Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Osawa, Zenjiro , Kobayashi, Kenji and Ogiwara, Yoshitaka(1972) 'Catalytic Action of Metallic Salts in Autoxidation and Polymerization. VII. Polymerization of Methyl Methacrylate by Cobalt(ll) or (III) Acetylacetonate-Dioxane Hydroperoxide', Journal of Macromolecular Science, Part A, 6: 8, 1665 — 1679

To link to this Article: DOI: 10.1080/10601327208056919

URL: http://dx.doi.org/10.1080/10601327208056919

J. MACROMOL. SCI.—CHEM., A6(8), pp. 1665-1679 (1972)

Catalytic Action of Metallic Salts in Autoxidation and Polymerization. VII. Polymerization of Methyl Methacrylate by Cobalt(II) or (III) Acetylacetonate-Dioxane Hydroperoxide

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ABSTRACT

Polymerization of methyl methacrylate by Co(II or III) acetylacetonate-dioxane hydroperoxide [abbreviated as $Co(acac)_2$, $Co(acac)_3$, and DOX HPO, respectively] was carried out in dioxane solvent, and the differences in polymerization rate and the degree of polymerization between two initiating systems were compared. $Co(acac)_2$-DOX HPO for the initiation of the polymerization system was more effective than $Co(acac)_3$-DOX HPO. The polymerization rate equations for both initiating systems obtained from kinetic data were as follows. For $Co(acac)_2$-DOX HPO initiating system:

$$R_p = k\,[M]^{3/2}\,[Co(acac)_2]^{1/7}\,[DOX\ HPO]^{1/5}$$

For Co(acac)$_3$-DOX HPO initiating system:

$$R_p = k[M][Co(acac)_3]^{1/3}[DOX\ HPO]^{1/2}$$

The degree of polymerization was dependent upon initial monomer, cobalt, and dioxane hydroperoxide concentrations, but it was extremely different between the two systems. In the case of the Co(acac)$_2$-DOX HPO initiating system, the degree of polymerization increased with conversion, which increased with time, but it was fairly low. On the other hand, the Co(acac)$_3$-DOX HPO initiating system produced polymers with higher degrees of polymerization, which was independent of conversion, and which increased with time.

INTRODUCTION

In the field of radical polymerization, studies on the elementary reaction mechanism and the newer initiators, including metallic compounds and metallic salts-peroxides initiating systems, have been made lately [1-16]. We have been studying the catalytic actions of metallic salts in autoxidation and polymerization [17-22].

In previous papers [17, 20] we reported that Co(II) acetylacetonate-dioxane hydroperoxide [Co(acac)$_2$-DOX HPO] and Co(III) acetylacetonate-dioxane hydroperoxide [Co(acac)$_3$-DOX HPO] initiating systems were much more effective for the polymerization of methyl methacrylate than Co(acac)$_2$— and Co(acac)$_3$—tert-butyl hydroperoxide initiating systems, and that cobaltous acetylacetonate was more effective than cobaltic acetylacetonate with the two hydroperoxides. The kinetic data on the decomposition of hydroperoxides catalyzed by Co(acac)$_2$ and Co(acac)$_3$ gave little information for interpretation of the polymerization process. Therefore, the dependences of the polymerization rate on monomer, Co(acac)$_2$, Co(acac)$_3$, and DOX HPO concentrations in the polymerization of methyl methacrylate were examined for the interpretation of the polymerization mechanism.

EXPERIMENTAL

Reagents

Commercial cobaltous acetylacetonate (Tokyo Kasei Co. Ltd.) was recrystallized from benzene-petroleum ether. Commercial cobaltic acetylacetonate was used without further purification. Purification of dioxane and methyl methacrylate was the same as in a previous paper [20]. Dioxane hydroperoxide was prepared by bubbling oxygen through dioxane under UV irradiation. The concentration of hydroperoxide was determined by iodometry. (Dioxane hydroperoxide is relatively unstable and its properties are unclear. Preparation conditions often affected the rate of hydroperoxide formation and also the polymerization rate.)

Polymerization

Polymerization was carried out in a glass tube under nitrogen at 50°C for various times using dioxane as solvent. The polymerization conditions are listed in Table 1. After polymerization, the contents of the tube were poured into a large amount of methanol to precipitate the polymer. The polymer obtained was purified by precipitation with the chloroform-methanol solvent systems. The degree of polymerization of the polymers was measured by viscometry in benzene solution at 25°C with the aid of the intrinsic viscosity molecular weight relationship of Fox et al. [23].

