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Takayuki Otsu[a]; Nobuaki Minamii[a]; Yukitoshi Nishikawa[a]
[a] Department of Applied Chemistry Faculty of Engineering, Osaka City University, Osaka, Japan

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Metal-Containing Initiator Systems. IX. Radical Polymerizations of Vinyl Monomers by Various Metal Acetylacetonates*

TAKAYUKI OTSU, NOBUAKI MINAMII, and YUKITOSHI NISHIKAWA

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Sugimotocho, Sumiyoshi-ku, Osaka
Japan

SUMMARY

A study of the polymerization of styrene, methyl methacrylate, acrylonitrile, vinyl acetate, and vinyl chloride initiated by various metal acetylacetonates [$Me(acac)_x$] has been made. It was found that $Mn(acac)_3$ was the most effective initiator, and $Co(acac)_3$, $Mn(acac)_2$, $Cu(acac)_2$, and $Cr(acac)_3$ showed moderate activity for the polymerization of methyl methacrylate at 60°C. However, the other, $Me(acac)_x$, had no effect or served as inhibitors. The addition of some additives such as halogen compounds did not accelerate polymerization of methyl methacrylate by $Mn(acac)_3$. From the results of polymerization and copolymerization of methyl methacrylate by $Mn(acac)_3$, it was concluded that the polymerization proceeded via an ordinary radical mechanism and the activation energy for initiation was 25.2 kcal/mole. The initiation mechanism of vinyl polymerization by $Me(acac)_x$ was studied on the basis of the complex formation with the monomer.

In 1965 Kastning et al. [1] reported that various metal acetylacetonates [$Me(acac)_x$] can initiate radical polymerization of vinyl

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monomers, and showed some excellent selectivities and stereospecificities for their polymerizations. However, when their results were re-examined by the present authors, some questionable results were observed. In the present paper, the detailed polymerizations of some vinyl monomers by various kinds of Me(acac)$_x$ were investigated and compared with the results by Kastning et al. [1].

Although many studies on vinyl polymerizations by some of the Me(acac)$_x$ have been made recently by Bamford and Lind [2], Izawa et al. [3], Uehara et al. [4] and Itakura et al. [5], no detailed investigations on the general behavior of vinyl polymerizations by various Me(acac)$_x$ have been undertaken.

EXPERIMENTAL

Materials

Reagent-grade samples of Me(acac)$_x$ were used without further purification.

Styrene (St), methyl methacrylate (MMA), acrylonitrile (AN), vinyl acetate (VAC), and vinyl chloride (VC) were purified by ordinary methods and distilled in a stream of nitrogen under reduced pressure before use. The other reagents were used after purification by ordinary methods.

Polymerization Procedure

Polymerizations and copolymerizations were carried out in a sealed tube under shaking in a thermostat maintained at a given temperature. After polymerization for a definite time, the resulting polymers, except poly(vinyl acetate), were precipitated by the addition of a large amount of methanol. In the case of polymers and copolymers of VAC, petroleum ether was used as a precipitant. The resulting polymers were then filtered, washed with the excess precipitant, and dried under vacuum at ca. 40°C. The conversion was calculated from the weight of the dried polymer.

Analysis of the Polymers

Infrared spectra of the polymers were determined by using the Nihonbunko IR-G spectrometer.

Syndiotacticities of the poly(methyl methacrylates) were also determined by their infrared spectra according to the method described in the previous paper [6].

The composition of the copolymers of methyl methacrylate with styrene and vinyl acetate was calculated from their elementary analysis on carbon. Monomer reactivity ratios were then determined by the method of Fineman and Ross [7].

RESULTS AND DISCUSSION

Effects of $Me(acac)_x$ on MMA Polymerization

The results of bulk polymerization of MMA initiated by various $Me(acac)_x$ at 80°C are shown in Table 1.

Table 1. Results of Bulk Polymerization of MMA Initiated by $Me(acac)_x$ at 80°C: $[Me(acac)_x] = 0.53$ wt. % to MMA

Me in $Me(acac)_x$	Time, hr	Conversion, %	Rp, %/hr	Syndiotacticity, %
Mn(III)	0.5	15.11	30.22	39
Co(III)	1.5	4.82	3.21	43
Mn(II)	1.5	4.25	2.83	53
Cu(II)	2.0	4.64	2.32	48
Cr(III)	2.0	5.61	2.24	—
Al(III)	8.0	2.89	0.36	—
Ni(II)	10.0	1.82	0.18	46
Fe(III)	11.0	3.87	0.35	47
Co(II)	11.0	3.53	0.32	42
TiO(II)	11.0	2.88	0.26	41
Zr(IV)	11.0	2.18	0.20	42
Zn(II)	11.5	2.56	0.22	—
None	15.5	3.08	0.20	42
VO(II)	20.0	2.48	0.12	—
Li(I)	20.0	1.87	0.09	—
$Ti(II)TiCl_6$	20.0	1.47	0.07	—
Na(I)	20.0	0.66	0.03	—
Mg(II)	30.3	3.28	0.11	—
V(III)	30.3	0.15	0	—
MoO_2(II)	30.3	0.12	0	—

