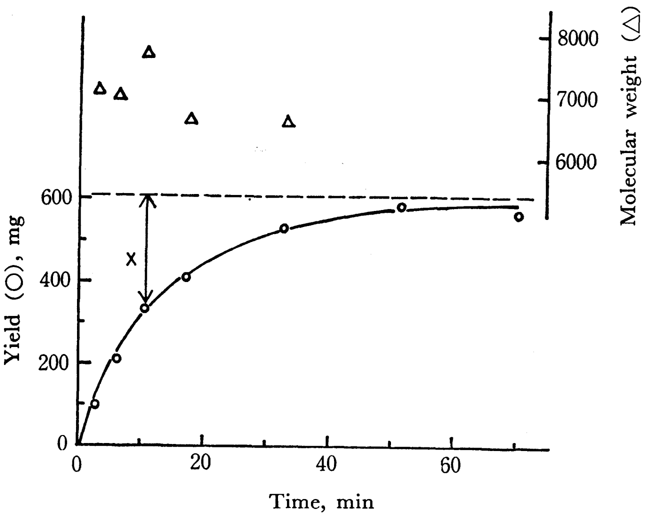


Fig. 1. Polymerization of acrylonitrile with $Fe(C_2H_5)_2(dipy)_2$ at 27.5°C; yield (○) *versus* time and molecular weight (△) of the polymer *versus* time. Acrylonitrile = 12.6 m*l*; dimethylformamide = 51 m*l*; $Fe(C_2H_5)_2(dipy)_2$ = 0.19 g; dipyridyl = 1.24 g.

nitrile can be regarded to be constant during the polymerization. Figure 1 indicates that the molecular weight of the polymer is virtually independent of time. As our spectroscopic study revealed[6], the concentration of $Fe(C_2H_5)_2(dipy)_2$ decreases with time in the presence of an olefin. The decrease of the concentration of the ethyl-iron complex should be responsible for the decrease of the polymerization rate. In fact the polymerization stops when the deep blue color of $Fe(C_2H_5)_2(dipy)_2$ disappears. Since the molecular weights of the polymers obtained at different conversions remain virtually constant, the yield of the polymer can be regarded as proportional to the number of polymer chains. The number of polymer chains produced from a single ethyl-iron complex (initiator efficiency) is shown in Table 2. The initiator efficiency increases with the increase of the monomer concentration approaching unity. The polymer yield is thus considered to be proportional to the ethyl-iron complex decomposed at a certain monomer concentration. If we plot the logarithms of the value *x* (Fig. 1) *versus* time a linear relationship is observed (Fig. 2) indicating the validity of the following equation.

$$-\frac{dx}{dt} = \bar{k}x \qquad (1)$$

The value *x* can be regarded to correspond to the remaining concentration of the ethyl-iron complex. The change of the slope $\bar{k}$ (Fig. 2) against the acrylonitrile concentration is plotted in Fig. 3. The value $\bar{k}$ increases with the increase of the acrylonitrile concentration approaching a limiting value of 0.2 min^{-1} in the presence of a small amount of dipyridyl added. Addition of a large amount of dipyridyl suppresses

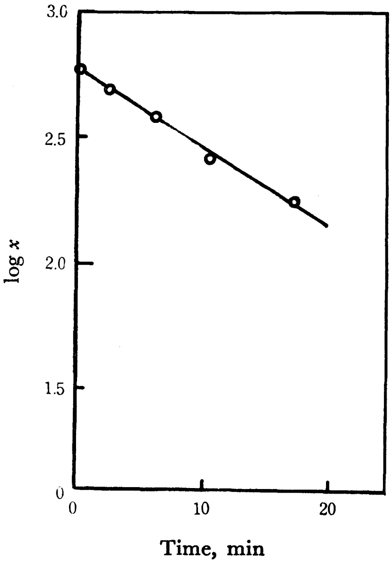


Fig. 2. The plot of logarithm of x (Fig. 1) versus time.

