

Heterogeneous Mixture of Metals and Organic Halides as Initiator for Vinyl Polymerization

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Vinyl monomers were polymerized by action of the heterogeneous mixtures of metals and organic chlorides. Zinc was the most efficient of all the metals investigated, and aralkyl chlorides were found to be superior components to alkyl ones. Addition of hydroquinone did not affect the polymerization. The possibility was suggested that some Grignard-type compounds form in the reaction mixture to induce the anionic polymerizations of vinyl monomers.

INTRODUCTION

It has been reported by one of the present writers and the co-workers¹⁾ that vinyl monomers enter into polymerization by catalytic action of a heterogeneous mixture of benzyl chloride and copper; the degree of polymerization gradually increases with the elapsing time of polymerization.

In the present paper, further observations on the initiating actions of various metal-organic chloride systems are described, together with some remarks about the selective affinity of vinyl monomers toward metals in the course of polymerization. Organic halides can not initiate vinyl polymerization until, for example, certain specific amines are used in conjunction with them²⁾.

When metals are used in admixture with organic chlorides, some Grignard-type substances possibly form to induce the polymerization of vinyl compounds. The ease of the reaction between metal and the chloride as well as the solubility of the reaction product, may be important factors controlling the polymerization reactions.

EXPERIMENTAL

1. Materials

All the vinyl monomers used were purified by appropriate methods and were further distilled under reduced or ordinary pressure immediately before use.

Some of the organic chlorides used were prepared according to the standard methods given in the literature (see Table 3) and others were the commercial substances, the purest available. These chlorides were dried over anhydrous calcium chloride and distilled before use.

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Metals were successively washed with dilute nitric acid and water and then were dried *in vacuo* to constant weights.

2. Polymerization

A 25-ml. test tube was charged with 2.50 ml. of a monomer, 0.005 to 0.02 g.-atom of metal and 0.01 to 0.02 mole of organic chloride. The tube was flushed with oxygen-free, dry nitrogen for 5 minutes and sealed. After all the tubes in any given batch of experiments had been sealed, they were maintained at $60 \pm 0.1^\circ\text{C}$. by immersion in a thermostat. At the end of the definite polymerization times, the tubes were opened and the formed polymers were precipitated with methanol. For polyvinyl acetate, *n*-hexane was used as precipitant. The crude polymers were made free from metal by redissolving in a large amount of chloroform, followed by filtration and reprecipitation. The metal-free polymers were gently warmed in water so as to remove unreacted monomer or occluded solvent by steam distillation, and then they were dried to constant weights in a vacuum oven at 55°C .

The polymerization degrees, P , of polymethyl methacrylate and polystyrene were viscometrically determined with the aid of the following equations:

Polymethyl methacrylate (in chloroform at 20°C)³¹

$$[\eta] = 3(\eta_{rel}^{1/3} - 1)C$$

$$P = ([\eta] - 0.0095) / 0.47 \times 10^{-4}$$

Polystyrene (in benzene at 20°C)⁴¹

$$[\eta] = 3(\eta_{rel}^{1/3} - 1)C$$

$$P = [\eta] / 1.8 \times 10^{-4}$$

where η_{rel} refers to the relative viscosity of the polymer solution, a concentration of which is C (g./l.).

RESULTS

1. Polymerization of Methyl Methacrylate

The data on the polymerization of methyl methacrylate initiated by several metals in admixture with *t*-butyl chloride are given in Table 1. Zinc was found more useful there than any other metal. The degree of polymerization remained nearly constant for each run. However, when magnesium was used, it increased gradually with the elapsing time; after 30 hours it amounted to 13,600. When Se, Pb, Cu, Ti, Bi, or Cr was used as a component of the mixture catalyst, no polymer was obtained under the essentially identical conditions as in Table 1.

As it is seen in Table 1, addition of hydroquinone did not affect the polymerization. This fact suggests the possibility that the propagation process is an ionic reaction.

