LETTER TO THE EDITORS

*Synthetic Linear Polymers. VIII. Metal Resinates in the Bulk Polymerization of Methyl Methacrylate Accelerated by Metal Redox Systems**

The polymerization of vinyl compounds is considerably accelerated by peroxides, especially in the presence of reducing agents. The latter may be the ion of a multivalent metal or some other reducing agent, e.g., a tertiary amine,[1] aliphatic or aromatic sulfinic acids[2,3] or α-oxy- or α-aminosulfones.[4]

Experiments have shown that not all reducing agents are able to form an effective redox system with a given peroxide for polymerization, e.g., the benzoyl peroxide–benzoin system is by itself ineffective for the polymerization of vinyl monomers. If suitable metal compounds are added to the system, a very effective, so-called metal–redox system can be obtained. The metals are effective not only in ionized form, but also as the metalloorganic compound soluble in the monomer.

The efficiency of the metal–redox systems is greatly influenced by the composition of the metal compound. For example, Kern[5] observed different efficiencies, depending on the anion related to the metal, for metal–redox systems initiating the bulk polymerization of styrene. He employed the metals as stearate, oleate, hexahydrobenzoate, naphthenate, water-free chloride, ethylate, and acetonylacetonate. Danilov and co-workers[6] studied the redox bulk polymerization of styrene in the presence of benzoyl peroxide, Fe naphthenate, and α-oxyketones. In this system benzoin proved to be the most active of the ketone alcohols.

Strubell[7] studied the metal–redox bulk polymerization of methyl methacrylate and found the propionylacetonates of various metals (Fe, Cu, Pb, Co, Ni, Mn, Hg) to be effective in the benzoyl peroxide–benzoin system.

In the course of our experiments the application of metal resinates was examined in the metal–redox bulk polymerization of methyl methacrylate and styrene. The initiators used were: benzoyl peroxide, di-*tert*-butyl peroxide, cyclohexyl hydroperoxide, and *tert*-butyl hydroperoxide; the activator was benzoin, and the metal components were Fe, Pb, Mn, Cu, and Co resinates.

It was established that the metal resinates were effective for the metal–redox bulk polymerization of methyl methacrylate and styrene.

The accelerating effect on the polymerization of such three-component redox systems depends on many factors (e.g., the type, the molar ratio of components, the employed concentrations) which gives the possibility of a wide range of changing experimental conditions. The comparison of different systems with one another is very difficult, and also the exact investigation of the effect of all factors requires much experimental work because of the great number of experimental possibilities (at a given temperature, the measurement of conversion with time, gelation time, viscosity change with time, etc.) Our experiments therefore, were confined to investigating the effect of some essential features.

* For the preceding paper in this series, "Synthetic Linear Polymers, VII," see *Periodica Polytechnica* [Chem. Ser.] **3,** 37 (1959).

1. Comparison of the Efficiency of Different Peroxides

Using different peroxides and benzoin in equimolar quantities we determined the conversions at different times in the presence of Fe and Pb resinates (Tables I and II).

TABLE I
Comparison of Efficiency of Various Peroxides in Equimolar Peroxide–Benzoin System (4.2×10^{-2} mole/l.) in the Presence of 0.4% Fe Resinate (Metal Content of Resinate 4.1%) at 40°C.

	Conversion, % at various times			
Peroxide[a]	10 min.	20 min.	30 min.	40 min.
t-BHP	17.0	18.3	21.2	35.4
p-CHP	16.4	17.0	19.6	21.2
BP	7.7	12.0	15.0	17.3
CHHP	5.4	5.4	8.7	14.5
AP	4.5	5.4	5.4	5.5

[a] Peroxide studied: *t*-BHP = *tert*-butyl hydroperoxide; *p*-CHP = *p*-cumene hydroperoxide; BP = benzoyl peroxide; CHHP = cyclohexyl hydroperoxide; AP = acetone peroxide.

TABLE II
Comparison of Efficiency of Various Peroxides in Equimolar Peroxide–Benzoin System (4.2×10^{-2} mole/l.) in the Presence of 0.7% Pb Resinate (Metal Content of Resinate, 4.2%) at 40°C.

	Conversion, %, at various times			
Peroxide	10 min.	20 min.	30 min.	40 min.
t-BHP	9.6	11.4	14.0	22.0
BP	5.8	6.7	8.0	9.6
CHHP	3.9	4.1	7.5	8.2
p-CHP	4.7	5.8	6.9	7.5
AP	2.7	2.9	3.1	3.1

The applied concentrations of Fe resinate (0.4%) and Pb resinate (0.7%) correspond to the equivalent quantities of metal in gram-atoms. The role of this latter will be mentioned later. On the basis of these experiments it can be established that the efficiency of initiation varies with the metal employed.

In the case of Fe resinate the order of the efficiency of peroxides is:

$$t\text{-BHP} > p\text{-CHP} > \text{BP} > \text{CHHP} > \text{AP}$$

In the case of Pb resinate this order is:

$$t\text{-BHP} > \text{BP} > \text{CHHP} > p\text{-CHP} > \text{AP}$$

The experimental data show that the above-mentioned order may also change at different stages of the reaction, which shows the different characters of the kinetic course of polymerization. The appearance of a gel indicates a defined extent of the polymerization, so that a comparison may be based upon the determination of gelation times. For simplicity in the following part of our experiments the method of Matsui[8] was used to determine gelation times, though the exactness of this method is limited.