Table 2. Effects of concentration of monomers and dipyridyl on the molecular weights of polymers and the number of polymer chains produced from a single-iron complex

[Monomer][a) (mol/*l*)		[dipy][b) (mol/*l*)	$FeEt_2(dipy)_2$ (mmol)	Temp. (°C)	Time	Yield (g)	Mol. wt. $\times 10^{-3}$	n[c)
AN	2.0	0	0.071	10	25 min	1.45	104	0.20
AN	15.1	0	0.047	10	2 days	3.06	205	0.32
AN	1.26	7.0×10^{-3}	0.045	23	1 day	0.17	6.7	0.56
AN	2.42	7.1×10^{-3}	0.049	23	1 day	0.48	12	0.82
AN	4.15	7.4×10^{-3}	0.045	23	1 day	0.81	18.5	0.97
AN	0.69	0.155	0.95	23	1 day	0.60	~1.0[d)	~0.63[d)
AN	1.38	0.147	0.90	23	1 day	0.92	~1.2[d)	~0.85[d)
AN	3.01	0.130	0.77	23	1 day	2.24	~2.1[d)	~1.4[d)
MMA	9.40	0	0.30	30	3 days	0.53	126	1.4×10^{-2}
MMA	8.55	0	0.38	30	3 days	0.58	107	1.4×10^{-2}
MMA	7.80	0	0.33	30	3 days	0.15	94	0.49×10^{-2}

a) [Monomer]=concentration of the monomer; AN=acrylonitrile; MMA=methacrylate.
Solvent: dimethylformamide for acrylonitrile and tetrahydrofuran for methyl methacrylate.
b) [dipy]=concentration of added dipyridyl.
c) The number of polymer chains produced from a single ethyl-iron complex (initiator efficiency).
d) Since the molecular weights of the polymers in these cases were very low, only approximate values could be obtained by viscometry.

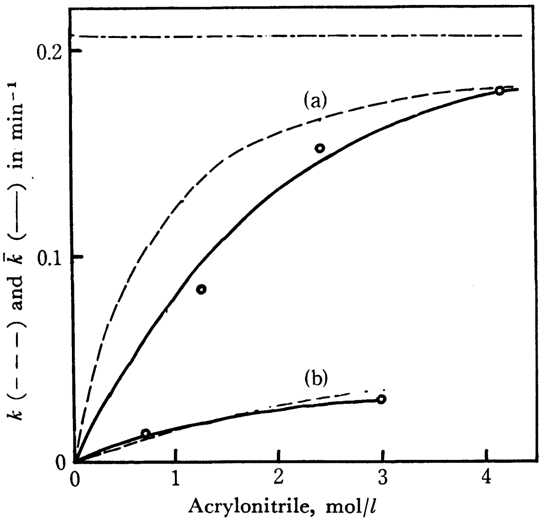


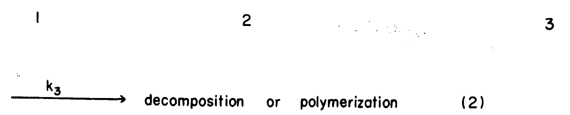
Fig. 3. Pseudo-first-order rate constants, k and $\bar{k}$, against the concentration of acrylonitrile at 23°C. (a), Concentration of dipyridyl was 7.2×10^{-3} mol/*l*; (b), Concentration of dipyridyl was about 0.14 mol/*l*. For k and $\bar{k}$ see the text. Solvent: dimethylformamide

