# Polymerization of Methyl Methacrylate by the Bis(benzoylacetonato)-Copper(II)-1,10-Phenanthroline System

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The addition of 1,10-phenanthroline accelerates the polymerization of methyl methacrylate by a $\beta$-diketonato chelate of Cu(II), Mn(II), Mn(III), Co(II), Co(III), and Fe(III), but has no effect on the chelate of Ni(II). The effect of 1,10-phenanthroline, which is composed of two pyridine units, is much greater than that of pyridine. The polymerization rate of methyl methacrylate by the bis(benzoylacetonato)Cu(II)-1,10-phenanthroline system may be represented as follows:

$$R_p \propto [\mathrm{MMA}]\{[\mathrm{Cu(II)}][\text{1,10-phenanthroline}]\}^{1/2}$$

The initiation reaction is assumed to be by a ligand-exchange reaction of bis(benzoylacetonato)Cu(II) with 1,10-phenanthroline, where a benzoylacetonyl ligand is displaced by 1,10-phenanthroline and Cu(II) is simultaneously reduced to Cu(I).

In has been reported that many additives accelerate vinyl polymerization by metallic chelates of $\beta$-diketone. Some additives, such as pyridine[1] and carbonyl compounds,[2] have been shown to coordinate to the central metal of chelate compounds through the lone-pair electrons and to increase the initiation rate of vinyl polymerization by tris(acetylacetonato)Mn(III) (Mn-(acac)$_3$, where acac represents an acetylacetonyl ligand). This implies that the greater the ability for coordination to metal, the greater the effect. The chelating agents form a class of compounds which have the greatest ability for coordination. Recently, Bamford and Ferrar have briefly mentioned that ethylene and propylene diamines have a remarkable effect on polymerization by Mn(acac)$_3$. It has been found that 1,10-phenanthroline (phen) has much greater effects on the polymerization of methyl methacrylate (MMA) by metallic chelates of $\beta$-diketone than pyridine does. Phen is a chelating agent which is composed of two pyridine units. The effect of phen on bis(benzoylacetonato)Cu(II) (Cu(ba)$_2$, where ba denotes a benzoylacetonyl ligand) is studied in some detail.

## Experimental

*Reagent.* The pyridine, MMA, and solvents were dried over **3A** molecular sieves and were distilled under reduced pressure just before use. The chelate compounds were commercially obtained and were used without further purification. The metallic chelates of acetylacetone were manufactured by the Dojindo Co., Ltd. The Cu(ba)$_2$ was supplied by Eastman Organic Chemicals. The recrystallization of phen was carried out from a benzene solution (mp 94°C). The dipyridyl was recrystallized from an ethanol-water system(mp 69°C).

*Procedure.* The chelate, the chelating agent, MMA, and benzene were mixed under atmospheric conditions. After the mixture had been placed in a glass tube and degassed by repeated freezing, evacuating, and thawing, it was sealed off. Polymerization was then carried out in the dark. The temperature was controlled within ±0.1°C. The polymer thus produced was precipitated in methanol containing a small amount of hydroquinone and hydrogen chloride, filtered, and dried *in vacuo* to a constant weighs. Conversions were then calculated on the weight of the polymer.

## Results and Discussion

1. *Effect of Chelating Agent.* The effects of phen and dipyridyl are compared with those of pyridine in Table 1. Phen has an accelerative effect on the polymerization of MMA by all the chelates of $\beta$-diketone examined other than Ni(acac)$_2$. Dipyridyl has an effect on Mn(acac)$_2$, Mn(acac)$_3$, Cu(ba)$_2$, Co(acac)$_2$, and Co(acac)$_3$, but has no effect on Fe(acac)$_3$ and Ni(acac)$_2$. Pyridine accelerates the polymerization of MMA by Mn(acac)$_2$, Mn(acac)$_3$, Co(acac)$_2$, and Co-(acac)$_3$, but has no effect on Cu(ba)$_2$, Fe(acac)$_3$, and Ni(acac)$_2$. Pyridine, however, has greater effects on the chelates of Mn and Co than dipyridyl does.

TABLE 1. EFFECTS OF CHELATING AGENT

| Chelate | | Conversion (%) | | | |
|---|---|---|---|---|---|
| type | concentration $\times 10^2$ mol/$l$ | no additive | phen $2\times10^{-2}$ mol/$l$ | dipyridyl $2\times10^{-2}$ mol/$l$ | pyridine $4\times10^{-2}$ mol/$l$ |
| Cu(ba)$_2$ | 2.07 | trace | 16.9 | 1.97 | 0 |
| Mn(acac)$_2$ | 1.19 | 3.42 | 35.6 | 7.02 | 13.4 |
| Mn(acac)$_3$ | 0.568 | 13.8 | 59.5 | 15.6 | 34.7 |
| Co(acac)$_2$ | 3.11 | 2.36 | 10.7 | 6.96 | 8.41 |
| Co(acac)$_3$ | 2.25 | 4.79 | 5.35 | 5.82 | 7.29 |
| Fe(acac)$_3$ | 2.27 | 0 | 3.67 | 0 | 0 |
| Ni(acac)$_2$ | 3.11 | trace | trace | 0 | 0 |

