The Additive Effect of Triphenylphosphine on the Polymerization of Vinyl Monomers by Copper(II) Chelates

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Various copper(II) chelates were found to be effective initiators in the polymerization reaction of the methyl methacrylate in the presence of triphenylphosphine. The conversion increases with an increase in the concentration of triphenylphosphine, reaching a constant level at the ratio of 1: 2 between copper chelates and triphenylphosphine. Di-μ-methoxo-bis(ethylacetoacetato)dicopper(II) was the most effective initiator. The dependence of the rate of the polymerization on the square root of the concentration of the complexes suggests that the polymerization by this initiation system proceeds *via* a radical mechanism. It can be assumed that the copper chelate coordinated the triphenylphosphine and that homolytic fission occurred to give a free ligand radical, accompanied by the reduction of the central copper atom. Stable copper(I) mixed chelates were obtained under conditions similar to those of the polymerization.

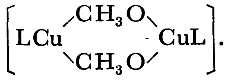
The radical polymerization of vinyl monomers by using copper acetylacetonate [Cu(acac)$_2$] and its derivatives as catalysts has been reported.[1–3] The solvent effects and effects resulting from the additives, as well as a high order with respect to the monomer, are characteristic of these polymerization reactions. These characteristics indicate the participation of monomers and additives in the initiation step. Recently, Bamford and Ferrar[4] showed by radiochemical investigations that donor additives enhance the rates of the initiation of free radical polymerization by transition-metal acetylacetonate and that the propagating chain carries one acetylacetonate residue, but that the fragments derived from the additives are incorporated in the polymer to only a minor extent.

In the present study, various copper(II) chelates were found to be effective initiators in the polymerization reaction of the vinyl monomer in the presence of triphenylphosphine.

During the initiating step, a ligand displacement is supposed to occur, with the simultaneous reduction of Cu(II)→Cu(I). Various Cu(I) triphenylphosphine mixed chelates were separated.

Experimental

Materials. The monomer was purified by the usual method and was distilled under reduced pressure before use. The triphenylphosphine was recrystallized several times from ether. The methoxo-copper(II) chelates were synthesized according to the method of Bertrand[5]; that is, the copper chelate, CuL$_2$, was allowed to react with potassium hydroxide in methanol to produce the methoxo complexes,



$$\left[\mathrm{LCu}\begin{smallmatrix}\diagup \mathrm{CH_3O} \diagdown \\ \diagdown \mathrm{CH_3O} \diagup\end{smallmatrix}\mathrm{CuL}\right].$$

Polymerization Procedure. A copper chelate, the monomer, and the solvent were placed in a glass tube. After the tube had been degassed by repeated freezing, evacuating, and thawing, it was sealed off. Polymerization was carried out under shaking in a thermostat maintained at a given temperature. The resulting polymers were precipitated in methanol containing hydrochloric acid, filtered, and dried *in vacuo* to a constant weight.

Measurements. The NMR spectra were measured in order to determine the tacticities of the poly(methyl methacrylates) according to the method of Kato.[6]

Polarographic measurements were carried out in acetonitrile with a Yanagimoto potential-controlled Polarograph at 25°C. Tetrabutylammonium perchlorate was used as the supporting electrolyte, and Triton X was added to each solution in order to diminish the maximum wave.

Result and Discussion

Additive Effect of Triphenylphosphine. Copper(II) acetylacetonate and di-μ-methoxo-bis(acetylacetonato)-dicopper(II) [Cu(acac)OCH$_3$]$_2$ each has its own accelerative effect on the polymerization of various vinyl monomers in organic solvents. Tables 1 and 2 show the remarkable accelerative effects of triphenylphosphine on the polymerization of methyl methacrylate (MMA) by copper(II) chelates. The accelerative effects of μ-methoxo copper(II) complexes were superior to those of the original copper(II) chelates. The methoxo ethyl acetoacetate chelate was the most effective.

The stereoregularity of the resulting polymer was calculated from the NMR spectra. The syndiotacticities were slightly higher than those of ordinary polymers

Table 1. Additive effect of the triphenylphosphine on the polymerization of MMA

Chelate	Chelate concentration (mol/*l*)	Triphenylphosphine concentration (mol/*l*)	Conversion (%/hr)
Cu(acac)$_2$	0.01	0	2.18
Cu(acac)$_2$	0.01	0.04	5.00
[Cu(acac)OCH$_3$]$_2$	0.01	0	5.40
[Cu(acac)OCH$_3$]$_2$	0.01	0.04	12.05

Solvent: acetonitrile, [MMA]: 5 mol/*l*, Temp: 70°C, 4 hr.

