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Effect of Carbonyl Compounds on Polymerization by Metal Acetylacetonates

Kyoji KAERIYAMA

Research Institute for Polymers and Textiles, Sawatari, Kanagawa-ku, Yokohama

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Some ketones and aldehydes have an accelerative effect on the polymerization of various monomers by various metal chelates of acetylacetone. The conversion increases with an increase in the concentration of these additives in a correspondingly increasing polymerization time. A radical is formed by the equimolar reaction of cyclohexanone and manganese(III) acetylacetonate and by the reaction of two aldehyde molecules and a molecule of the chelate. The order with a monomer is lowered from 1.64 to 1.13 and to 1.07 by the addition of cyclohexanone and caproic aldehyde respectively. The relation between the polymerization rate and the square root of the chelate concentration is linear without any additive; concave and convex curves are obtained for the systems containing cyclohexanone and caproic aldehyde respectively. The apparent activation energy is lowered from 19.9 kcal/mol to 13.9 and to 14.3 in the presence of cyclohexanone and caproic aldehyde respectively. The effectiveness of ketones is dependent on the nucleophilicity. A mechanism of the initiation reaction which interprets the molar ratio of reactants, the kinetical parameters, and the spectral data is proposed.

Metal acetylacetonates (Macac$_n$) have already been used as initiators for the polymerization of unsaturated compounds.[1-4] The polymerization proceeds *via* radical intermediates. The substituents on the acetylacetone ligand are shown to have an appreciable effect on the initiator activity of the chelate.[5-7] A solvent effect[7] and a high order with a monomer[6,7] are characteristic of a polymerization by Macac$_n$. This indicates the participation of monomers and solvents in the initiation reaction and suggests the presence of additives, a small amount of which accelerates the polymerization by the reaction of the additives with the chelate

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[1] E. M. Arnett and M. A. Mendelsohn, *J. Amer. Chem. Soc.*, **84**, 3821 (1962).

[2] E. G. Kastning, H. Naarmann, H. Reis and C. Berding, *Angew. Chem.*, **77**, 313 (1965).

[3] Y. Nishikawa and T. Otsu, *Kogyo Kagaku Zasshi*, **72**, 751 (1969).

[4] K. Uehara, Y. Kataoka, K. Kamei, M. Tanaka and N. Murata, *ibid.*, **72**, 1831 (1969).

[5] K. Uehara, T. Matsumura, Y. Murata, M. Tanaka and N. Murata, *ibid.*, **72**, 1825 (1969).

[6] Y. Nishikawa and T. Otsu, *ibid.*, **72**, 1836 (1969).

[7] C. H. Bamford and D. J. Lind, *Proc. Roy. Soc.*, *Ser. A*, **302**, 145 (1968).

prior to that of monomers and solvents. In fact, the addition of pyridine has been found to accelerate the polymerization of styrene by the metal chelate of β-diketone.[8] The effect of carbon tetrachloride has also been discussed.[2,7,9]

The present author has previously shown that the addition of carbonyl compounds accelerates the polymerization of styrene by ceric salt in an organic solvent.[10] In the present study, the effect of ketone and aldehyde on polymerization by Macac$_n$ is investigated.

Experimental

Materials. The monomers, aldehydes, and ketones were distilled under reduced pressure just prior to use. The metal acetylacetonates were commercially obtained (Dotite Reagent) and were used without further purification.

Procedure. In a glass tube we placed a chelate solution in benzene, additives, monomers, and a solvent, in that order, under atmospheric conditions. After the tube had been degassed by repeated freezing, evacuating and thawing, it was sealed off. Polymerization was then carried out in the dark under a mild shaking. The polymer thus produced was precipitated in methyl alcohol containing hydroquinone and hydrogen chloride, filtered, and dried *in vacuo* to a constant weight.

The absorption spectra were measured by a Hitachi recording spectrophotometer, Model EPS-3T.