Table 2 shows the data on the methyl methacrylate polymerization induced by varying amounts of zinc and *t*-butyl chloride. When a varying amount of zinc was used in admixture with a constant amount (1.00 mmole) of *t*-butyl chloride, the polymerization yield after 17 hrs. increased with an increasing

Table 1. Polymerization^a of methyl methacrylate by various metals and *t*-butyl chloride.

Metal	Time, hrs.	Yield, %	<i>P</i>
Mg	5	0.1	—
	20	8.5	6,000
	30	36.4	13,000
	45	97.6	14,240
Fe	15	2.1	2,500
	20	4.9	2,300
	30	21.7	2,000
	30 ^b	18.6	2,200
	45	38.3	2,000
Zn	5	10.5	—
	15	16.8	—
	20	19.2	2,200
	20 ^b	21.1	1,900
	30	24.9	1,700
	45	32.4	2,100
Al	20	5.4	4,700
	30	5.9	5,200
	45	6.5	5,700
Sb	10	6.9	4,600
	30	13.1	5,600
	45	14.0	4,800

^a Monomer, 2.50 ml. (23.7 mmoles); *t*-butyl chloride, 10.0 mmoles; metal, 10.0mg.-atom; temperature, 60±0.1°C.

^b Fifty milligrams (0.45 mmoles) of hydroquinone was added.

Table 2. Dependence of the methyl methacrylate polymerization upon the amounts of catalyst components^a.

<i>t</i> -BuCl, mmoles	Zn, mg-atom	Time, hrs.	Yield, %	<i>P</i>
1.00	0	17	0	—
1.00	1.00	17	6.2	4,200
1.00	2.00	17	12.1	2,600
1.00	5.00	17	11.0	3,260
1.00	10.0	17	11.2	2,710
1.00	1.00	20	21.7	9,180
2.00	2.00	20	33.8	9,400
5.00	5.00	20	24.3	—
10.0	10.0	20	19.2	—

^a Monomer, 2.50 ml. (23.7 mmoles); temperature, 60±0.1°C.

amount of zinc up to 2.00 mg.-atom and, beyond this limiting amount, it remained almost constant. The situation might have arisen from a limiting solubility of some active species which formed through the reaction between zinc and *t*-butyl chloride to initiate the ionic polymerization. When more than 2 mmoles of *t*-butyl chloride was used for the polymerization of 23.7 mmoles of

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 Table 3. Polymerization^a of methyl methacrylate by various organic chlorides in admixture with metallic zinc or iron.

Organic chloride	Zn		Fe		Reference for Synthesis
	Yield, %	<i>P</i>	Yield, %	<i>P</i>	
<i>t</i> -Butyl chloride	33.8	9,400	11.5	1,670	5
α -Chloromethylnaphthalene	16.1	830	24.1	2,100	6
Chloromethylether	17.2	1,070	5.6	9,600	7
<i>p</i> -Methylbenzyl chloride	4.9	3,150	10.0	7,100	8
Benzyl chloride	0	—	4.1	7,600	—
<i>i</i> -Propyl chloride	3.9	18,300	—	—	9
<i>n</i> -Propyl chloride	3.3	16,200	3.9	14,240	9
Chloroform	3.7	15,790	4.3	16,250	—
Carbon tetrachloride	4.3	11,190	—	—	—
None	1.2	4,600	1.6	4,200	—
<i>t</i> -Butyl chloride only ^b	0	—	0	—	—

^a Monomer, 2.50 ml. (23.7 mmoles); chloride, 2.00 mmoles; metal, 2.00 mg.-atom; time, 20 hrs.; temperature, 60±0.1°C.

^b In the absence of metal.

methyl methacrylate, the polymerization yield even decreased, which might be due to the decrease in the concentration of the monomer in the reaction mixture.

Table 3 summarizes the comparison data on methyl methacrylate polymerization initiated by different organic chlorides in admixture with metallic zinc or iron. Inspection of the data in Table 3, shows a crude generality that *t*-butyl chloride, α -chloromethylnaphthalene, chloromethylether and *p*-methylbenzyl chloride are superior catalyst components to the remaining chlorides, *i.e.*, that the polar nature of chlorides seems to favor the initiation. However, the order of polymerization degrees of the resulting polymers were roughly reversed with respect to that of the polymerization rates. This was also found to be the case with the polymerization of styrene. At least for the methyl methacrylate polymerization with zinc as the metallic component of the binary catalyst, *t*-butyl chloride seems to be the most efficient chloride component both in the rate of polymerization and in the polymerization degree of the resulting polymer.