It was found that $Mn(acac)_3$ was the most excellent initiator, and $Co(acac)_3$, $Mn(acac)_2$, $Cu(acac)_2$, and $Cr(acac)_3$ showed moderate initiating activity for MMA polymerization. However, the other

$Me(acac)_x$ were not as effective or even served as an inhibitor. This order for initiating activity of $Me(acac)_x$ was in agreement with that reported by Kastning et al. [1] and by Izawa et al. [3].

As can be also seen from Table 1, the initiating activities of $Me(acac)_x$ which involved the central metals of higher valency state were higher than those of the corresponding lower valency state. The observed activity order of $Me(acac)_x$ was independent of their stability constant (in water) and thermal stabilities and of the ionization potentials or electronegativities of their central metals, as was pointed out by Izawa et al. [3].

The abnormally high initiator activity of $Mn(acac)_3$ might be based on its structural strain, as was stated by Morosin and Brathorde [8], but the exact reason was not clear.

Contrary to the results by Kastning et al. [1], the syndiotacticities of the resulting polymers were the same, independently of the kinds of $Me(acac)_x$ initiators, as shown in Table 1. It was also observed that the polystyrenes obtained by $Me(acac)_3$ and $Co(acac)_3$ at 60°C did not contain any isotactic fraction insoluble in methyl ethyl ketone [9]. Accordingly, it was concluded that the $Me(acac)_x$ did not induce stereospecific radical polymerization of vinyl monomers.

Initiator Activity of $Me(acac)_x$ toward Monomers

Table 2 shows the results of bulk polymerization of various monomers by $Mn(acac)_3$ and $Co(acac)_3$ at 60°C.

Table 2. Bulk Polymerization of Vinyl Monomers by $Me(acac)_3$ at 60°C: $[Me(acac)_3] = 0.53$ wt.% to Monomer

Me in $Me(acac)_3$	Rate of polymerization, %/hr			
	MMA	St	AN	VAC
Mn(III)	5.50	1.38	4.54	21.60
Co(III)	1.93	0.21	—	0.02

From Table 2 it was observed that the order in the initiator activity of $Mn(acac)_3$ toward various monomers was in agreement with that of azobisisobutyronitrile. In the initiating order by $Co(acac)_3$, however, similar correlation was not observed.

It is interesting to note that some of $Me(acac)_3$ can induce the polymerizations of some aldehydes such as formaldehyde [10] and chloral [11], and of trioxane [12].

Effects of Additives on MMA Polymerization by $Mn(acac)_3$

Kastning et al. [1] reported that the polymerization of MMA by $Mn(acac)_3$ was accelerated by the addition of halogen compounds, etc. To confirm this point, the effects of some aliphatic and aromatic chloro, nitro, and cyano compounds on the same polymerization were investigated. The results are shown in Table 3.

Table 3. Effects of Additives on the Bulk Polymerization of MMA Initiated by $Mn(acac)_3$ at 60°C: $[Mn(acac)_3] = 0.53$ wt.% to MMA

Additives (A)	[A], wt.%	Time, hr	Polymer yield, %	R_p, %/hr
Chloroform	0.32	2.0	14.38	7.19
	0.53	2.0	14.07	7.04
	1.37	2.0	10.70	5.35
Carbon tetrachloride	0.5	2.0	11.46	5.73
n-Amyl chloride	0.5	2.75	27.31	9.99
Trichloroethylene	0.5	2.75	15.76	5.73
Chlorobenzene	0.5	3.33	17.64	5.30
Nitromethane	0.5	3.33	15.73	4.72
Nitrobenzene	0.5	2.00	13.38	6.69
Acetonitrile	0.5	3.33	14.37	4.32
Benzonitrile	0.5	2.00	9.67	4.84
None	—	2.00	16.20	8.10

As can be seen from Table 3, the rate of polymerization (R_p) had no effect or decreased with the presence of these additives. This result was quite different from that of Kastning et al. (1) but agreed with that of Bamford and Lind [2].