the polymerization rate as shown by (b) in Fig. 3. We see a striking resemblance between this and the decomposition pattern of $Fe(C_2H_5)_2(dipy)_2$.[6) In Fig. 3 are also shown the change of pseudo-first-order rate constants k for decomposition of $Fe(C_2H_5)_2(dipy)_2$ with the concentrations of monomers (*cf.* Fig. 3 of the preceding paper[6)). The agreement between the rate constants indicates that the rate of polymerization of acrylonitrile by $Fe(C_2H_5)_2(dipy)_2$ is proportional to the decomposition rate of the ethyl-iron complex. This result implies that the initiation is the rate-determining step followed by rapid propagation and termination processes. The molecular weight of the polymer is independent of the initiator concentration[7) but is affected by the monomer concentration, the coordinating ability of the solvent employed and the concentration of dipyridyl added. Table 3 shows the effect of solvent on the molecular weight of poly(methyl methacrylate). Employment of a strongly coordinating solvent decreases the molecular weight of the polymer obtained. Table 2 shows that the molecular weight of the polymer increases with monomer concentration but decreases with the increase of dipyridyl concentration. These results suggest the competitive coordination of the monomer, dipyridyl and solvent toward an iron complex with a growing polymer chain.

Table 3. Effects of solvent on the molecular weight of poly(methyl methacrylate) at 30°C. Catalyst$=Fe(C_2H_5)_2(dipy)_2$. [dipy]=0 $[Fe(C_2H_5)_2(dipy)_2]=23\sim 28$ mmol/*l*

MMA (M)	Solvent	Molecular weight
4.68	Benzene	91000
6.36	Tetrahydrofuran	78000
3.06	Tetrahydrofuran	60000
4.68	Acetonitrile	46000

Dealing with the kinetics of decomposition of $FeR_2(dipy)_2$ we assumed the following activation mechanism of the metal-alkyl bond:[6)



(2)

If the above mechanism is valid, an inhibiting effect

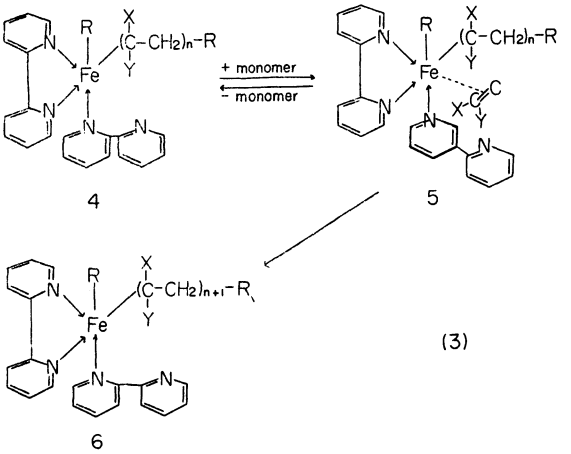
TABLE 4. INHIBITION OF POLYMERIZATION BY THE ADDITION OF DIPYRIDYL

Monomer (m*l*)	Solvent[a] (m*l*)	Dipyridyl (g)	Temp. (°C)	Time	Yield (%)
MMA 8.0	THF 16	0	30	46 hr	34
MMA 6.5	THF 13	0.30	30	46 hr	21
MMA 5.5	THF 11	0.80	30	46 hr	0
AN 5.0	DMF 20	0	30	30 min	23
AN 5.0	DMF 20	9.0	30	30 min	1.6

a) THF: tetrahydrofuran; DMF: dimethylformamide.

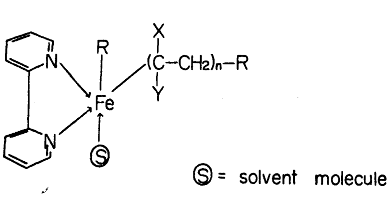
of dipyridyl for polymerization is expected. Table 4 substantiates this expectation showing that the polymerization of methyl methacrylate was completely inhibited and that of acrylonitrile severely retarded by the addition of dipyridyl.

If the polymerization proceeds through an insertion mechanism[7)], the coordinated monomer is inserted between one of the two iron-alkyl bonds in complex **3** generating a growing species **4** ($n=1$) as shown below.



(3)

Propagation processes might proceed further by coordination and insertion reactions of monomer molecules as shown in Eq. (3). The partially dissociated dipyridyl ligand may remain attached to iron as in **4**, **5**, and **6**, but the possibility that one dipyridyl is completely displaced as shown below can not be excluded.