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[1] Y. Nishikawa and T. Otsu, *Kogyo Kagaku Zasshi*, **72**, 1836 (1969) and references therein.

[2] K. Uehara, Y. Kataoka, M. Tanaka, and N. Murata, *ibid.*, **73**, 1053 (1970) and references therein.

[3] K. Kaeriyama, This Bulletin, **43**, 1511 (1970).

[4] C. H. Bamford and A. N. Ferrar, *Chem. Commun.* **1970**, 315 *Proc. Roy. Soc.* (London), **A321**, 425 (1971).

[5] J. A. Bertrand, R. I. Kaplan, *Inorg. Chem.*, **4**, 1657 (1965).

[6] Y. Kato, H. Watanabe, and A. Nishioka, This Bulletin, **37**, 1762 (1964).

TABLE 2. ADDITIVE EFFECT OF THE TRIPHENYLPHOSPHINE ON THE POLYMERIZATION OF MMA BY VARIOUS CHELATES

Chelate	Chelate concentration (mol/*l*)	Triphenylphosphine concentration (mol/*l*)	Rate of polymerization (mol/*l*/sec)
$Cu(acac)_2$	0.001	0.004	1.83×10^{-5}
$[Cu(acac)OCH_3]_2$	0.001	0.004	2.86×10^{-5}
$Cu(eacac)_2$	0.001	0.004	7.55×10^{-5}
$[Cu(eacac)OCH_3]_2$	0.001	0.004	8.70×10^{-5}
$Cu(dpm)_2$	0.001	0.004	0.43×10^{-5}
$[Cu(dpm)OCH_3]_2$	0.001	0.004	1.21×10^{-5}
$Cu(SA)_2$	0.001	0.004	0.97×10^{-5}
$[Cu(SA)OCH_3]_2$	0.001	0.004	1.32×10^{-5}
$Cu(3\text{-}foc)_2$	0.001	0.004	2.51×10^{-5}

Polymerization condition; solvent: acetonitrile, [MMA]: 5 mol/*l*, Temp: 70°C, 4 hr.
eacac=ethylacetoacetato, dpm=dipivaloylmethanato, SA=salicylaldehydato, 3-foc=3-formyl camphor.

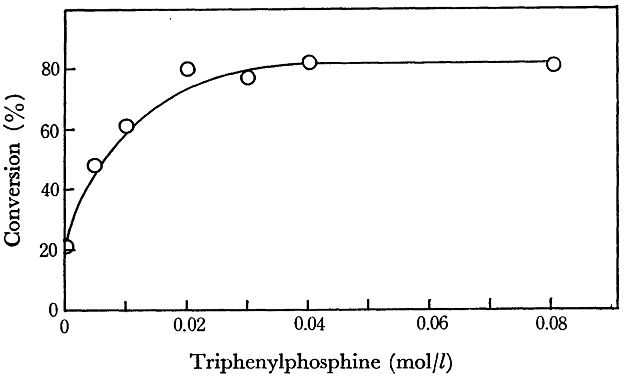


Fig. 1. The dependence of the concentration of triphenylphosphine. Solvent: acetonitrile, $[Cu(acac)OCH_3]_2$: 0.01 mol/*l*, [MMA]: 5 mol/*l*, at 70°C, 4 hr.

obtained by radical polymerization. (74.0%, polymerized by $[Cu(eacac)OCH_3]_2$ at 20°C; 68.8%, polymerized by $Cu(acac)_2$ at 50°C; 65.6%, at 70°C.)

Figure 1 shows the dependence of the conversion on the concentration of triphenylphosphine. The conversion increases with an increase in the concentration of triphenylphosphine, reaching a constant level at the ratio of 1 : 2 of the copper chelate and triphenylphosphine. Above this ratio, the polymerizing mixture loses its blue color at the end of the polymerization. In the absence of copper(II) chelates, traces of the polymer were obtained in the presence of 0.1 mol/*l* of triphenylphosphine ([MMA]: 5 mol/*l*).