2. Polymerization of Styrene

The data on polymerization of styrene initiated by the mixtures of metals and *t*-butyl chloride are collected in Table 4, where it is seen that, when Fe, or Ti was used in admixture with *t*-butyl chloride, the polymerization reaction proceeds at a noticeable rate to give polystyrene of the low molecular weight. Likewise, Cu, Sn, Bi and Cr also gave the low polymers of styrene. A mixture of zinc and *t*-butyl chloride gave a viscous liquid which might be the polymer of much lower molecular weight. When Mg or Se was used under similar conditions, the polymerization yield was in essential agreement with that of the controlled sample listed in the bottom of Table 4.

Table 4. Polymerization^a of styrene by various metals in admixture with *t*-butyl chloride.

Metal	Time, hrs.	Yield, %	<i>P</i>
Zn	10	Liquid substance	
Fe	1	8.7	16
	5	87.8	18
	10	92.3	18
	20	100.0	18
Ti	1	8.0	14
	6	70.5	18
	10	81.4	21
	20	100.3	14
Cu	10	21.8	31
	20	61.9	21
	30	80.5	24
Sn	10	11.7	26
	20	28.3	21
	30	37.3	18
Bi	30	44.3	14
Cr	30	25.1	60
Sb	30	5.7	110
Pb	30	1.8	970
Al	30	1.7	880
Mg	30	0.5	1,210
Se	30	0.2	1,300
None	30	0.3	1,240

^a Monomer, 2.50 ml. (23.7 mmoles) ; *t*-butyl chloride, 10.0 mmoles ; metal, 10.0 mg.-atom ; temperature, 60±0.1°C.

In Table 4 the polymerization data of styrene by different organic chlorides in admixture with metallic iron are compared. The chlorides investigated may be divided into two groups—the one, *i.e.*, a group comprising α -chloromethyl-

 Table 5. Polymerization^a of styrene by various organic chlorides in admixture with metallic iron.

Organic chloride	Time, hrs.	Yield, %	<i>P</i>
α -Chloromethylnaphthalene	5	100	16
<i>t</i> -Butyl chloride	5	95.2	24
<i>p</i> -Methylbenzyl	5	84.2	17
Chloromethylether	20	13.1	1,040
Benzyl chloride	20	4.6	1,230
<i>i</i> -Propyl chloride	20	4.5	1,620
Chloroform	20	3.3	1,720
<i>n</i> -Propyl chloride	20	2.2	1,850
None	20	2.2	1,100
<i>t</i> -Butyl chloride only ^b	30	0.3	1,240

^a Monomer, 2.50 ml. (23.7 mmoles) ; chloride, 2.00 mmoles ; metal, 2.00 mg.-atom ; temperature, 60±0.1°C.

^b In the absence of metal.

naphthalene, *t*-butyl chloride and *p*-methylbenzyl chloride caused rapid polymerizations of styrene to give the low molecular weight polymers and the other allowed the same monomer to enter into rather tedious polymerization giving high polymers instead. Comparison of the data in Table 5 with the results given in Table 3 shows that the order of efficiency of different chlorides for styrene polymerization roughly agrees with that for the polymerization of methyl methacrylate. The selective affinity of monomers toward the catalyst mixture seems to lie in the monomer—metal relation rather than in the monomer—halide relation.

3. Polymerizations of the Other Monomers

The catalytic actions of the binary mixtures consisting of various metals and chlorides were also studied with respect to methyl acrylate, acrylonitrile and vinyl acetate.