Results and Discussion

Effect of the Additive. The effects of various additives on the polymerization of styrene by Mnacac$_3$ are shown in Table 1. All the additives used have an accelerative effect. Since caproic aldehyde and cyclohexanone are the most effective of the additives examined, these two reagents will be mainly used as additives in the following parts of this paper.

TABLE 1. EFFECTS OF ADDITIVES ON POLYMERIZATION OF STYRENE BY Mnacac$_3$

Additive	Conversion (%)
Cyclohexanone	18.6
Diethyl ketone	7.78
Benzophenone	4.34
Isobutyl methyl ketone	6.03
Caproic aldehyde	29.5
Benzaldehyde	12.9
Ethyl acetate	4.42
Diethyl ether	4.82
Tetrahydrofuran	6.50
Ethyl alcohol	8.95
Methyl alcohol	10.69
—	3.66

[Mnacac$_3$] $=1.42\times10^{-2}$ mol/l; [Additive] $=0.483$ mol/l; [styrene] $=3.49$ mol/l; solvent: benzene; at 60°C for 9.0 hr

Table 2 shows the effects of additives on the polymerization by various Macac$_n$. Accelerative effects can be seen in all the chelates used, but there is a large difference in the degree of the effects and in the conversions between the chelates.

The effects of additives on the polymerization of various monomers are shown in Table 3. Methyl

TABLE 2. EFFECTS OF ADDITIVES ON POLYMERIZATION OF STYRENE BY VARIOUS Macac$_n$

Run	Chelate	Additive	Conversion (%)
A	Mnacac$_2$	Caproic aldehyde	3.33
A	Mnacac$_2$	Cyclohexanone	9.39
A	Mnacac$_2$	—	0.86
B	Mnacac$_3$	Caproic aldehyde	18.4
B	Mnacac$_3$	Cyclohexanone	13.1
B	Mnacac$_3$	—	2.69
C	Coacac$_2$	Caproic aldehyde	5.39
C	Coacac$_2$	Diethyl ketone	1.06
C	Coacac$_2$	Cyclohexanone	1.59
C	Coacac$_2$	—	1.00
D	Feacac$_3$	Caproic aldehyde	1.55
D	Feacac$_3$	Ethyl alcohol	1.11
D	Feacac$_3$	Cycloheptanone	0.86
D	Feacac$_3$	—	0.47

[additive] $=0.483$ mol/l; solvent: benzene; at 60°C for 6.0 hr

Run A: [Mnacac$_2$] $=1.98\times10^{-2}$ mol/l; [styrene] $=3.49$ mol/l

Run B: [Mnacac$_3$] $=1.42\times10^{-2}$ mol/l; [styrene] $=3.49$ mol/l

Run C: [Coacac$_2$] $=1.95\times10^{-2}$ mol/l; [styrene] $=4.36$ mol/l

Run D: [Feacac$_3$] $=1.42\times10^{-2}$ mol/l; [styrene] $=3.49$ mol/l

TABLE 3. EFFECT OF CARBONYL COMPOUNDS ON POLYMERIZATION OF VARIOUS MONOMERS

Monomer	(mol/l)	Additive	Conversion (%)
Methyl methacrylate	4.70	—	24.4
Methyl methacrylate	4.70	Cyclohexanone	70.9
Acrylonitrile	7.60	—	15.8
Acrylonitrile	7.60	Cyclohexanone	45.2
Acrylonitrile	7.60	Caproic aldehyde	88.0
Styrene	3.49	—	3.66
Styrene	3.49	Cyclohexanone	18.6
Styrene	3.49	Caproic aldehyde	29.5

[Mnacac$_3$] $=1.42\times10^{-2}$ mol/l; [additive] $=0.483$ mol/l; solvent: benzene; at 60°C for 9.0 hr

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[8] K. Uehara, Y. Kataoka, M. Tanaka, and N. Murata, *Kogyo Kagaku Zasshi*, **72**, 754 (1969).

[9] T. Otsu, Y. Nishikawa and S. Aoki, *ibid.*, **71**, 1067 (1968).