TABLE 3. SOLVENT EFFECTS ON THE POLYMERIZATION RATE IN $[Cu(acac)OCH_3]_2$–PPh_3 SYSTEM

Solvent	Rate of polymerization (mol/*l*/sec)
Acetonitrile	7.09×10^{-5}
Chloroform	2.88×10^{-5}
Dimethylformamide	3.24×10^{-5}
Pyridine	2.29×10^{-5}
Tetrahydrofuran	4.03×10^{-5}

$[Cu(acac)OCH_3]_2$: 0.005 mol/*l*, $[PPh_3]$: 0.02 mol/*l*, [MMA]: 5 mol/*l*, at 70°C, 4 hr.

Table 3 shows the solvent effects on the reactivity of the Cu(II)-chelate-triphenylphosphine system. The rates of polymerization are in the following order: $CH_3CN>THF>DMF>CHCl_3>Py$. The effectiveness of the solvent might be due to the stabilization of the univalent copper. The univalent copper is known to

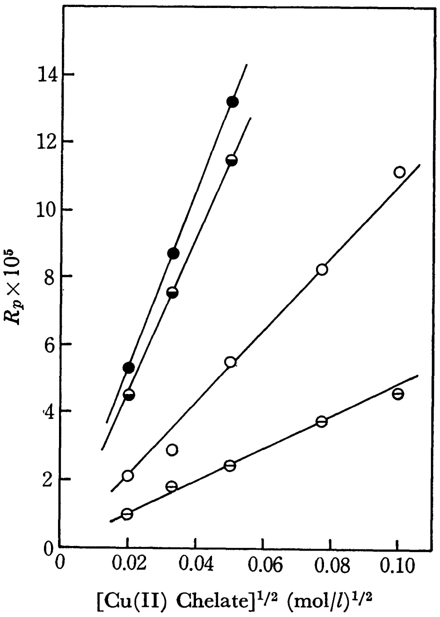


Fig. 2. The dependence of the polymerization rate on the square root of the concentration of the copper(II) chelates. [MMA]: 5 mol/*l*, Solvent: acetonitrile, at 70°C, 2 hr. $[Chelate]/[PPh_3]=1/4$
●: $[Cu(eacac)OCH_3]_2$, ◒: $Cu(eacac)_2$, ○: $[Cu(acac)OCH_3]_2$, ⊖: $Cu(acac)_2$.

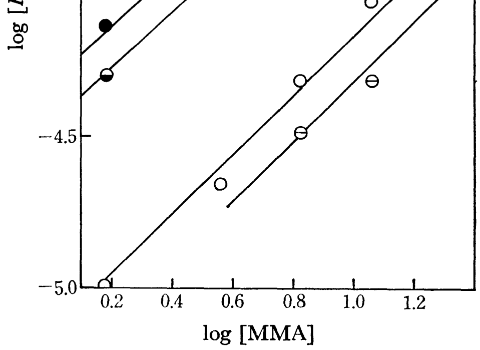


Fig. 3. The dependence of the polymerization rate on the MMA concentration.
[Chelate]: 0.005 mol/*l*, $[PPh_3]$: 0.02 mol/*l*, Solvent: acetonitrile, at 60°C, 1 hr.
●: $[Cu(eacac)OCH_3]_2$, ◒: $Cu(eacac)_2$, ○: $[Cu(acac)OCH_3]_2$, ⊖: $Cu(acac)_2$.

TABLE 4. POLYMERIZATION RATE OF VARIOUS MONOMERS

Monomer	Chelate	Chelate concentration (mol/*l*)	PPh_3 concentration (mol/*l*)	Solvent	Temp. (°C)	Time (hr)	Conversion (%/hr)
Ethyl acrylate	$Cu(acac)_2$	0.05	0.2	bulk	50	5	2.4
	$[Cu(acac)OCH_3]_2$	0.05	0.2	bulk	50	3	30.7
Acrylonitrile	$Cu(acac)_2$	0.05	0.2	bulk	50	5	1.6
	$[Cu(acac)OCH_3]_2$	0.05	0.2	bulk	50	3	9.3
Styrene	$Cu(acac)_2$	0.005	0.02	benzene	70	10	0.4
	$[Cu(acac)OCH_3]_2$	0.005	0.02	benzene	70	10	0.4
	$[Cu(eacac)OCH_3]_2$	0.005	0.02	benzene	70	10	2.6
	$Cu(3\text{-foc})_2$	0.005	0.02	benzene	70	10	2.2