RESULTS AND DISCUSSION

A (Co(acac)$_2$-DOX HPO Initiating System

The dependence of time-conversion curves on monomer, Co(acac)$_2$, and DOX HPO concentrations are shown in Figs 1-3, respectively.

As shown in Figs. 1-3, the polymerization rate of the

TABLE 1. Polymerization Conditions

A:	$\mathrm{Co(acac)_2}$-DOX HPO initiating system (total volume 10 ml)	
A-1	Monomer conc	3.74 to 0.47 mole/liter
	$\mathrm{Co(acac)_2}$ conc	2.5×10^{-3} mole/liter (const)
	DOX HPO conc	1.0×10^{-2} mole/liter (const)
A-2	$\mathrm{Co(acac)_2}$ conc	2.5×10^{-3} to 1.0×10^{-4} mole/liter
	Monomer conc	3.74 moles/liter (const)
	DOX HPO conc	1.0×10^{-2} mole/liter (const)
A-3	DOX HPO conc	2.0×10^{-2} to 1.0×10^{-3} mole/liter
	Monomer conc	3.74 moles/liter (const)
	$\mathrm{Co(acac)_2}$ conc	2.5×10^{-3} mole/liter (const)
B:	$\mathrm{Co(acac)_3}$-DOX HPO initiating system (total volume 12 ml)	
B-1	Monomer conc	4.68 to 1.56 moles/liter
	$\mathrm{Co(acac)_3}$ conc	2.5×10^{-3} mole/liter (const)
	DOX HPO conc	1.0×10^{-2} mole/liter (const)
B-2	$\mathrm{Co(acac)_3}$ conc	5.0×10^{-3} to 2.5×10^{-4} mole/liter
	Monomer conc	3.90 moles/liter (const)
	DOX HPO conc	1.0×10^{-2} mole/liter (const)
B-3	DOX HPO conc	2.5×10^{-2} to 2.5×10^{-3} mole/liter
	Monomer conc	3.90 moles/liter (const)
	$\mathrm{Co(acac)_3}$ conc	2.5×10^{-3} mole/liter (const)

$\mathrm{Co(acac)_2}$-DOX HPO initiating system is very fast and is affected by the three variables examined: namely, monomer, $\mathrm{Co(acac)_2}$, and DOX HPO concentrations. Therefore, the dependence of the polymerization rate upon $[\mathrm{M}]$, $[\mathrm{Co(acac)_2}]$, and [DOX HPO] were calculated. The dependence of rate upon $[\mathrm{M}]$ is unusual and differs from conventional radical polymerization initiating system such as benzoyl peroxide. The polymerization rate is proportional to $[\mathrm{M}]^{3/2}$, which suggests that monomer participates in the initiation process. The polymerization rates are proportional to $[\mathrm{Co(acac)_2}]^{1/7}$ and $[\mathrm{DOX\ HPO}]^{1/5}$, respectively. From the above, the polymerization rate can be expressed by

$$R_p = K[\mathrm{M}]^{3/2}[\mathrm{Co(acac)_2}]^{1/7}[\mathrm{DOX\ HPO}]^{1/5}$$

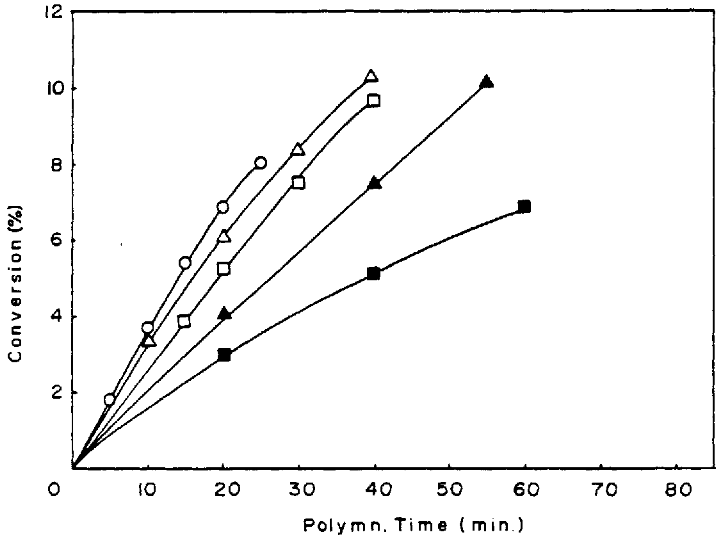

FIG. 1. Time vs conversion, initiation by Co(acac)$_2$-DOX HPO, dependence on monomer concentration. [Co(acac)$_2$]: 2.5×10^{-3} mole/liter; [DOX HPO]: 1.0×10^{-2} mole/liter; [monomer]: (○) 3.74, (△) 2.81, (□) 1.87, (▲) 0.94, (■) 0.47 mole/liter.