Kinetic Studies of the Polymerization of MMA by $Mn(acac)_3$

Figure 1 shows time-conversion relations on the bulk polymerization of MMA by the different concentration of $Mn(acac)_3$ at 60°C. In these cases straight lines were obtained with the absence of induction periods.

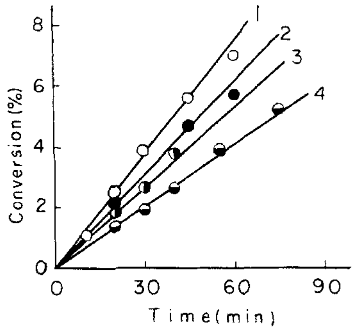


Fig. 1. Time-conversion relations for the bulk polymerization of MMA by $Mn(acac)_3$ at 60°C: $[Mn(acac)_3] = 1.85 \times 10^{-2}$ (1), 1.42×10^{-2} (2), 0.99×10^{-2} (3), and 0.57×10^{-2} mole/liter (4).

The relationships between R_p and the concentration of $Mn(acac)_3$ are shown in Fig. 2, from which R_p was found to be proportional to the square-root concentration of $Mn(acac)_3$ initiator. This result suggests that the polymerization by this initiator proceeds via a radical intermediate.

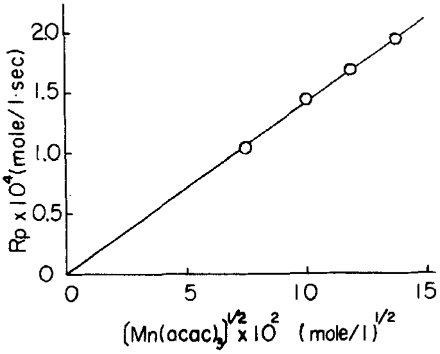


Fig. 2. Relationship between R_p and the concentration of $Mn(acac)_3$ at 60°C.

Time-conversion relations for the polymerizations carried out using the different MMA concentration in benzene are also shown in Fig. 3. Some induction periods were observed, and these increased with increasing concentration of benzene in MMA. The reason for the appearance of such induction periods is not obvious at the present time.

From the slopes of the straight lines in Fig. 3, the dependency of the concentration of MMA on R_p was determined approximately.

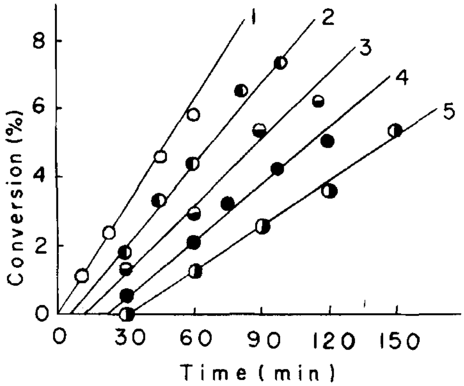


Fig. 3. Time-conversion relations for the polymerization of MMA by $Mn(acac)_3$ [1.42×10^{-2} mole/liter] at 60°C: [MMA] = 9.30 (1), 7.44 (2), 5.58 (3), 3.72 (4), and 1.86 moles/liter (5) in benzene.

The results are shown in Fig. 4, from which R_p was found to increase with the 1.44 power of the MMA concentration. This value was different from that (1.0) reported by Bamford and Lind [2] but was in agreement with that (1.4) obtained for copper ethyl acetoacetate [13].

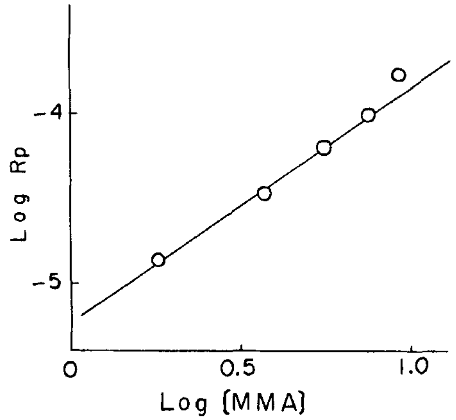


Fig. 4. Relationship between R_p and the MMA concentration in benzene at 60°C.

From the above kinetic results, the following rate equation was obtained:

$$R_p = 5.51 \times 10^{-5} [MMA]^{1.44} [Mn(acac)_3]^{0.5}$$

This rate equation might suggest that the initiation occurred via the complex formation between Me(acac)$_3$ and MMA, and the produced growing radical was propagated with the successive reaction of MMA followed by bimolecular termination as well as ordinary radical polymerization.