[MMA]=2.82 mol/$l$; solvent: benzene; at 60°C for 8 hr

It has been described that the effect of ketones is dependent on the nucleophilicity.[2] The effects of pyridine homologs on the polymerization of styrene decreases in this order: pyperidine>pyridine>2,6-lutidine.[1] This order is consistent with the ability of coordination to the central metal. In the present case also, it is reasonable to assume that the effects of pyridine homologs are dependent on the ability of coordi-

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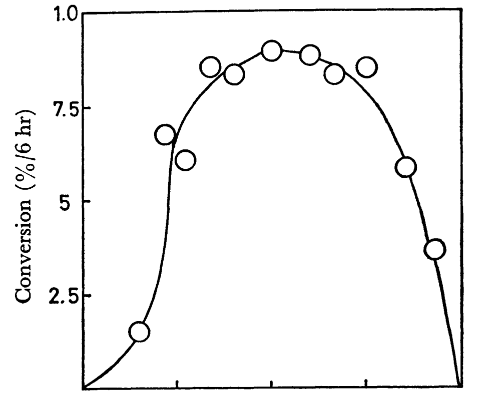
[1] K. Uehara, Y. Kataoka, M. Tanaka, and N. Murata, *Kogyo Kagaku Zasshi*, **70**, 1945 (1967).

[2] K. Kaeriyama, This Bulletin, **43**, 1511 (1970). K. Kaeriyama and Y. Yamazaki, *Kogyo Kagaku Zasshi*, **74**, 1718 (1971).

[3] C. H. Bamford and A. N. Ferrar, *Chem. Commun.*, **1970**, 315.

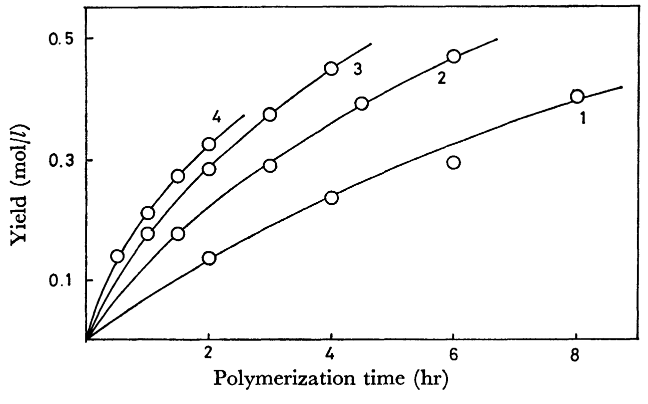
nation to the central metal, as can be anticipated from the viewpoint of nucleophilicity and steric hindrance. The average p$K$ values for pyridine, dipyridyl, and phen are 5.21, 4.36, and 4.87 respectively.[4] Pyridine is the most nucleophilic. Steric hindrance of coordination to the central metal of chelate compounds probably decreases in this order: phen>dipyridyl>pyridine. Nevertheless, phen is the most effective. Pyridine has smaller effects than phen. The noticeable effect of phen, which has two coordination sites in a molecule, is attributable to the chelating effect of phen.



Molar fraction of Cu(ba)$_2$

Fig. 1. Dependence of conversion on molar fraction of chelate.
[Cu(ba)$_2$]+[phen]=2.1×10$^{-2}$ mol/$l$
[MMA]=2.82 mol/$l$; at 60°C in benzene

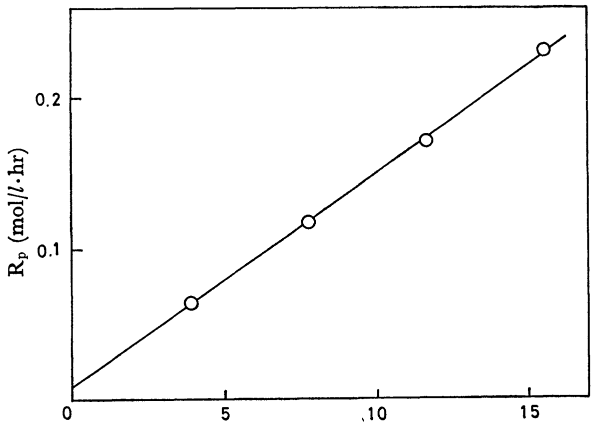
2. *Dependence on Molar Fraction of Cu(ba)$_2$.* Conversions at a constant polymerization time are shown as a function of the molar fraction of Cu(ba)$_2$ in Fig. 1. It is apparent from the figure that the binary system is very active in the initiation of MMA polymerization, although neither component shows any appreciable effect. In the case of the Mn(acac)$_3$-phen system,[5] a clear peak is observed at the molar fraction of 0.5. In the present combination, no sharp peak appears, but a wide plateau can be seen in the range of the molar fractions from 0.33 to 0.75.