7

We observed the effects of solvents and alkyl groups on the stereoregularity of methyl methacrylate polymer and the presence of a penultimate effect on the polymer configurations[8)]. Penultimate effects in solvents of low coordinating abilities were explained by assuming a species in which a coordination site is occupied by the substituent of the penultimate unit displacing the solvent molecule in **7**. The role of the singly bonded dipyridyl ligand in **4** may be similar at that of a solvent in **7**. If the explanation is reasonable we can anticipate that the proportion of acetone-insoluble stereoblock polymers produced by a propagation process involving a penultimate effect[8)] will decrease by the addition of dipyridyl. Table 5 supports this view.

TABLE 5. EFFECT OF DIPYRIDYL ON THE FORMATION OF ACETONE-INSOLUBLE POLY(METHYL METHACRYLATE)

Dipyridyl added (g)	$Fe(C_2H_5)_2(dipy)_2$ (g)	Acetone-insoluble fraction (%)
0	0.50	10.7
0	0.81	7.56
0.30	0.67	2.90
0.30	0.68	5.06
0.50	1.45	2.18

Methyl methacrylate=10 m*l*, Benzene=20 m*l*, Temperature=30°C, Time=2 days.

For an explanation of the difference in stereochemical configuration of poly(methyl methacrylate) obtained with $Fe(CH_3)_2(dipy)_2$ and $Fe(C_2H_5)_2(dipy)_2$, we previously assumed a difference in steric effects between the methyl and ethyl groups bonded to iron. However, an inductive effect of the alkyl group may also be involved. The higher rate constant (k_1) for the breakage of one Fe–N bond of dipyridyl from $Fe(C_2H_5)_2(dipy)_2$ than for the methyl homolog has been explained by the inductive effect of the alkyl group in the preceding paper[6)]. If a similar situation holds in the complete dissociation of one dipyridyl ligand from **4** giving **7**, the formation of an acetone-insoluble poly(methyl methacrylate) will be favored for the ethyl-iron complex than for the methyl complex in agreement with the experimental result that the acetone-insoluble stereoblock polymer was obtained with the ethyl complex but not with the methyl homolog.[8)]

Copolymerization. We observed previously that acrylonitrile unit is introduced into a polymer chain preferentially to methyl methacrylate which has a less coordinating ability toward the iron complex[7)]. We deal herewith with more quantitative aspect of copolymerization. From copolymerization experiments

TABLE 6. MONOMER REACTIVITY RATIOS IN COPOLYMERIZATIONS OF VINYL MONOMERS WITH $Fe(C_2H_5)_2(dipy)_2$.

M_1	M_2	r_1	r_2	$r_1 \times r_2$
Methacrylonitrile	Acrylonitrile	0.17 ± 0.03	17 ± 2	3.0 ± 0.9
Methacrylonitrile	Methyl acrylate	0.23 ± 0.06	3.4 ± 0.4	0.78 ± 0.23
Methacrylonitrile	Methyl methacrylate	4.2 ± 1.2	0.16 ± 0.05	0.73 ± 0.40
Acrylonitrile	Methyl methacrylate	25 ± 5	0.09 ± 0.04	2.6 ± 1.6

of vinyl monomers with $Fe(C_2H_5)_2(dipy)_2$, monomer reactivity ratios were obtained by using Fineman-Ross' method[10]. The values are summarized in Table 6.