[10] K. Kaeriyama, This Bulletin, **41**, 722 (1968); *Polymer*, **10**, 11 (1969).

methacrylate and acrylonitrile are polymerized better than styrene. Accelerative effects are, thereby, observed in all the monomers used. It is apparent that some ketones and aldehydes have an accelerative effect on the polymerization of many unsaturated monomers by a variety of metal chelates.

The dependence of the conversion on the concentration of additives is shown in Fig. 1. The conversion increases monotonically with an increase in the concentration of the additive, and it is higher in the presence of caproic aldehyde than in the presence of cyclohexanone in all the concentrations examined. In the run with the highest concentration of caproic aldehyde, the polymerizing mixture lost its color at the end of the polymerization. This indicates the complete decomposition of the chelate. In the run with the second highest concentration of the aldehyde, the color faded. No color change could be observed in the other runs.

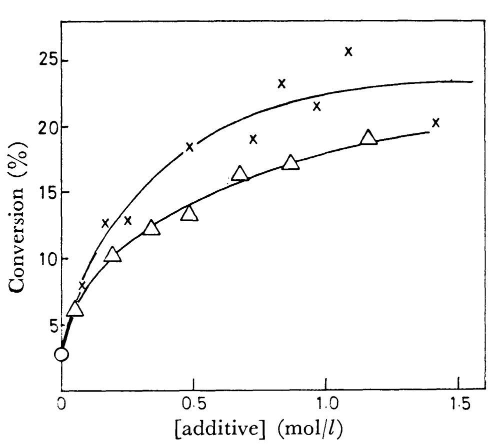

Fig. 1. Dependence of conversion on the concentration of additives.
[styrene] = 3.49 mol/l; [Mnacac$_3$] = 1.42 × 10^{-2} mol/l; solvent; benzene; at 60°C for 6.0 hr.
-△- cyclohexanone, -×- caproic aldehyde

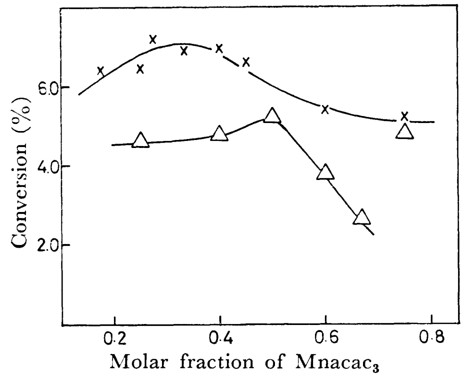

Fig. 2. Dependence of conversion on molar fraction of Mnacac$_3$.
[Mnacac$_3$] + [additive] = 3.0 × 10^{-2} mol/l
[styrene] = 3.49 mol/l; solvent: benzene;
at 60°C for 7.0 hr.
-△- cyclohexanone, -×- caproic aldehyde

Figure 2 represents the conversion of styrene as a function of the mole fraction of Mnacac$_3$. The maxima do not appear sharp compared with those of other systems, for example, the amide-carbon tetrachloride system.[11] The maxima appear at the optimum fraction, which corresponds to the ratio of the reactants participating in the initiation reaction. In the case of cyclohexanone, the maximum is observed at the equimolar ratio. This implies that a chelate molecule and a cyclohexanone molecule participate in the initiation reaction. In the presence of caproic aldehyde, the maximum seems to be at the molar fraction of 0.33. This suggests that a radical is generated from one manganese tris-acetylacetonate molecule and two caproic aldehyde molecules.

Kinetics. Because a small deviation from a straight line is observed in time-conversion plots, the initial rates of polymerization can be evaluated by graphically determining a tangent at time 0. No change in or fading of the color of polymerizing mixture could be observed in the runs described here.

