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Metal-Containing Initiator Systems. XVI. Radical Polymerization with Metal Carboxylates

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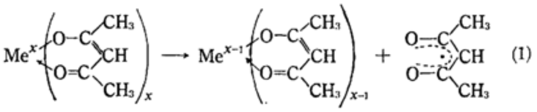
The polymerization of vinyl monomers with metal carboxylates has been investigated in benzene at 60°C. Cobalt(III) cyclohexanecarboxylate behaved as an effective initiator of the polymerization, and its activity was higher than that of corresponding salts of manganese (III) and copper(II), and than that of cobalt(III) acetylacetonate in the polymerizations of styrene (St) and methyl methacrylate (MMA). It was found that the overall rate of polymeriaztion (R_p) of MMA with cobalt(III) cyclohexanecarboxylate was expressed by the following equation, indicating that the polymerization proceeded through a free redical intermediate:

$$R_p = k[\mathrm{MMA}]^{1.4}[\mathrm{Co(III)}]^{0.5}$$

The free radical propagation of this polymerization was also supported by the results of the copolymerizations of St with MMA and with vinyl acetate; *i.e.*, the resulting copolymer composition curves agreed with the typical free radical ones. It was assumed that the initiation of polymerization occurred by means of a radical produced by the homolysis of the metal-oxygen bond in the carboxylate. The reaction order with respect to MMA in the above equation, which was higher than unity, suggested the participation of the MMA molecule in initiating the radical formation.

It is well known that some metal acetylacetonates can act as free radical initiators of vinyl polymerization. The initiation of polymerization has been considered to take place with a ligand radical resulting from the homolysis of the metal-oxygen bonds in metal acetylacetonates (Eq. (1)).[1–3]


(1)

In previous papers,[3–5] the initiation of vinyl polymerizations by various metal acetylacetonates and copper(II) ethyl acetoacetate was investigated, and it was suggested that it occurs *via* the participation of the monomer used.

It can be predicted that certain metal carboxylates which consist of a similar structure of metal acetylacetonates may serve in a similar manner to initiate the vinyl polymerization. Indeed, lead tetraacetate[6] and ferric laurate[7] have been found to initiate the polymerization of methyl methacrylate (MMA).

The present paper will describe the polymerization of vinyl monomers with metal cyclohexanecarboxylates, especially that of MMA with cobalt(III) cyclohexanecarboxylate.

Experimental

Materials. The monomers and the solvents were purified by ordinary methods and were redistilled before use.

Copper(II) cyclohexanecarboxylate was prepared by the reaction of sodium cyclohexanecarboxylate with copper sulfate. Cobalt(III) cyclohexanecarboxylate was obtained through the reaction of sodium cyclohexanecarboxylate with cobalt sulfate in the presence of hydrogen peroxide, much as in the preparation of cobalt(III) acetylacetonate.[8] Manganese(III) cyclohexanecarboxylate was also prepared according to the method used for the preparation of manganese(III) acetylacetonate;[9] *i.e.*, sodium cyclohexanecarboxylate was reacted with manganese chloride in the presence of potassium permanganate. All of the metal cyclohexanecarboxylates

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1) E. M. Arnett and M. A. Mendelsohn, *J. Am. Chem. Soc.*, **84**, 3821, 3824 (1962).

2) E.-G. Kastning, H. Naarmann, H. Reis and Ch. Berding, *Angew. Chem.*, **77**, 313 (1965).

3) C. H. Bamford and D. J. Lind, *Proc. Roy. Soc.*, **A 302**, 145 (1968).

4) T. Otsu, M. Minamii and Y. Nishikawa, *J. Macromol. Sci.*, **A2**, 902 (1968).

5) T. Otsu, Y. Nishikawa and S. Aoki, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **71**, 1067 (1968).

6) S. Aoki, R. Nakatani and T. Otsu, *ibid.*, **71**, 1756 (1968).

7) V. Lingamurty and S. R. Palit, *J. Sci. Ind. Res.* (*India*), **18B**, 140 (1959).

8) B. E. Bryant and W. C. Fernelius, "Inorganic Syntheses," Vol. V, p. 188, (1957).

9) R. G. Cherles, *ibid.*, Vol. VII, p. 183, (1963).

obtained were thoroughly washed with water; they were then dried in a vacuum desiccator:

$Cu(OCOC_6H_{11})_2$; light blue powder, Cu (calcd) 20.0%, Cu (found) 20.7%.

$Co(OCOC_6H_{11})_3$; dark green powder, Co (calcd) 13.4%, Co (found) 13.8%.