The results can be explained by assuming the competitive coordination to the iron complex and the ensuing insertion reactions between metal-carbon bonds.

$$\begin{aligned}
&\text{Fe-m}_1\text{-}\sim\sim + M_1 \underset{k_{11}^{(-1)}}{\overset{k_{11}^{(1)}}{\rightleftharpoons}} \underset{\overset{\vdots}{M_1}}{\text{Fe-m}_1\text{-}\sim\sim} \xrightarrow{k_{11}^{(2)}} \text{Fe-m}_1\text{-m}_1\text{-}\sim\sim \\
&\text{Fe-m}_1\text{-}\sim\sim + M_2 \underset{k_{12}^{(-1)}}{\overset{k_{12}^{(1)}}{\rightleftharpoons}} \underset{\overset{\vdots}{M_2}}{\text{Fe-m}_1\text{-}\sim\sim} \xrightarrow{k_{12}^{(2)}} \text{Fe-m}_2\text{-m}_1\text{-}\sim\sim \\
&\text{Fe-m}_2\text{-}\sim\sim + M_1 \underset{k_{21}^{(-1)}}{\overset{k_{21}^{(1)}}{\rightleftharpoons}} \underset{\overset{\vdots}{M_1}}{\text{Fe-m}_2\text{-}\sim\sim} \xrightarrow{k_{21}^{(2)}} \text{Fe-m}_1\text{-m}_2\text{-}\sim\sim \\
&\text{Fe-m}_2\text{-}\sim\sim + M_2 \underset{k_{22}^{(-1)}}{\overset{k_{22}^{(1)}}{\rightleftharpoons}} \underset{\overset{\vdots}{M_2}}{\text{Fe-m}_2\text{-}\sim\sim} \xrightarrow{k_{22}^{(2)}} \text{Fe-m}_2\text{-m}_2\text{-}\sim\sim
\end{aligned} \tag{4}$$

$$k_{11} = \frac{k_{11}^{(1)}k_{11}^{(2)}}{k_{11}^{(-1)}},\ k_{12} = \frac{k_{12}^{(1)}k_{12}^{(2)}}{k_{12}^{(-1)}},\ k_{21} = \frac{k_{21}^{(1)}k_{21}^{(2)}}{k_{21}^{(-1)}},\ k_{22} = \frac{k_{22}^{(1)}k_{22}^{(2)}}{k_{22}^{(-1)}} \tag{5}$$

$$r_1 = \frac{k_{11}}{k_{12}},\ r_2 = \frac{k_{22}}{k_{21}} \tag{6}$$

In these equations dipyridyl ligands and the other alkyl group are omitted for the sake of simplification. M_1 and M_2 are coordinating monomers and m_1 and m_2 represent monomer units taken into the polymer chains. We found a linear relationship between $\log k_{Ni}$, the logarithms of rate constants for the scission of Ni–R bonds of $NiR_2(dipy)$, and $\log K$, the logarithms of stability constants of Ni(dipy)(olefin)[5]. We have also found a linear relationship between the $\log k_{Ni}$ value for Ni–R scission and $\log (k_1k_2k_3/k_{-1}k_{-2})$ which represent the relative reactivities of olefins for the decomposition of $FeR_2(dipy)_2$ (*cf.* Eq. (2),[9] and Fig. 5 of the preceding paper[6]). From these two relationships, a linear relationship between $\log K$ and $\log (k_1k_2k_3/k_{-1}k_{-2})$ can be derived; $\log(k_1k_2k_3/k_{-1}k_{-2}) = 2.4 \log K - 4.3$. Therefore, it is reasonable to assume a linear relationship between $\log K$ and the logarithms of rate constants, k_{ij}, for insertion of a monomer (j) into the iron-carbon bond of the preceding monomer unit (i) already introduced into the polymer chain. These assumptions lead to the following relationships.

$$\begin{aligned}
\log k_{11} - \log k_{12} &= a_1(\log K_1 - \log K_2) \\
\log k_{21} - \log k_{22} &= a_2(\log K_1 - \log K_2)
\end{aligned} \tag{7}$$

where a_1 and a_2 are constants depending on the nature of the Fe–m_1 and Fe–m_2 bonds into which the coordinated monomer is to be inserted. From these equations $1/r_1$ and $r_1 \cdot r_2$ can be expressed as follows.