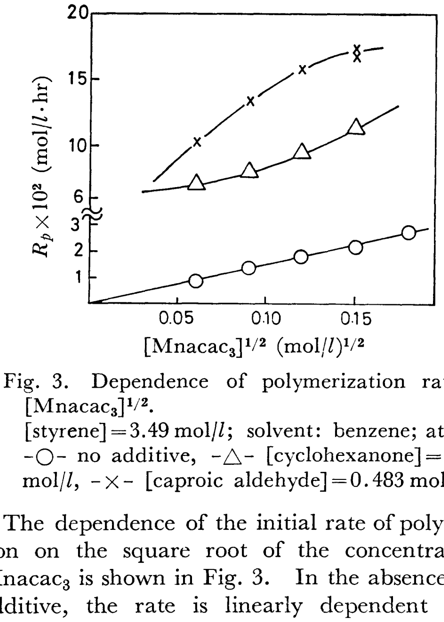

Fig. 3. Dependence of polymerization rate on [Mnacac$_3$]$^{1/2}$.
[styrene] = 3.49 mol/l; solvent: benzene; at 60°C
-○- no additive, -△- [cyclohexanone] = 0.483 mol/l, -×- [caproic aldehyde] = 0.483 mol/l

The dependence of the initial rate of polymerization on the square root of the concentration of Mnacac$_3$ is shown in Fig. 3. In the absence of any additive, the rate is linearly dependent on the square root of the chelate concentration. The polymerization chain is terminated by the bimolecular reaction of polymer radicals. Bamford and Lind[7] have also reported that the polymerization rate of styrene and methyl methacrylate is proportional to the square root of the concentration of Mnacac$_3$. In the presence of cyclohexanone, the curve is concave. As is shown in Fig. 1, the polymerization rate increases with the concentration of cyclohexanone at a constant concentration of

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[11] K. Kaeriyama, This Bulletin, **42**, 3602 (1969).

Mnacac$_3$, because the ratio of cyclohexanone to the chelate increases. In the case of a constant concentration of cyclohexanone, the ratio of cyclohexanone to Mnacac$_3$ increases with a decrease in the concentration of the chelate. This is the reason why the rate is higher at low concentrations of the chelate than would be expected from the linear dependence on the square root of the chelate concentration. The possibility of the bimolecular termination can not be rejected. In the presence of caproic aldehyde, the curve is convex. If the termination is by the reaction of the polymer radical with the initiator, the polymerization rate is independent of the initiator concentration. In this case, both terminations, by the chelate and by bimolecular reaction of polymer radicals, take place. This is the reason why the curve is convex. Uehara *et al.* have described how the polymerization of acrylonitrile is terminated by copper chelates of β-diketones.[4)]

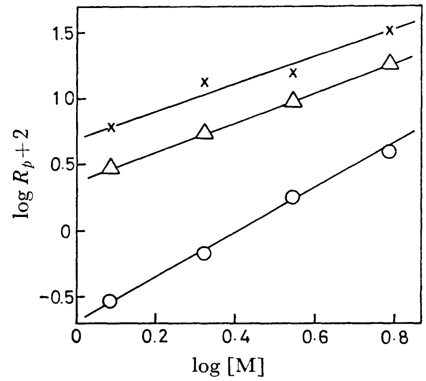

Fig. 4. Dependence of polymerization rate on styrene concentration.
[Mnacac$_3$] = 1.42×10^{-2} mol/*l*
solvent: benzene; at 60°C
-○- no additive
-△- [cyclohexanonoe] = 0.483 mol/*l*
-×- [caproic aldehyde] = 0.483 mol/*l*

Figure 4 presents logarithmic plots of the initial rate of polymerization as a function of the monomer concentration at constant concentrations of Mnacac$_3$ and additives. The order with the monomer is 1.64 in the absence of any additive. This high order is attributable to the participation of the monomer in the initiation reaction. The order is lowered to 1.13 and 1.07 by the addition of cyclohexanone and caproic aldehyde respectively. This shows that the additive limits the participation of the monomer in the initiation reaction to a lesser extent. Bamford and Lind[7)] have reported that the order with the monomer is dependent on the diluent, being 1.5 and 1.2 for toluene and ethyl acetate respectively. These findings are similar to those of present paper in the sense that the use of the carbonyl compound as the solvent lowers the order with the monomer. However, cyclanone is more effective than the ester. Uehara *et al.*[8)] have also described that the addition of pyridine lowers the order with styrene from 1.9 to 1.2.