$Mn(OCOC_6H_{11})_3$; dark brown powder, Mn (calcd) 12.6%, Mn (found) 13.3%.

Analytical-grade cobalt(III) acetylacetonate was used without further purification. Azobisisobutyronitrile was recrystallized from ethanol.

Polymerization. The polymerization was carried out in a sealed glass tube without diffused light in a thermostat maintained at given temperatures. The resulting polymer was isolated by pouring the polymerization mixture into a large amount of methanol.

The number-average molecular weight ($\bar{M}_n$) of the resulting polymers was determined from the intrinsic viscosity measurements in benzene at 30°C by using the following equations:[10]

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76} \text{ for poly (MMA)}$$

$$[\eta] = 1.13 \times 10^{-4} \bar{M}_n^{0.73} \text{ for polystyrene}$$

Results and Discussion

Initiating Activity of Metal Cyclohexanecarboxylates. Styrene and MMA were polymerized by using copper(II), cobalt(III) and manganese(III) cyclohexanecarboxylates as initiators in bulk at 60°C. The results are shown in Table 1. Cobalt(III) cyclohexanecarboxylate was observed to show the highest initiating activity among these cyclohexanecarboxylates. For the MMA polymerization the activity decreased in the order: $Co^{III} > Mn^{III} > Cu^{II}$; this order agreed with that of the redox potential of the corresponding metal ions in aqueous solutions.[11]

TABLE 1. BULK POLYMERIZATIONS OF STYRENE AND MMA WITH METAL CYCLOHEXANECARBOXYLATES AT 60°C

Carboxylate (1×10^{-2} mol/l)	Monomer	Time (hr)	Yield (%)	$\bar{M}_n \times 10^{-5}$
Cu^{II}	Styrene	8	1.2	7.34
	MMA	5	trace	—
Co^{III}	Styrene	8	2.7	6.68
	MMA	2.5	6.6	8.55
Mn^{III}	Styrene	8	trace	—
	MMA	5	2.3	8.94

As can be seen from Table 2, the initiating activity of cobalt(III) cyclohexanecarboxylate was found to be higher than that of cobalt(III) acetylacetonate in the polymerizations of the vinyl monomers used. However, in the polymerization of butadiene, the initiating activity of cobalt(III) cyclohexanecarboxylate was very low.

TABLE 2. BULK POLYMERIZATIONS OF VINYL MONOMERS WITH Co(III) CYCLOHEXANECAR BOXYLATE AND Co(III) ACETYLACETONATE AT 60°C

Monomer	Initiator	Time (hr)	Yield (%)
MMA	Carboxylate	5	11.0
	Acetylacetonate	5	2.2
Styrene	Carboxylate	5	1.9
	Acetylacetonate	5	1.0
Acrylonitrile[b]	Carboxylate	5	2.9
	Acetylacetonate	5	trace
Vinyl acetate	Carboxylate	2	2.0
	Acetylacetonate	2	trace
Butadiene[c]	Carboxylate	15	trace

a) Initiator 30 mg and monomer 10 ml were used.
b) Polymerized in 50 vol% benzene solution.
c) Polymerized in 70 vol% benzene solution using 100 mg of the carboxylate at 80°C.

Polymerization of MMA with Cobalt(III) Cyclohexanecarboxylate. The course of the MMA polymerization with cobalt(III) cyclohexanecarboxylate was investigated kinetically in bulk or in a benzene solution.

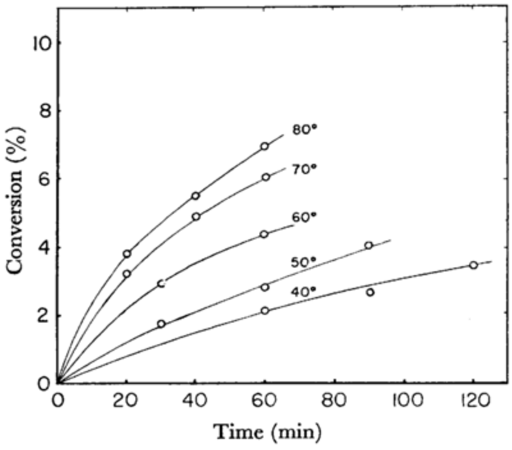

Fig. 1. Time-conversion curves in the bulk polymerization of MMA with cobalt(III) cyclohexanecarboxylate ([Co]=6.8×10^{-3} mol/l).