$$\log 1/r_1 = a_1(\log K_2 - \log K_1) \tag{8}$$

$$\log (r_1 \cdot r_2) = (a_1 - a_2)(\log K_1 - \log K_2) \tag{9}$$

Figure 4 shows the plot of $\log 1/r_1$ *versus* ($\log K_2 - \log K_1$), where M_1 is methacrylonitrile chosen as the reference. The roughly linear relationship supports Eq. (8) and demonstrates a unique characteristic of the coordination polymerization. It can be seen from a comparison of r_1 values in Table 6 that the relative reactivity of methacrylonitrile is 0.17 of that of acrylonitrile and 4.2 times of that of methyl methacrylate. If we assume the validity of the proposed coordination mechanism the relative reactivity of acrylonitrile to methyl methacrylate is expected to be 25 in good agreement with the experimental value of 25±5.

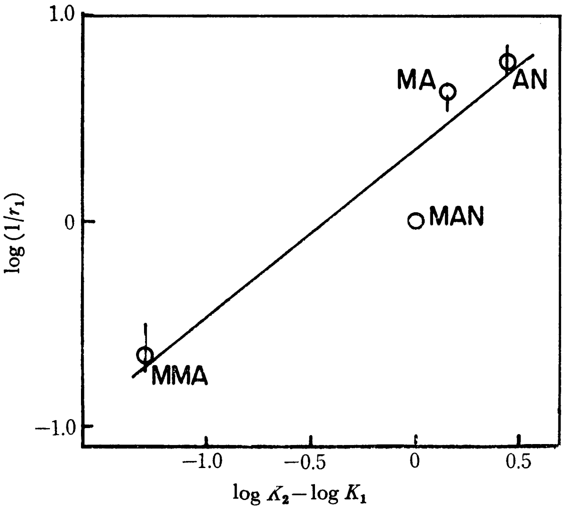


Fig. 4. Copolymerization of methacrylonitrile with olefins. M_1=methacrylonitrile as a reference. K represents the stability constant of the nickel–olefin π complex.[5]

Natta *et al.*[11] observed that $r_1 \cdot r_2$ values are very close to unity in the copolymerization of styrene derivatives with mixed catalysts prepared from aluminum alkyls and titanium halides and that $\log r_2$ values are inversely proportional to the Hammett constants of the substituents. In our system $\log r_2$ or $\log 1/r_1$ values increase with the increase of the Hammett constants of the substituent and hence with the increase of the $\log K$ values, but the $r_1 \cdot r_2$ values show significant deviations from unity. If a_1 should be equal to a_2 (Eq. (9)), $r_1 \cdot r_2$ should be unity. The observed deviations in our system suggest the considerable effects of the ultimate units in the growing polymer chains.

Termination Mechanism. The fact that molecular weights of poly(acrylonitrile) and poly(methyl methacrylate) are independent of the catalyst concentration suggests that the termination reaction is unimolecular as shown by

$$R_t = k_t[\text{Fe}^*] \tag{10}$$

where [Fe*] represents the concentration of growing polymer chains attached to the iron complex such as **4** or **7**. In the proposed coordination mechanism the rate of propagation can be expressed by

$$R_p = k_p[\text{Fe}^*][\text{M}] \tag{11}$$

---

[10] M. Fineman and S. Ross, *J. Polymer Sci.*, **5**, 259 (1950).

[11] G. Natta, F. Danusso, and D. Sianesi, *Makromol. Chem.*, **30**, 238 (1959); F. Danusso, *Chem. Ind.* (Milan), **44**, 611 (1962).