The relations between conversion and the degree of polymerization are shown in Figs. 4-6.

As shown in Figs. 4-6, the degree of polymerization increases with increasing conversion for each series. Furthermore, the degree of polymerization increases with increasing monomer concentration, and increases with decreasing Co(acac)$_2$ and DOX HPO concentrations.

B Co(acac)$_3$-DOX HPO Initiating System

The dependence of time-conversion curves on monomer, Co(acac)$_3$, and DOX HPO concentrations are shown in Figs. 7-9, respectively.

As shown in Figs. 7-9, the polymerization rate of the Co(acac)$_3$-DOX HPO initiating system is slower than that of the Co(acac)$_2$-DOX HPO initiating system. The dependencies of the polymerization rate on [M], [Co(acac)$_3$], and [DOX HPO] were calculated from

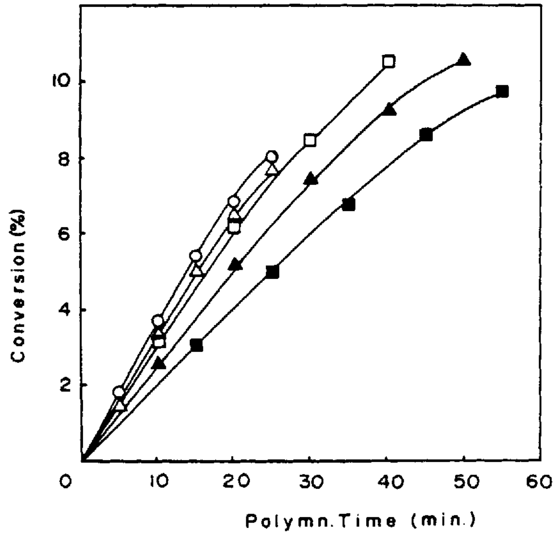

FIG. 2. Time vs conversion, initiation by $Co(acac)_2$-DOX HPO, dependence on $Co(acac)_2$ concentration. [Monomer]: 3.74 mole/liter; [DOX HPO]: 1.0×10^{-2} mole/liter; $[Co(acac)_2]$: (○) 2.5×10^{-3}, (△) 1.0×10^{-3}, (□) 5.0×10^{-4}, (▲) 2.0×10^{-4}, (■) 1.0×10^{-4} mole/liter.

Figs. 7-9. The results obtained differ from those of the $Co(acac)_2$-DOX HPO initiating system, i.e., the polymerization rate is directly proportional to the initial monomer concentration and is proportional to the one-third power of the $Co(acac)_3$ concentration. The rate is also proportional to the one-half power of the DOX HPO concentration. Therefore, the polymerization rate of the $Co(acac)_3$-DOX HPO initiating system can be expressed as

$$R_p = K[M][Co(acac)_3]^{1/3}[DOX\ HPO]^{1/2}$$

The kinetic results indicate that in the $Co(acac)_3$-DOX HPO initiating system, monomer does not participate for the initiation process and the dependencies of the polymerization rate on both $Co(acac)_3$ and DOX HPO are greater than those of the $Co(acac)_2$-DOX HPO initiating system.

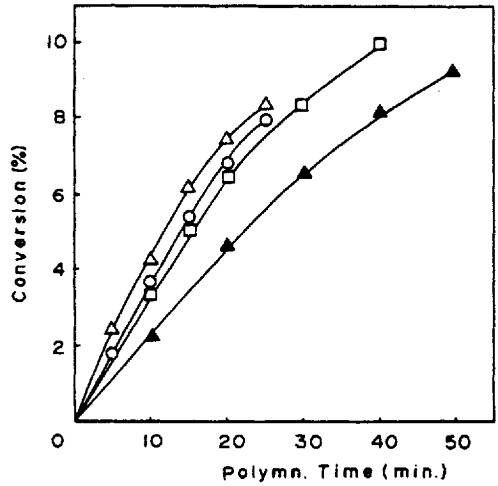

FIG. 3. Time vs conversion, initiation by $Co(acac)_2$-DOX HPO, dependence on DOX HPO concentration. [Monomer]: 3.74 moles/liter; $[Co(acac)_2]$: 2.5×10^{-3} mole/liter; [DOX HPO]: (△) 2.0×10^{-2}, (○) 1.0×10^{-2}, (□) 5.0×10^{-3}, (▲) 1.0×10^{-3} mole/liter.