Arrhenius plots are shown in Fig. 5. The apparent activation energies and frequency factors are summarized in Table 4. The additives lower the apparent activation energy by *ca.* 6 kcal/mol. The frequency factors are very low, especially in the presence of cyclohexanone. This is characteristic of the polymerization by these initiator systems.

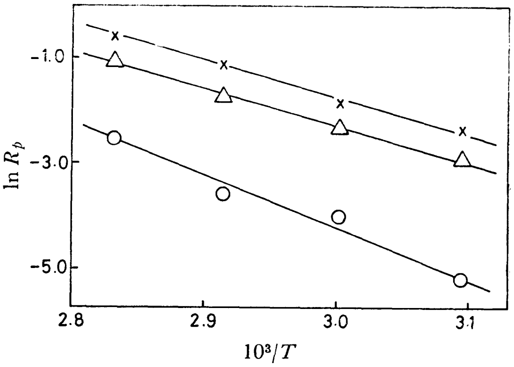

Fig. 5. Dependence of polymerization rate on temperature.
[M] = 3.49 mol/*l*; [Mnacac$_3$] = 1.42×10^{-2} mol/*l*
solvent: benzene; -○- no addititive
-△- [cyclohexanone] = 0.483 mol/*l*
-×- [caproic aldehyde] = 0.483 mol/*l*

TABLE 4. SUMMARY OF PARAMETERS FOR FIG. 5

	No additive	Cyclo-hexanone	Caproic aldehyde
Activation energy (kcal/mol)	19.9	13.9	14.3
Frequency factor (mol/*l*·sec)	5.6×10^7	3.6×10^4	1.1×10^5

Spectra. The absorption spectra of Mnacac$_3$ in visible regions are shown in Fig. 6. Because the spectra in benzene and a benzene-styrene mixture (50 vol%) are completely identical, it can be said that styrene does not coordinate to Mnacac$_3$. The behavior of Mnacac$_3$ is different from that of the copper chelate.[6)] The spectra in a cyclohexanone solution are essentially identical with those in a benzene solution, although a small deviation can be observed. The spectra in a caproic aldehyde solution are shifted to shorter wavelengths and show higher absorption coefficients. It is apparent that they are different from those in the benzene and cyclohexanone solutions. This can be attributed to the coordination of caproic aldehyde to Mnacac$_3$.

Initiation Mechanism. Although the coordination of cyclohexanone with Mnacac$_3$ can not be deduced from the spectral data, it is clear that

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12) M. Tamres and S. Searles, *J. Amer. Chem. Soc.*, **81**, 2100 (1959).