Figure 1 shows the time-conversion relations in the bulk polymerization of MMA at different temperatures. The linear relationship between the polymer yield and the time was not observed even at the initial stage of the polymerization, and the rate of polymerization decreased gradually with the time, much as in the MMA polymerization with lead tetraacetate.[6] Therefore, as a matter of convenience, the rate of polymerization was estimated approximately from the ratio of the polymer yield and the time at about a 5% polymer yield.

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10) "Polymer Handbook," J. Brandrup and E. H. Immergut Ed., Interscience, New York (1966).

11) "Handbook of Chemistry," N. A. Lange Ed., McGraw-Hill, New York (1961).

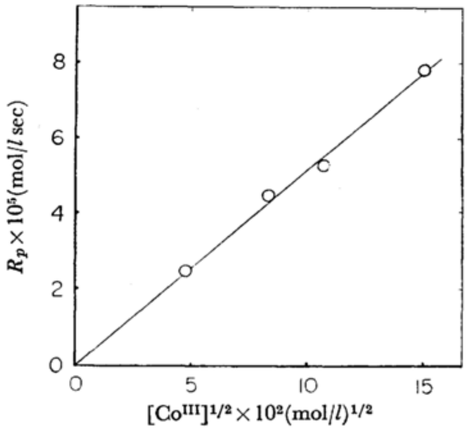


Fig. 2. Relationship between R_p and $[\mathrm{Co^{III}}]^{1/2}$ at 60°C ([MMA]=4.7 mol/l in benzene).

Figure 2 shows the straight-line relationship between the rate of polymerization and the square-root concentration of the initiator at a constant MMA concentration in benzene at 60°C. Figure 3 shows the log-log plot between the rate of polymerization and the monomer concentration at a constant initiator concentration in benzene at 60°C. From this figure, the kinetic order with respect to the MMA concentration was found to be 1.4.

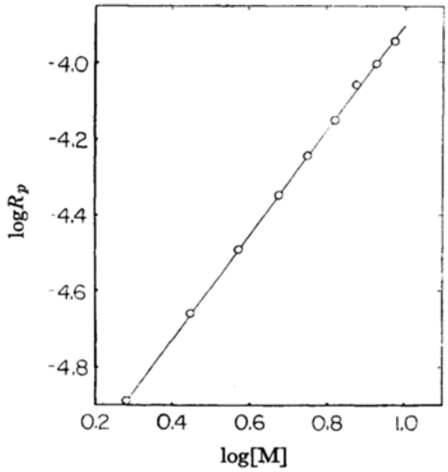


Fig. 3. Relationship between R_p and [MMA] in benzene at 60°C ($[\mathrm{Co^{III}}]=6.8\times10^{-3}$ mol/l).

Therefore, the overall rate of polymerization (R_p) of MMA with cobalt(III) cyclohexanecarboxylate was expressed by the following equation:

$$R_p = k[\mathrm{MMA}]^{1.4}[\mathrm{Co}]^{0.5} \qquad (2)$$

The observed order with respect to the initiator concentration in Eq. (2) indicated that this polymerization proceeded through a free radical intermediate. The order of the MMA concentration, which was higher than unity, suggests that the MMA molecule participates in the radical formation from the cobalt(III) initiator.

The poly(MMA) obtained by using the metal cyclohexanecarboxylates showed the same infrared spectra as the typical radical polymer, indicating that there was no difference in stereoregularity between them.

Copolymerization of Styrene with MMA or Vinyl Acetate. Styrene (M_1) was copolymerized with MMA or vinyl acetate by using cobalt(III) cyclohexanecarboxylate as an initiator in bulk at 60°C. The monomer-copolymer composition curves obtained are shown in Fig. 4. From this figure the monomer reactivity ratios in these copolymerization systems were determined to be $r_1=0.40$ and $r_2=0.50$ for the styrene-MMA system, and $r_1=55$ and $r_2=0$ for the styrene-vinyl acetate system. These values were in accordance to those obtained by using peroxides and azo compounds as radical initiators,[10] indicating that this cobalt(III) initiator did not influence the propagation step of the radical polymerization.

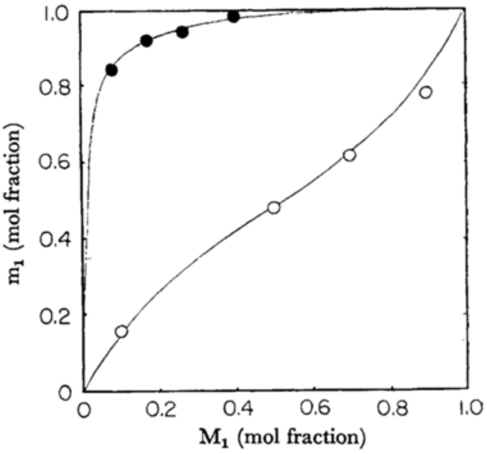


Fig. 4. Monomer-copolymer composition curves in the copolymerizations of styrene (M_1) with MMA (—○—) and with vinyl acetate (—●—) at 60°C.