The degree of polymerization vs conversion curves are shown in Figs. 10-12.

As shown in Figs. 10-12, the trends of the degree of polymerization of the $Co(acac)_3$-DOX HPO initiating system are extremely characteristic; i.e., no increase in the degree of polymerization with conversion which increases with time is observed. The degree of polymerization is almost controlled by the initial monomer, $Co(acac)_3$, and DOX HPO concentrations, and it increases with an increase in the initial monomer concentration, and decreases with an increase in the initial $Co(acac)_3$ and DOX HPO concentrations.

As mentioned above, remarkable differences in polymerization rate and the degree of polymerization were observed between $Co(acac)_2$-DOX HPO and $Co(acac)_3$-DOX HPO initiating system. In a previous paper [20] we discussed the polymerization mechanism on the basis of Co(II,III)-catalyzed decomposition of DOX HPO, and the apparent activation energies for the polymerization. Apparently the remarkable differences in polymerization rate between the $Co(acac)_2$-DOX HPO and $Co(acac)_3$-DOX HPO

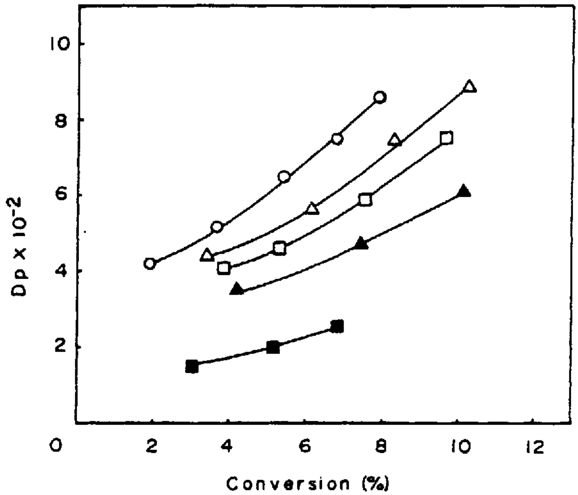

FIG. 4. Conversion vs degree of polymerization, initiation by $Co(acac)_2$-DOX HPO, dependence on monomer concentration. $[Co(acac)_2]$: 2.5×10^{-3} mole/liter; [DOX HPO]: 1.0×10^{-2} mole/liter; [monomer]: (○) 3.74, (△) 2.81, (□) 1.87, (▲) 0.94, (■) 0.47 mole/liter.

initiating systems are dependent upon differences in the decomposition rate of DOX HPO. That is, $Co(acac)_2$ is a much more effective catalyst for the decomposition of the hydroperoxide than is $Co(acac)_3$. Almost all dioxane hydroperoxide was decomposed and produced a large number of primary radicals at the initial stage of the polymerization. The primary radicals produced initiate the polymerization. Therefore, a relatively large number of growing polymer radicals were involved in the polymerization system, indicating that there is high probability of the termination reactions between polymer radicals and primary radicals, and between polymer radicals themselves. Furthermore, kinetic evidence indicates the presence of the interactions between monomer and initiators.

On the other hand, the decomposition of dioxane hydroperoxide in the $Co(acac)_3$ system was much slower than in the $Co(acac)_2$ system and occurred continuously during the polymerization. This means that the concentrations of primary radicals and