[Styrene]: 5 mol/*l*, 3-foc=3-formylcamphor.

be stabilized by acetonitrile.[7]

Kinetics. From the straight line in the time-conversion plots, the rates of polymerization were evaluated by graphically determining a tangent at a given time. The dependences of the rate of polymerization on the square root of the concentrations of the four complexes are shown in Fig. 2. Figure 3 shows the rate of polymerization as a function of the monomer concentration at a constant concentration of copper chelates and additives. From the slopes of these straight lines, the order with respect to the monomer was found to be 1.0. Judging from this order, the coordination of the monomer to the copper chelate cannot be considered at the initiation step. It can be assumed that the Cu(II) chelate coordinated the triphenylphosphine and that homolytic fission occurred to give a free-ligand radical or an alkoxy radical, accompanied by the reduction of the central copper atom.

The reduction potentials of the copper(II) chelates were measured and plotted against the rate of polymerization. A good linearity was obtained (see Fig. 4).

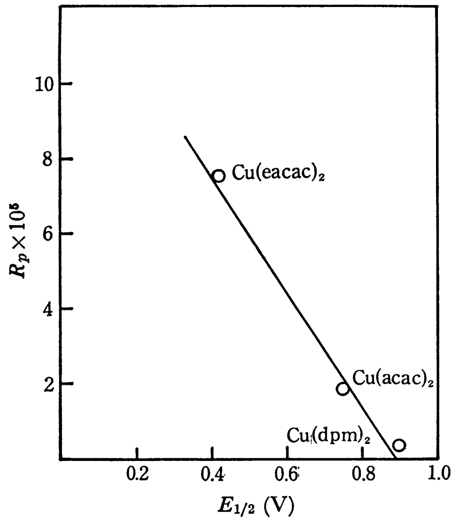


Fig. 4. The relationship between the reduction potentials of the copper(II) chelates and the rate of polymerization (Table 2).
Solvent: acetonitrile, [Chelate]: 0.001 mol/*l*, $[(C_4H_9)_4NClO_4]$: 0.1 mol/*l*, [Triton X]: 0.1%.

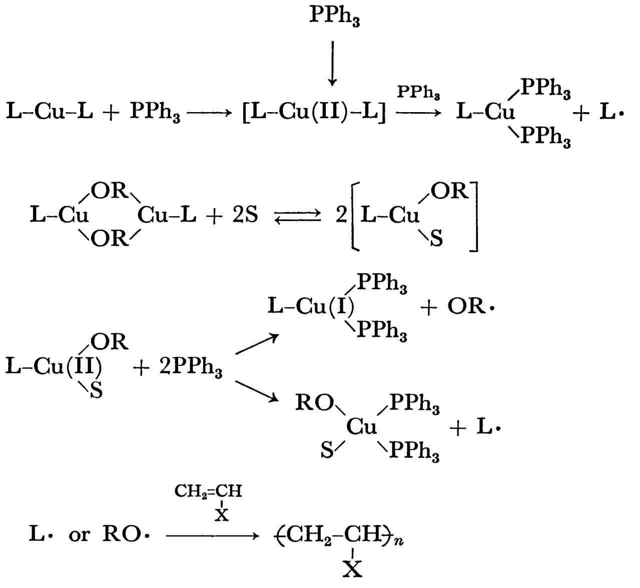
TABLE 5. THE ISOLATED Cu(I) CHELATES

Cu(I) Chelate	Color	Mp (°C)
$Cu(acac)(PPh_3)_2$	colorless	177—179
$Cu(SA)(PPh_3)_2$	yellow	175
$Cu(3\text{-foc})(PPh_3)_2$	colorless	105—107

(3-foc=3-formylcamphor)

Reactivity of Other Monomers. As is shown in Table 4, these initiation systems were effective with styrene, acrylonitrile, and ethyl acrylate.

Reaction of Triphenylphosphine with Cu(II) Chelates. As is shown in Table 5, stable Cu(I) mixed chelates were obtained under conditions similar to those of the polymerization. The details of the preparations and the properties of the copper(I) mixed chelates will be reported in a separate paper.[8] The initiation reactions can be summarized schematically as follows:



(L=bidentate ligand)
(S=solvent)

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[8] T. Shono, Y. Fujii, and K. Shinra, *Chem. Lett.*, **1**, 163 (1972).