The effect of temperature on this polymerization was also investigated. The rates of bulk polymerization obtained at the temperature range between 30 and 80°C were plotted against the reciprocal polymerization temperatures, as shown in Fig. 5. From this figure apparent activation energy for overall polymerization by Mn(acac)$_3$ was calculated as 16. 5 kcal/mole. Accordingly, the activation energy for initiation was obtained as 25. 2 kcal/mole using the reported rate constants [14] for propagation and termination. This value was in agreement with that obtained by Bamford and Lind [2].

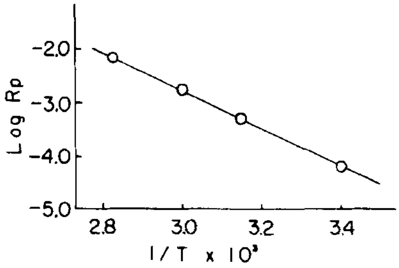


Fig. 5. Arrehnius plots of log R_p versus 1/T for bulk polymerization of MMA.

Copolymerizations by Me(acac)$_x$

Kastning et al. [1] have stated that the copolymerization reactivity of some vinyl monomers by Me(acac)$_x$ was different from that by ordinary radical initiator. To check this point, the copolymerization of St (M_1) and MMA (M_2) by Co(acac)$_3$ was investigated. The results are shown in Table 4.

As can be seen from Fig. 6, the copolymer composition curve obtained by Co(acac)$_3$ was in good agreement with that by azobisisobutyronitrile. The obtaining monomer reactivity ratios were as follows:

$r_1 = 0.63, r_2 = 0.35$ by Co(acac)$_3$

$r_1 = 0.52, r_2 = 0.46$ by AIBN [15]

This result is different from that of Kastning et al. [1] and suggests that the polymerization by Co(acac)$_3$ proceeds via ordinary radical mechanism.

Table 4. Results of Copolymerization of St (M_1) and MMA (M_2) by $Co(acac)_3$ at 60°C: $[Co(acac)_3] = 0.50$ wt. % to Total Monomer (10 ml)

$[M_1]$ in feed monomer, mole %	Time, hr	Yield, %	Copolymer obtained	
			C, %	$[M_1]$, mole %
90.19	10.42	3.67	87.89	86.59
74.75	12.50	2.50	82.96	70.60
60.15	12.50	2.75	76.66	60.24
50.01	12.50	2.82	77.38	53.23
19.99	10.42	3.18	70.87	33.15

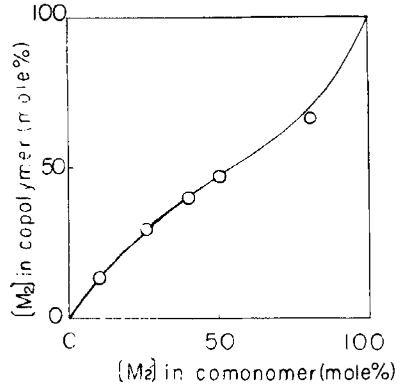


Fig. 6. Copolymer composition curve for the copolymerization of St (M_1) and MMA (M_2) by $Co(acac)_3$ at 60°C: $[Co(acac)_3] = 1.40 \times 10^{-2}$ mole/liter.

Table 5 shows the results of the copolymerization of St and VAC or VC by $Mn(acac)_3$ at 80°C. The styrene contents in the copolymers of St (M_1) with VAC (M_2) obtained were in fairly good agreement with those calculated from $r_1 = 55$ and $r_2 = 0.01$ [16] but did not differ from those reported by Kastning et al. [1]. Similar conclusion was made on the copolymer composition of the system of St and VC (Table 5). However, it was noted that the rates of these copolymerizations by $Mn(acac)_3$ might be higher than those by ordinary radical initiator.

Table 5. Results of Copolymerization of St(M_1) and VAC or VC (M_2) by Mn(acac)$_3$ at 80°C: [Mn(acac)$_3$] = 0.50 wt.% to Total Monomer (10 ml) in the Presence of n-Amyl Chloride (0.50 wt.%)

M_2	M_1 in feed monomer, mole %	Time, hr	Yield, %	Copolymer obtained	
				C, %	[M_1], mole %
VAC	46.94	4.0	16.41	91.37	90.20
"	30.04	5.0	12.36	90.65	88.70
"	20.07	6.5	15.06	88.36	83.93
VC	48.29	15.0	31.01	3.18[a]	91.00

[a] Cl %.