Polymerization time (hr)

Fig. 2. Dependence of yield on polymerization time.
[MMA]=3.57 mol/$l$; at 70°C in benzene
{[Cu(ba)$_2$][phen]}$^{1/2}$
1. 3.89×10$^{-3}$ mol/$l$ 2. 7.77×10$^{-3}$ mol/$l$
3. 11.7×10$^{-3}$ mol/$l$ 4. 15.5×10$^{-3}$ mol/$l$

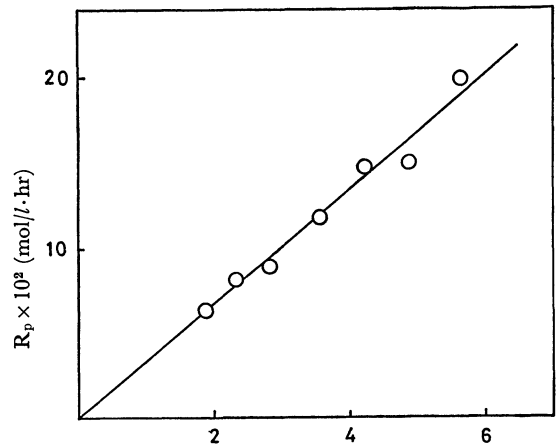
3. *Dependence on Initiator Concentration.* The dependence of the polymer yield on the polymerization time is shown at different concentrations of the initiator in Fig. 2. No linear relation between the yield and the time can be observed even in the initial stage of polymerization. Therefore, according to the Aoki-Matsumura-Otsu method,[6] the rate of polymerization was estimated approximately from the ratio of the polymer yield and the time at a 5% polymer yield.



{[Cu(ba)$_2$][phen]}$^{1/2}$×(mol/l)

Fig. 3. Dependence of polymerization rate on initiator concentration.
[MMA]=3.57 mol/$l$; at 70°C in benzene

The rate of polymerization thus obtained is shown as a function of the concentrations of Cu(ba)$_2$ and phen in Fig. 3. The molar concentration of Cu(ba)$_2$ is equal to that of phen in each run. The rate of polymerization is linearly dependent on the square root of [Cu(ba)$_2$][phen]. This suggests that termination is not by a reaction of a polymer radical with the chelate, but by a bimolecular reaction of polymer radicals. This conclusion is also supported by the experimental evidence that Cu(ba)$_2$ has no effect on the polymerization of MMA initiated by azo-bis-isobutyronitrile.



[MMA] (mol/$l$)

Fig. 4. Dependence of polymerization rate on concentration of MMA.
[Cu(ba)$_2$]=[phen]=7.77×10$^{-3}$ mol/$l$ at 70°C in benzene

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[4] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London (1965).

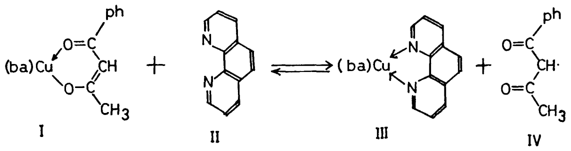
[5] K. Kaeriyama, *Makromol. Chem.*, in press.

[6] S. Aoki, S. Matsumura, and T. Otsu, This Bulletin, **42**, 2574 (1969).

The line does not pass through the point of origin. This deviation is probably attributable to the fact that the rate is not strictly determined at the initial stage of polymerization from the linear relation between the time and conversion.

4. *Dependence on the Monomer Concentration.* The dependence of the polymerization rate on the MMA concentration is shown in Fig. 4. It is apparent that the rate of polymerization is linearly proportional to the concentration of MMA. The monomer does not participate in the initiation reaction at all. This is the first case, in which MMA does not participate in the initiation reaction of the polymerization by metallic chelates of β-diketones.

5. *Initiation Reaction.* It has been reported by many workers that the initiation reaction of vinyl polymerization by metallic chelates of β-diketone proceeds by means of the elimination of a ligand from the chelate, which accompanies the reduction of the central metal.[1,2,7,8] Electron-donating additives coordinate to the metal of the chelate and accelerate the elimination of the β-diketonyl radical from the chelate.[1-3] This increases the initiation rate of polymerization. Phen also coordinates to Cu and accelerates the polymerization of MMA. Phen is a chelating agent and coordinates at two sites. The initiation reaction can be represented as follows:



where ph represents a phenyl group. The reaction is a ligand-exchange reaction between the benzoylacetonyl group and phen, and Cu(II) is simultaneously reduced to Cu(I). Radical polymerization is initiated by the benzoylacetonyl radical thus produced. This exchange reaction reasonably explains why phen has a greater effect on Cu(ba)$_2$ than pyridine. It also supports the initiation reaction that the carbonyl group can be detected by IR spectroscopy in polystyrene produced by the initiator system. One of the driving forces for the formation of the radical is the precipitation of III from the polymerizing mixture, which shifts the equilibrium toward the right side.

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7) C. H. Bamford and D. J. Lind, *Proc. Roy. Soc.*, **A302**, 145 (1968).

8) T. Otsu, Y. Nishikawa, and S. Aoki, *Kogyo Kagaku Zasshi*, **71**, 1067 (1968).