Thus from a comparison of Eqs. (10) and (11) the molecular weight of the polymer is expected to be proportional to the monomer concentration. The linear relationship between the molecular weight of poly(acrylonitrile) and the concentration of the monomer in Fig. 5 supports the above assumptions. The fact that the addition of dipyridyl (Fig. 5) and the employment of solvents with greater coordinating abilities caused the decrease of molecular weight suggests that coordination of a solvent and dipyridyl instead of a monomer destabilizes the bond between iron and the growing polymer chain to induce the unimolecular termination process. Further insight into the termination mechsnism was obtained by employing a deuterated monomer and analyzing the gas evolved in the termination process.[12]

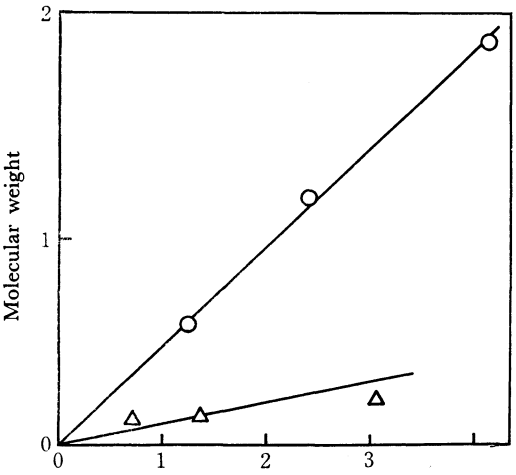
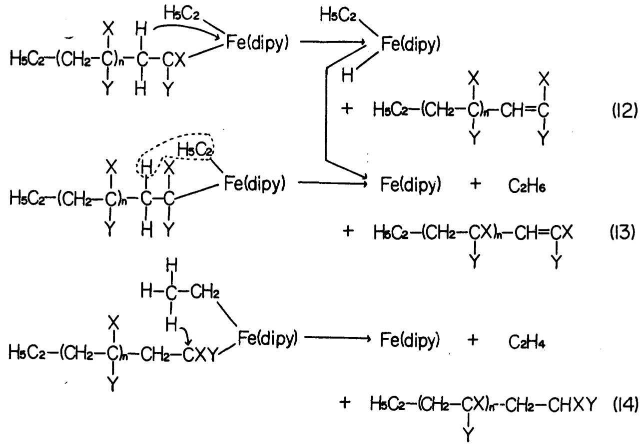


Fig. 5. Effect of the concentration of acrylonitrile and dipyridyl on the molecular weight of poly(acrylonitrile), (○) [dipy]≒7.2×10⁻³, (△) [dipy]≒0.14 mol/*l*.

In the polymerization of *cis*-β-d_1-methyl methacrylate (78% isotopic purity) with $Fe(C_2H_5)_2(dipy)_2$, the evolution of ethane and ethylene was observed to take place in a molar ratio 1 : 2.5. Analysis of the ethane by mass spectroscopy indicated that it contained 32% of C_2H_5D and 68% of C_2H_6 (average of two experiments). The possibility of direct hydrogen abstraction of the methyl methacrylate monomer by the ethyl groups of $FeEt_2(dipy)_2$ can be excluded since the content of C_2H_5D in ethane evolved in the thermal decomposition of $FeEt_2(dipy)_2$ in benzene-d_6 at room temperature and at 80°C did not exceed the natural abundance of C_2H_5D. The NMR spectrum of the recovered deuterated monomer after the polymerization was identical with that of the deuterated monomer used for the experiment. Thus the source of ethane-d_1 is considered to be the ethyl group of $FeEt_2(dipy)_2$ and the β-hydrogens of the growing poly(methyl methacrylate-d_1) chain.

In a previous paper[8] we concluded that one of the alkyl groups of $FeR_2(dipy)_2$ remains attached to iron during the propagation process. The fact that the initiator efficiency (*n* in Table 2) does not exceed unity (except for one case where the accuracy of the molecular weight determination is not very great) also supports the conclusion. If we assume that ethane-d_1 was formed through an abstraction of β-hydrogens in the ultimate unit of the growing polymer chain attached to iron by the remaining ethyl-group, the theoretical content of C_2H_5D is 39%, which agrees with the experimental value. An experiment carried out with a 1 : 1 mixture of the normal methyl methacrylate and methyl methacrylate-d_1 showed a corresponding decrease in the amount of C_2H_5D in the evolved gas in comparison to C_2H_6.