End Groups of Polystyrenes Obtained by Me(acac)$_x$

Figure 7 shows the infrared spectra of the polystyrenes obtained by different amounts of Mn(acac)$_3$ at 80 and 110°C. The low molecular weight polystyrene which was obtained by using 10.0 wt.% Mn(acac)$_3$ to St was found to show a strong absorption band at 1700 cm^{-1} due to a carbonyl group. However, the high molecular weight polystyrene produced by using 0.5 wt.% Mn(acac)$_3$ at 80°C did not show this carbonyl band. These results might be expected from the

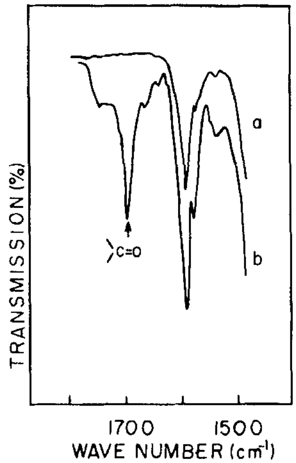


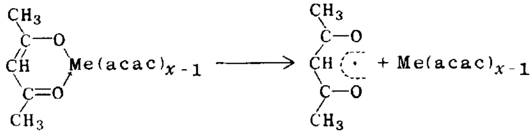
Fig. 7. Infrared spectra of polystyrenes obtained by Mn(acac)$_3$: (a) [Mn(acac)$_3$] = 1.42 × 10^{-2} mole/liter at 60°C; (b) [Mn(acac)$_3$] = 0.284 mole/liter at 110°C.

general features that the carbonyl group in the initiator fragment derived from Mn(acac)$_3$ existed in an end group of the polymer.

Initiation Mechanism of Polymerization by Me(acac)$_x$

From the kinetic results of polymerization and copolymerization by Me(acac)$_x$ and from the results of the polymer structure obtained, it was clear that Me(acac)$_x$ could induce the ordinary radical polymerization of vinyl monomers and did not give any stereospecificity of the resulting polymers. These observations did not coincide with those reported in the previous paper [1].

As was pointed out by Arnett and Mendelsohn [17], the initiation mechanism by Me(acac)$_x$ is considered to occur through the homolysis of their metal-oxygen bonds:



This mechanism was supported by Bamford and Lind [2] from the observed rate equation, i.e., $R_p = k'[\mathrm{MMA}]$.

If this mechanism is correct, the acetylacetonate radical must be produced as an initiating radical; at the same time the central metal ion of Me(acac)$_x$ must be reduced. From the present study, the former possibility was supported by the infrared spectrum of low molecular weight polystyrene obtained by Mn(acac)$_3$. The latter might be confirmed from the fact that the color of the polymerizing mixture involving St and Mn(acac)$_3$ changed from a blackish-brown to a yellowish-brown. Similar conclusions have been suggested by several authors [2, 3, 5].

However, Izawa et al. [3] pointed out that radical formation of Me(acac)$_3$ was not observed in nonpolar solvent.
This result and the present observations that the activation energy for initiation of MMA by Mn(acac)$_3$ was as small as 25. 2 kcal/mole and that the dependency of the MMA concentration on R_p was close to the 1. 5 power, which was also confirmed for the monomers (St) [18] and chelates [Cu(ethyl acetoacetate)$_2$] [19], may suggest that the monomer molecule must participate in the homolysis of Me(acac)$_x$, i.e., in the initiating radical production step:

$$\mathrm{Me(acac)}_x + \mathrm{M} \rightleftharpoons [\mathrm{M} \rightarrow \mathrm{Me(acac)}_x] \rightarrow$$

$$(\mathrm{acac})\text{-}\mathrm{M}\cdot + \mathrm{Me(acac)}_{x-1}$$

This mechanism for initiation coincides with all the experimental results described above.

Recently, Bamford and Lind [20] stated that the Mn(III) chelate of trifluoroacetylacetonate (facac) could initiate selectively the radical polymerization of vinyl monomers which were easily polymerized by an anionic mechanism. In this case the ligand anion dissociated from the chelate was added with the monomer, and then one electron transfer occured, as follows:

$$\mathrm{Mn(facac)_3} \rightleftharpoons \mathrm{(facac)^{-}Mn^{III}(facac)_2} \xrightarrow{M}$$

$$\mathrm{(facac)\!-\!M^{-}Mn^{III}(facac)_2} \rightarrow$$

$$\mathrm{(facac)\!-\!M^{\cdot}} + \mathrm{Mn^{II}(facac)_2}$$

The other evidence for such a complex formation might be obtained from the recent observations that some aldehydes [10, 11] and cyclic oxides [12] could polymerize through a coordinated anionic mechanism to give high polymers. Accordingly, it was concluded that the initiation of vinyl polymerizations by $\mathrm{Me(acac)_x}$ proceeded via complex formation with the monomer, followed by homolysis of the metal-oxygen bond in the $\mathrm{Me(acac)_x}$ to give an initiating radical.

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