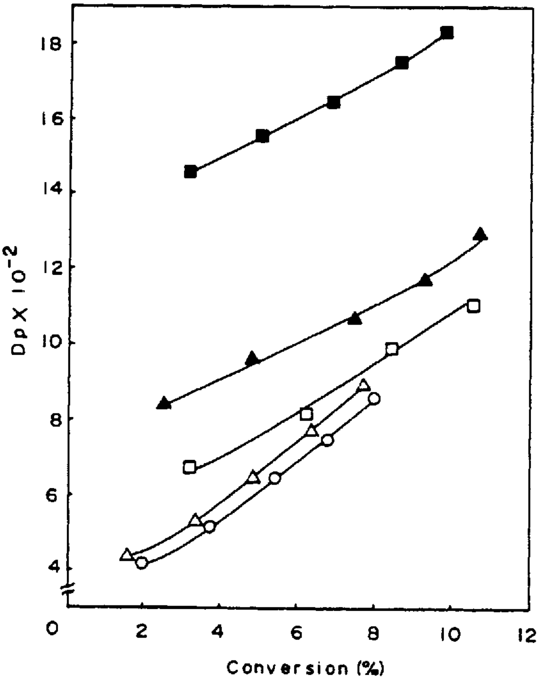

FIG. 5. Conversion vs degree of polymerization, initiation by $Co(acac)_2$-DOX HPO, dependence on $Co(acac)_2$ concentration. [Monomer]: 3.74 moles/liter; [DOX HPO]: 1.0×10^{-2} mole/liter; [$Co(acac)_2$]: (○) 2.5×10^{-3}, (△) 1.0×10^{-3}, (□) 5.0×10^{-4}, (▲) 2.0×10^{-4}, (■) 1.0×10^{-4} mole/liter.

growing polymer radicals are lower. Therefore, the termination reactions between primary radicals themselves, and between polymer radicals and primary radicals, are relatively less probable and are rather steady. The speculation mentioned for the catalytic decomposition of dioxane hydroperoxide seems to be rational when one takes into account the degree of polymerization. As shown in Figs. 4-6, the degree of polymerization in the $Co(acac)_2$-DOX HPO initiating system increases gradually with time, and is fairly low. On the other hand, in the case of the $Co(acac)_3$-DOX HPO initiating system the degree of

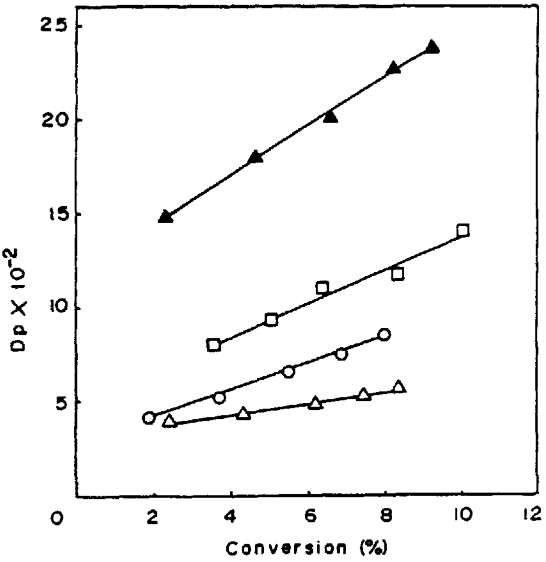

FIG. 6. Conversion vs degree of polymerization, initiation by $Co(acac)_2$-DOX HPO, dependence on DOX HPO concentration. [Monomer]: 3.74 moles/liter; [$Co(acac)_2$]: 2.5×10^{-3} mole/liter; [DOX HPO]: (△) 2.0×10^{-2}, (○) 1.0×10^{-2}, (□) 5.0×10^{-3}, (▲) 1.0×10^{-3} mole/liter.

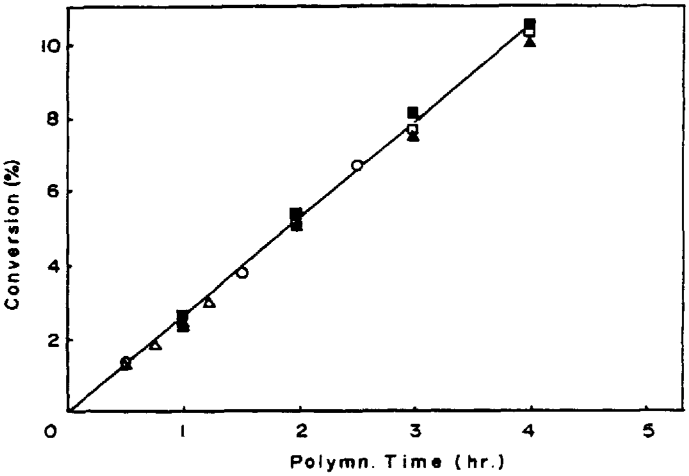

FIG. 7. Time vs conversion, initiation by $Co(acac)_3$-DOX HPO, dependence on monomer concentration. [$Co(acac)_3$]: 2.5×10^{-3} mole/liter; [DOX HPO]: 1.0×10^{-2} mole/liter; [monomer]: (△) 4.68, (○) 3.90, (□) 3.12, (▲) 2.34, (■) 1.56 moles/liter.