2. Comparison of the Efficiency of Metal Resinates

a. Comparison on the Basis of Equal Concentration of Resinates

A comparison of the efficiency of the Cu and Fe resinates in the presence of CHHP and benzoin (BN) is shown in Table III.

TABLE III
Comparison of CHHP–BN–Cu Resinate and CHHP–BN–Pb resinate Systems for Polymerization of Methyl Methacrylate at 15°C.

Resinate[a]	Molar ratio CHHP: BN	Resinate, wt.-%	Concn. metal, gram-atom/ 2.5 ml. monomer	Gelation time, hr.
Pb	2.55:1	0.40	10.5×10^{-6}	48
		0.48		51
		0.56		57
Cu	2.55:1	0.40	5.71×10^{-6}	28
		0.48		28
		0.56		30

[a] Metal contents of the resinates: Cu, 5.19%; Pb, 19.5%.

Comparing the gelation times for the same amount of metal resinates (in weight-per cents) shows that the Cu has almost double the efficiency of Pb. Considering that the Pb resinate used contained about twice the quantity of metal (in gram-atoms), the difference in the efficiencies of the two metals is even greater.

As the metal resinates contained the metals in different quantities, it seemed more favorable to compare them in systems containing the same amount of metal (in gram-atoms).

b. Determination of the Efficiency in Systems of Equal Metal Concentration (in Gram Atoms)

A comparison of the efficiency of Fe, Pb, Co, Mn, and Cu resinates in the BP–BN systems is shown in Table IV.

TABLE IV
Order of Efficiency on the Basis of Similar Gram-Atom Metal Content for Polymerization at 22°C. for 1 Hr. Methyl Methacrylate in the Presence of the Equimolar Benzoyl Peroxide–Benzoin System (4.2×10^{-2} mole/l.)[a]

Metal resinate	Metal content of resinate, %	Concentration of metal resinate, wt. %	Conversion, %
Fe	4.1	0.80	5.2
Pb	4.2	2.89	4.7
Co	11.6	1.15	2.2
Mn	14.0	3.08	1.8
Cu	10.8	1.86	None

[a] Metal resinate content: 1.39×10^{-5} g.-atom metal/2.5 ml. monomer.

The metal resinates employed contained in every case 1.39×10^{-5} g.-atom metal 2.5 ml. monomer. The comparison was made on the basis of the extent of conversion after 1 hr. at 22°C. The order of the efficiency was:

$$\text{Fe} > \text{Pb} > \text{Co} > \text{Mn}$$

Comparison of Tables III and IV shows that in the presence of CHHP–BN Cu is more effective, while in the presence of BP–BN the Cu is ineffective under the given experimental conditions. In this latter case, however, Pb shows relatively considerable accelerating effect.

c. Determination of the Efficiency with Optimum Concentrations of the Resinates

In the case of a given metal resinate the conversion and the gelation time depend also on the concentration of the

TABLE V
Optimum Concentrations of Metal Resinates for Polymerization of Methyl Methacrylate at 40°C. for 1 Hr. in the Presence of the Equimolar Benzoyl Peroxide–Benzoin System (4.2×10^{-2} mole/l.)

Metal resinate	Metal contents of resinates, %	Conversion, %, at various metal resinate concentrations									
		0.3 wt.-%	0.5 wt.-%	0.6 wt. %	0.9 wt.-%	1.0 wt.-%	1.5 wt.-%	2.0 wt.-%	4.0 wt.-%	4.5 wt.-%	5.0 wt.-%
Fe	4.1	14.7	17.1	15.4	15.1	—	16.1	22.8	—	—	—
Pb	4.2	6.3	11.0	9.1	—	11.5	13.6	16.4	—	—	—
Mn	14.0	—	1.9	8.4	10.5	—	9.9	—	8.2	—	—
Co	11.6	—	0.5	0.1	0.4	3.3	—	4.0	—	—	—
Cu	10.82	—	—	—	—	—	—	—	0.3	1.1	2.3

metal resinate. Plots of the conversion and the gelation time against the concentration of metal resinate show considerable differences for different metals. Such curves generally have a maximum, but instances can be found also in which the efficiency can be considered independent of the concentration of metal resinate. Applying the optimum concentration of each system containing the metal-resinate, the comparison of the conversions obtained with these systems gives an efficiency order independent of the concentrations of the resinates.

In the presence of BP–BN under the conditions given in Table V, this order has been found to be:

$$Fe > Pb > Mn > Co > Cu$$

The mole ratio of the peroxide and benzoin is also an important factor in deciding the efficiency of the metal–redox system. It was found that in many cases the optimum mole ratio was 1:1, but sometimes at a different mole ratio, another maximum could be obtained.

The bulk polymerization was studied in such cases also when a small quantity (several per cent) of polymer (polymethyl methacrylate) was previously added to the monomer, but no considerable accelerating effect on the polymerization was observed (c.f. Melville and Watson[9]).

In a similar manner we also investigated the redox systems containing metal resinates in the bulk polymerization of styrene. They were found to be effective in this case too.

In our experiments the bulk polymerization was carried out as before.[10]

The conversion was determined both by precipitation and partly by refractive index measurements.

The peroxides used were purified by recrystallization. The monomers were freshly distilled before using. The metal-resinates were made according to Hadert.[11]

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Received June 27, 1960