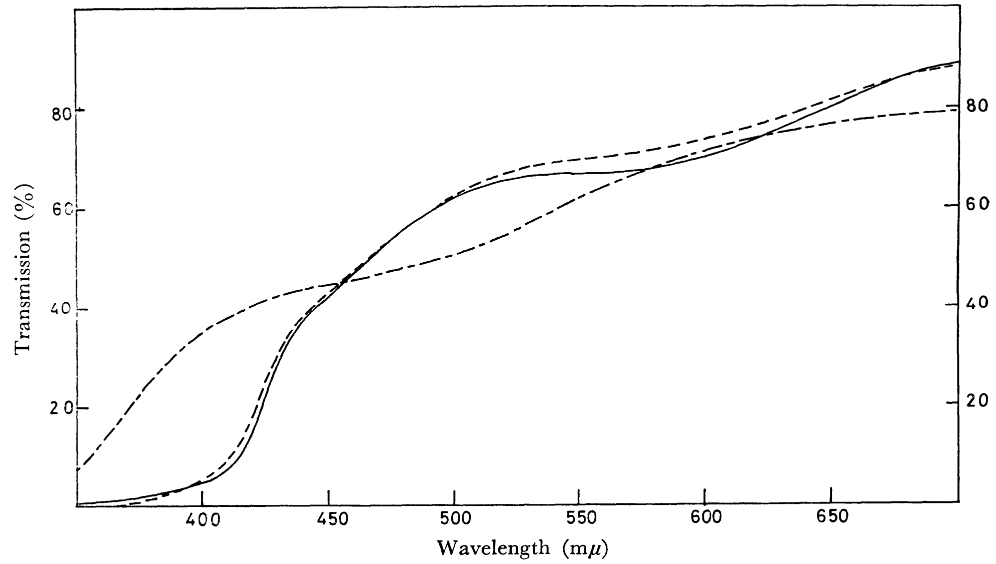

Fig. 6. Spectra of Mnacac$_3$.
[Mnacac$_3$]$=7.7\times10^{-4}$ mol/*l*
—— in benzen; ---- in cyclohexanone; —-—- in caproic aldehyde

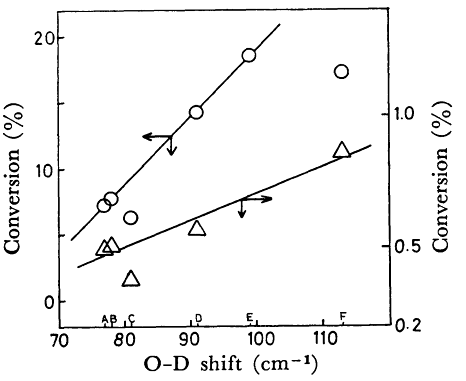

Fig. 7. Dependence of conversion on O-D shift.
[styrene]$=3.49$ mol/*l*; solvent: benzene: at 60°C
[additive]$=0.483$ mol/*l*
A : methyl ethyl ketone B : diethyl ketone
C : acetone D : cyclopentanone
E : cyclohexanone F : cycloheptanone
-○- [Mnacac$_3$]$=1.42\times10^{-2}$ mol/*l*, 9.0 hr
-△- [Feacac$_3$]$=1.42\times10^{-2}$ mol/*l*, 6.0 hr

ketone interacts with the chelate and accelerates the polymerization. Ketones are arranged in the order of nucleophilic tendency. Figure 7 shows the relation between the conversion and the O–D shift in IR spectra. The O–D shift of monodeuterated methanol, which is cited from the report of Tamres and Searles,[12] is due to a hydrogen bond with ketone and depends on the nucleophilicity of the ketone. Acetone deviates from the line. It also deviates from the linear relation between the O–D shift and the heat of mixing with chloroform because of association. The deviation of cycloheptanone can be interpreted in terms of the difference in bulkiness between methanol and the chelate molecule. Cycloheptanone deviates only in reaction with manganese chelate, which has a stronger interaction with the ketone. It appears from Fig. 7 that conversion is dependent on the nucleophilicity of ketone. These results and the spectral data suggest that ketone coordinates to the chelate in an activation state.

The initiation reactions can be summarized schematically as on the next page. Styrene does not coordinate to I judging from the spectra. I is activated into II, which reacts with the monomer to generate the radical IV. The mechanism shouldlead to an order of 1.5 with the monomer. The observed order of 1.64 can, therefore, not be explained. A possible explanation is to suppose another reaction in which II reacts with two molecules of monomer. In the presence of the ketone I reacts with the ketone to form an activated complex V, which in turn decomposes into VI and VII. The mechanism predicts the linear dependence on the monomer concentration. The observed order is attributable to the simultaneous reaction *via* II. The above explanation is consistent with the spectral data and the equimolar reaction of the chelate with ketone.