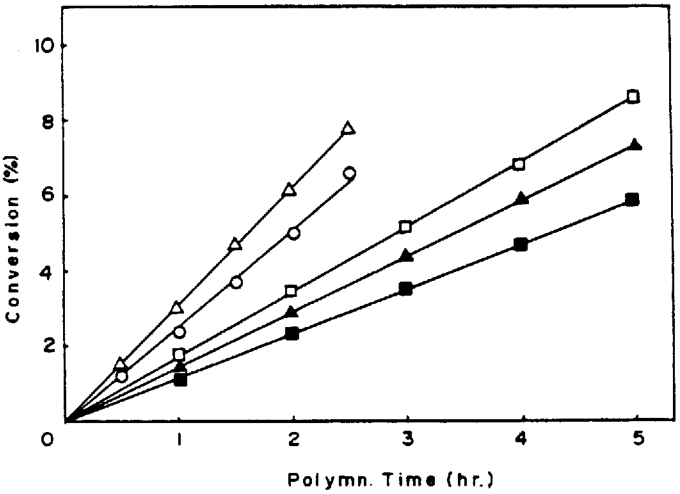

FIG. 8. Time vs conversion, initiation by $Co(acac)_3$-DOX HPO, dependence on $Co(acac)_3$ concentration. [Monomer]: 3.90 moles/liter; [DOX HPO]: 1.0×10^{-2} mole/liter; [$Co(acac)_3$]: (△) 5.0×10^{-3}, (○) 2.5×10^{-3}, (□) 1.0×10^{-3}, (▲) 5.0×10^{-4}, (■) 2.5×10^{-4} mole/liter.

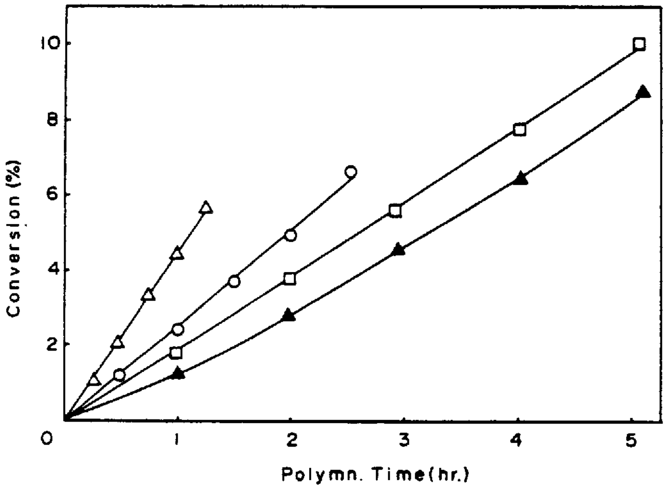

FIG. 9. Time vs conversion, initiation by $Co(acac)_3$-DOX HPO, dependence on DOX HPO concentration. [Monomer]: 3.90 moles/liter; [$Co(acac)_3$]: 2.5×10^{-3} mole/liter; [DOX HPO]: (△) 2.5×10^{-2}, (○) 1.0×10^{-2}, (□) 5.0×10^{-3}, (▲) 2.5×10^{-3} mole/liter.