Absorption Spectra of Cobalt(III) Cyclohexanecarboxylate. Cobalt(III) cyclohexanecarboxylate showed the characteristic absorption maximum at about 650 mμ based on the $\mathrm{Co^{III}}$ ion.

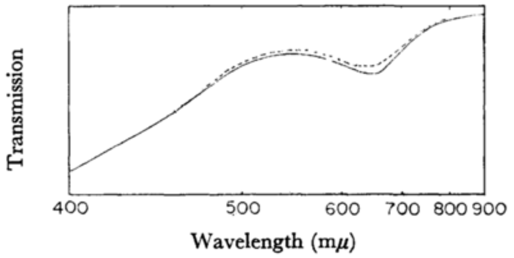


Fig. 5. Absorption spectra of cobalt (III) cyclohexanecarboxylate in benzene-MMA mixture (9 : 1). (——): Before heating, (------): After heating

The intensity of this absorption peak did not change upon heating in benzene at 80°C for 18 hr. As can be seen from Fig. 5, however, it decreased slightly upon being heated in a benzene-MMA mixture. This result indicates that cobalt(III) cyclohexanecarboxylate does not decompose in benzene, much like cobalt(III) acetylacetonate,[12] but it decomposes in the presence of the MMA monomer.

Chain Transfer to Cobalt(III) Cyclohexanecarboxylate. Figure 6 shows the plot between the rate of the polymerization of MMA and the reciprocal degree of polymerization ($1/\bar{P}_n$) of the polymer obtained. Although this plot gave a straight line when azobisisobutyronitrile was used as an initiator, that obtained by using cobalt(III) cyclohexanecarboxylate showed a concave curve, indicating that considerable chain transfer to the cobalt(III) initiator occurred. According to the treatment by Tobolsky *et al.*,[13] the apparent chain transfer constant of this initiator toward the poly(MMA) was estimated to be 0.06.

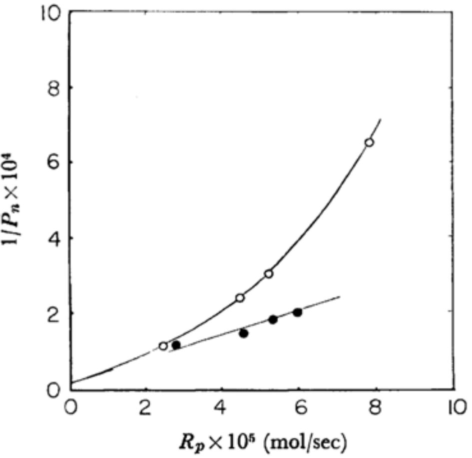
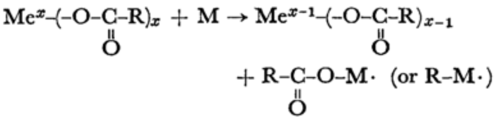


Fig. 6. $1/\bar{P}_n$ *vs.* R_p.
(—○—): Polymerized with cobalt(III) cyclohexanecarboxylate,
(—●—): Polymerized with azobisisobutyronitrile
(Polymerization conditions were the same with in Fig. 2.)

Conclusions

The following conclusions were derived from the results presented above: (i) cobalt(III) cyclohexanecarboxylate could serve as an effective free radical initiator of the MMA polymerization; (ii) this carboxylate did not influence the propagation step in the radical polymerization of MMA, and (iii) this carboxylate decomposed to produce the initiating radical species when the MMA monomer participated.

The initiation with cobalt(III) cyclohexanecarboxylate in the MMA polymerization might resemble that of metal acetylacetonates.[4,5] The polymerization was thought to be initiated with a radical produced by the homolysis of the metal-oxygen bond in metal carboxylate, with the participation of the MMA monomer, as follows:



$$\mathrm{Me}^{x}\text{-}(\text{-O-}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\text{-R})_x + \mathrm{M} \rightarrow \mathrm{Me}^{x-1}\text{-}(\text{-O-}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\text{-R})_{x-1} + \mathrm{R}\text{-}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\text{-O-M}\cdot \;\text{(or R-M}\cdot\text{)}$$

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[12] J. Itakura, H. Tanaka and H. Ito, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **70**, 1227 (1967).

[13] B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).