Thus we believe that the termination involving the formation of ethane and ethylene takes place through one of the following courses:



where $X{=}CH_3$, $Y{=}COOCH_3$ for methyl methacrylate.

The coordinated solvent molecule or dipyridyl ligand as in **7** and **4** are omitted for the sake of simplification. From the available data it has not been determined yet whether the elimination (Eq. (12)) leaving the alkyl-iron hydride takes place first followed by an intramolecular elinination of RH, or the alkyl group abstracts the β-hydrogen directly as in Eq. (13). In a similar type of polymerization of methyl methacrylate by tris(allyl)chromium, Ballard *et al.*[2] proposed a termination mechanism in which the addition of an allyl group to the carbonyl group of the ultimate monomer unit was involved. The type of termination seems to be unlikely in our system.

Experimental

Materials. Dialkylbis(dipyridyl)iron(II) was prepared as previously described[4,6]. Methyl *cis*-β-d_1-methacrylate was prepared from methyl acetylene, deuterium chloride, nickel tetracarbonyl and methanol-d_1 by the method of Jones[13] and was purified by distillation 4-times, NMR: τ3.93 β-*cis* proton, (a complex peak with a relative area 0.22); τ4.47 β-*trans* proton (a quartet with a relative area 1); τ6.27 ester methyl proton (a singlet with a relative area 2.9); τ8.07 α-methyl proton (a doublett with a relative area 2.9). The deuterated monomer had 78% isotopic purity based on NMR. Monomers and solvents were purified

---

[12] T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Polymer Sci.*, part B, **9**, 281 (1971).

[13] E. R. Jones, T. T. Shen, and M. C. Whiting, *J. Chem. Soc.*, **1959**, 230.

and stored as previously reported[6].

Polymerization. Polymerization was mostly carried out in a sealed ampoule in which the catalysts, olefin and solvent were transferred in an atmosphere of nitrogen or by trap-to-trap distillation *in vacuo*. After the set time of polymerization, the ampoule was opened and the content poured into acidic methanol. The precipitate was filtered, washed with methanol and dried. The kinetic study on acrylonitrile was carried out in a Schlenk type flask around which thermostatted water was circulated or in a dilatometer immersed in a thermostatted water bath. Acrylonitrile, catalyst, dipyridyl, and dimethylformamide were transferred in an atmosphere of nitrogen. The time-dependent yield was measured by pipetting out each fraction of the solution from the Schlenk type flask at set time or by reading the decrease of the volume of solution in the dilatometer. The density of poly(acrylonitrile) in the solution was measured by comparing the final decrease of volume with the weight of the recovered polymer. The density at 25°C was 1.05 g/m*l*. Poly(methyl methacrylate) was extracted in a Soxhlet extractor with acetone for 1 week and separated into acetone-soluble and acetone-insoluble fractions.

Compositions of the Copolymers. Compositions of the copolymers were calculated from microanalyses of carbon, hydrogen and nitrogen performed by Mr. T. Saito with a Yanagimoto CHN Autocorder Type MT-2.

Molecular Weight. The molecular weights of polymer were measured by viscometry by using the following equations: for poly(methyl methacrylate)[14], $[\eta]=3.80\times10^{-5}\,M_w^{0.79}$; for poly(acrylonitrile)[15], $[\eta]=1.66\times10^{-4}\,M_w^{0.81}$; for poly(methacrylonitrile)[16], $[\eta]=9.55\times10^{-4}\,M_w^{0.56}$.

Mass Analysis. The gas evolved in the polymerization of methyl *β-cis-d*$_1$-methacrylate was analyzed with a Hitachi type RMU-5B Mass Spectrometer by Mr. H. Sakurai.

---

14) J. -Y. Chine, L. -H. Shin, and K. -I. Shin, *Acta Chim. Sinica*, **23**, 213 (1957).

15) J. Bisschops, *J. Polymer. Sci.*, **17**, 81 (1955).

16) N. Fuhrman and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **76**, 5281 (1954).