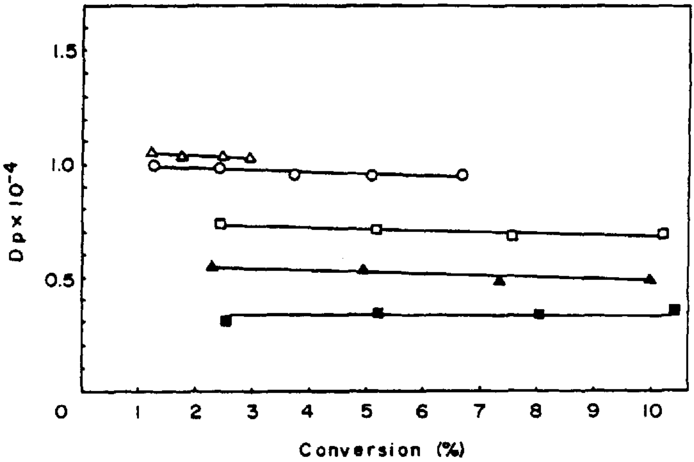

FIG. 10. Conversion vs degree of polymerization, initiation by Co(acac)$_3$-DOX HPO, dependence on monomer concentration. [Co(acac)$_3$]: 2.5×10^{-3} mole/liter; [DOX HPO]: 1.0×10^{-2} mole/liter; [monomer]: (△) 4.68, (○) 3.90, (□) 3.12, (▲) 2.34, (■) 1.56 moles/liter.

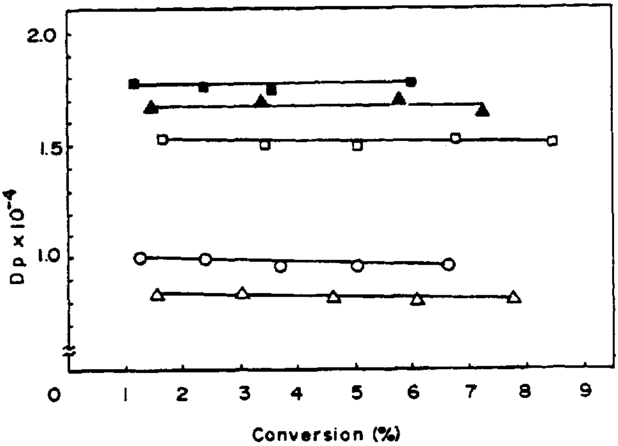

FIG. 11. Conversion vs degree of polymerization, initiation by Co(acac)$_3$-DOX HPO, dependence on Co(acac)$_3$ concentration. [Monomer]: 3.90 moles/liter; [DOX HPO]: 1.0×10^{-2} mole/liter; [Co(acac)$_3$]: (△) 5.0×10^{-3}, (○) 2.5×10^{-3}, (□) 1.0×10^{-3}, (▲) 5.0×10^{-4}, (■) 2.5×10^{-4} mole/liter.

polymerization is much higher than that of the Co(acac)$_2$-DOX HPO initiating system and does not increase with conversion, which increase with time (See Figs. 10-12).

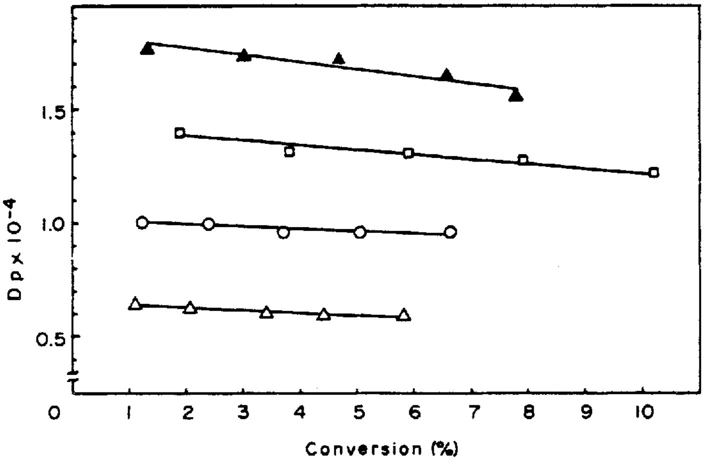

FIG. 12. Conversion vs degree of polymerization, initiation by Co(acac)$_3$-DOX HPO, dependence on DOX HPO concentration. [Monomer]: 3.90 moles/liter; [Co(acac)$_3$]: 2.5 × 10^{-3} mole/liter; [DOX HPO]: (△) 2.5 × 10^{-2}, (○) 1.0 × 10^{-2}, (□) 5.0 × 10^{-3}, (▲) 2.5 × 10^{-3} mole/liter.

In the metallic salts-catalyzed thermal oxidative degradation of polymer and the decomposition of hydroperoxide, the kind of metal plays an extremely important role [24]. In this paper we demonstrated the differences of cobaltous and cobaltic acetylacetonate in the polymerization of methyl methacrylate by a metal-peroxide binary initiating system. The results obtained by a number of metal acetylacetonates-cyclic ether hydroperoxides initiating systems will be published in the near future.

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Accepted by editor March 17, 1972
Received for publication June 22, 1972