Otsu *et al.* reported that metal β-diketonates induced a coordination polymerization of aldehyde.[13] Chloral was most easily polymerized; when *n*-butyl aldehyde and chloral were copolymerized by Cu bis-(ethyl acetoacetate), a copolymer

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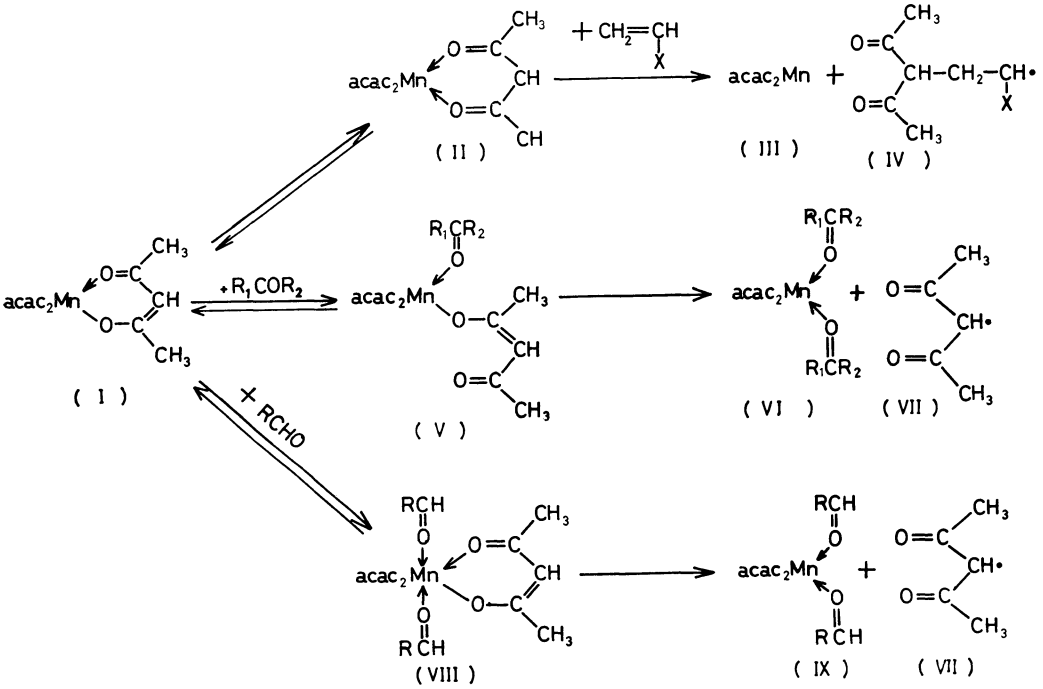
[13] T. Otsu, S. Watanuma and Y. Nishikawa, *Kogyo Kagaku Zasshi*, **72**, 1857 (1969); *Makromol. Chem.*, **115**, 278 (1968).



Scheme 1

containing a small amount of *n*-butyl aldehyde units was produced. They also reported that Mnacac$_3$ did not induce the polymerization of chloral. In the present study, no polymer of caproic aldehyde was detected by precipitation in benzene or methanol. No copolymerization of caproic aldehyde with styrene was deduced from the IR data. Although caproic aldehyde is not polymerized by Mnacac$_3$, it has a stronger interaction with the chelate than cyclohexanone. In the presence of caproic aldehyde, two aldehyde molecules coordinate to the chelate in the ground state and VIII is formed. The decomposition of VIII generates the radical VII. This route is compatible with the spectral data and with the optimum molar ratio of the reactants.

The bond between manganese and the acetylacetone ligand is weakened by the coordination of aldehyde, and a acetylacetone ligand in VIII reacts with the polymeric radical. This indicates that the chelate terminates the polymerization of styrene in the presence of caproic aldehyde, as has been described in the section on the dependence on the initiator concentration.

The polymers produced by the present initiator systems do not have stereoregularity, the IR data indicate.[14]

The author is grateful to Dr. M. Suzuki and Dr. A. Okada for their interest and encouragement during this work.

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[14] J. P. Luongo and R. Salovey, *J. Polym. Sci., Part A-3*, 2759 (1965).