Methyl acrylate polymerized only when zinc was used as an admixture with *t*-butyl chloride. Polymerization of 10 ml. of this monomer at 60°C with a mixture catalyst of 1.00 mmole of *t*-butyl chloride and 5.00 mg.-atom of zinc gave well-defined polymers at the yields of 16.6%, 21.8%, 20.0% and 29.2% after the reaction times of 5, 10, 22 and 30 hours, respectively.

For acrylonitrile, zinc was the only effective metal. The most efficacious catalyst system was the one consisting of zinc and α -chloromethylnaphthalene. With 5.00 mmoles of α -chloromethylnaphthalene and 5.00 mg atom of zinc as a binary catalyst, 10 ml. of acrylonitrile was polymerized at 60°C for 20 hours to give 7.3% yield of the polymer yellow in color, the polymerization degree being 2100.

Vinyl acetate could also be polymerized by action of zinc used in admixture with *t*-butyl chloride or with any of aralkyl chlorides. Several hours after the beginning of the polymerization, the reaction mixtures colored in dark brown. A similar color of the collected polymer did not disappear by repeated reprecipitation using methanol as solvent and *n*-hexane as precipitant.

DISCUSSION

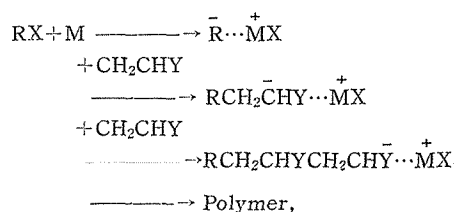
Beaman¹⁰ has undertaken an investigation of the low temperature polymerization of acrylic monomers by action of Grignard reagents and described that the reaction proceeded with too vigorous exothermicity to be controlled. An anionic chain mechanism has also been suggested for the propagation step.

With the present binary mixtures of metallic magnesium and organic chlorides as catalyst, the polymerization of methyl methacrylate proceed at a moderate rate giving a high polymeric substance. This might be due to the slow formation of the Grignard reagent or, in other words, from the low concentration of the reagent in the course of polymerization reaction. Also in the cases where the remaining metals are employed in admixture with the chlorides, some Grignard-type compounds possibly form in the reaction mixtures with more or less easiness, inducing the polymerizations of vinyl compounds. It is

thus to be understood that the polar chlorides favored the polymerization. The ease of the reaction between metal and the chloride might, therefore, be considered as an important factor to control the polymerization reactions.

Another controlling factor for the polymerization will be the solubility of the Grignard-type compounds in monomer-chloride mixtures. As already mentioned, the rate of the methyl methacrylate polymerization increased with an increasing amount of zinc up to a certain limiting quantity, but, beyond this limit, it remained almost constant. This constant rate will be due to the saturation of *t*-butylzinc chloride in the reaction mixture.

Polymerization catalyzed by the binary mixtures of metals (M) and organic halides (RX) may be considered to proceed according to the following scheme :



where the chain may propagate through the stepwise addition of monomer molecule toward the polar reaction site of the growing polymer molecule. The different efficiencies of metals for the polymerizations may partly be ascribed to the selective affinities of monomers toward the metallic cations constituting the reaction centers of the active polymer molecules.

REFERENCES

- (1) J. Furukawa, K. Sasaki and E. Murakami, *Polymer Chem. Japan*, **11**, 71 (1954).
- (2) T. Fueno, T. Tsuruta and J. Furukawa, *J. Polymer Sci.*, **15**, 594 (1955).
- (3) I. Sakurada, *Polymer Chem. Japan*, **2**, 253 (1945).
- (4) I. Sakurada, *ibid.*, **2**, 260 (1945).
- (5) H. Gilman, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, 1948, p. 144.
- (6) R. C. Fuson and C. H. McKeever, "Organic Reactions," Vol. 1, John Wiley and Sons, Inc., New York, 1947, p. 70.
- (7) Reference 5, p. 377.
- (8) G. Blanc, *Bull. soc. Chim. France*, **33**, 313 (1923).
- (9) J. Norris and H. B. Taylor, *J. Am. Chem. Soc.*, **46**, 753 (1924).
- (10) R. G. Beaman, *ibid.*, **70**, 3115 (1948).