The New Method of Polymerization of Vinyl Compounds. I.[1] On the Polymerization of Methyl Methacrylate with Copper or Cuprous Chloride and Acids at Room Temperature

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(Received June 16, 1952)

Introduction

We have discovered some new methods of polymerization of vinyl compounds, which are entirely different from the previous methods catalyzed by peroxides. Our methods are peculiar because they are able to perform polymerization very rapidly in good yield at room temperature. In this report we have treated the polymerization of methyl methacrylate with copper or cuprous chloride and acids. Copper has hitherto been considered in contradiction to our experimental results, as an anticatalyst in polymerization. For example, it has been applied as an inhibitor in the case of synthesis of methacrylate.

Experimental

In the following experiments we have applied methacrylic methyl ester as a vinyl monomer. We have, however, used aqueous solution of the ester in order to simplify experiments. As the solubility of this ester is only about 1% at room temperature, the polymerization in a considerably dilute solution is to be discussed in this report.

As an orientation, the accelerating power of the combination of the powder of metallic copper and various acids for polymerization are shown in Table 1.

The rate of polymerization, after about 1 weight % of the powder of metallic copper is thrown into the aqueous solution which contains 1% of methyl methacrylate and acid respectively is shown in the above Table. The reaction vessel was agitated vigorously at first and then allowed to stand. Generally speaking, the lower the molecular weight of organic acid is, the stronger the accelerating power for polymerization becomes, and in this case inorganic acids are not so useful. But as it will be shown later, this tendency as for the accelerating power is of course different when other kinds of metal or its lower valencial salts are used. What is important is that the polymerization is accelerated by the preceding system.

The course of the polymerization with the powder of metallic copper and formic acid is shown in Fig. 1.

(1) This paper was read in the annual meeting of the Chemical Society of Japan in April, 1952.

Table 1

The Accelerating Power of the System of the Powder of Metallic Copper and Various Acids for the Polymerization of the Methyl Methacrylate (at Room Temperature)

Formic acid	##	Lactic acid	+
Acetic acid	##	Benzoic acid	+
Propionic acid	#	Sulfuric acid	#
Butyric acid	+	Hydrochloric acid	#
Isovalerianic acid	+	Phosphoric acid	#
Oxalic acid	##		

where

means that the white precipitate (polymer) is produced within five minutes after the powder of metallic copper is thrown into the solution.

means that the white precipitate (polymer) is produced within thirty minutes after the powder of metallic copper is thrown into the solution.

\+ means that the white precipitate (polymer) is produced within several hours after the powder of metallic copper is thrown into the solution.

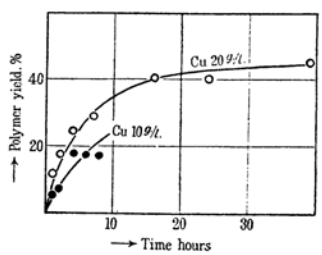

Fig. 1.

In the figure we have shown two examples with a different ammount of copper powder, i. e. 20 g./l. and 10 g./l. The solution contained 0.096 mol./l. methyl methacrylate and 0.115 mol./l. formic acid. Though an ammount of the copper powder has influence on the velocity of the polymerization, it is not easy to find any quantitative relations. It is worth notice that though the powder of metallic copper precipitates to the bottom of the vessel as a result of quiscence throughout the polymerization, separation of

polymers can be observed all over the solution (system) and that the induction period is not to be observed.

If we apply Cu_2Cl_2 instead of metallic copper, more rapid and more uniform polymerization will happen, as Cu_2Cl_2 is somewhat soluble in water. We have shown the influence of the amount of Cu_2Cl_2 and the concentration of formic acid on polymerization in Tables 2 and 3. In these experiments we have stirred the solution slowly.

Table 2

The temperature of polymerization: 40°C.
Methyl methacrylate :0.096 mol./l.
Formic acid :0.201 mol./l.

Time of polymerization (hours)	Amount of Cu_2Cl_2 (g./l.) 15 Yield (%)	$\bar{P}$	10 Yield (%)	$\bar{P}$	5 Yield (%)	$\bar{P}$
0.5	19.2	170	27.5	140	35.6	100
1.0	39.6	—	39.9	—	29.0	—
1.5	43.1	—	52.3	—	50.9	—
2.0	50.5	160	(36.7)	150	56.7	140
3.0	51.3	—	60.4	—	60.2	—
4.0	59.0	—	62.9	—	61.1	—
5.0	60.6	—	60.2	—	61.7	—
6.0	60.9	—	62.5	—		
7.0	62.7	—			64.0	—
8.0	60.9	140	55.5	140	62.9	130
24.0	62.7	140	(85.4)	130	69.6	120

Table 3

The temperature of polymerization: 40°C.
Methyl methacrylate :0.096 mol./l.
Formic acid :0.392 mol./l.

Time of polymerization (hours)	Amount of Cu_2Cl_2 (g./l.) 5 Yield (%)	$\bar{P}$	1 Yield (%)	$\bar{P}$	0.5 Yield (%)	$\bar{P}$
0.5	21.3	120	19.2	180	27.1	350
1.0	36.5	—	35.0	—	37.9	—
1.5	43.4	—	42.5	—	47.9	—
2.0	49.2	140	51.6	260	45.4	360
3.0	53.1	—	51.0	—	45.0	—
4.0	56.5	—	51.0	—		
5.0	58.8	—	50.8	—	44.7	—
6.0	58.8	—	49.8	—	44.0	—
7.0	62.3	—	49.1	—	44.6	370
8.0	54.8	140	49.0	240		
24.0	61.0	130	51.6	250	46.9	370

Though the concentration of the formic acid does not suffer a change such as can be detected by ordinary titration, the reaction mixture becomes green with the lapse of time. The polymerization stops in about two hours presumably in consequence of the exhaustion of Cu_2Cl_2; it proceeds again as shown in Fig. 2 when Cu_2Cl_2 is added anew (arrow in the Fig.).

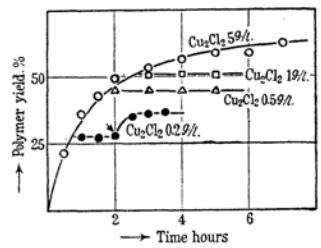

Fig. 2.

Discussion

In the reaction of the above experiments, free radical of hydrogen is produced, which can initiate the chain polymerization.

$$Cu + RCOOH \rightarrow Cu^+ + RCOO^- + H\cdot$$
$$Cu^+ + RCOOH \rightarrow Cu^{++} + RCOO^- + H\cdot$$

As H· is very unstable or reactive in comparison with benzoate radical, if the concentration of H· is somewhat high, the initiation and stabilization reaction happen at once and in an extreme case merely hydrogenation may be observed. The conditions of the above experiments allow a primary free radical to have enough time to repeat chain propagation about two hundred times before it stabilizes as the result of collision with another free radical. In other words the concentration of H· is very low in comparison with an ordinary polymerization, the catalyst of which is benzoyl peroxide. It is known that Cu or Cu_2Cl_2 is stable to acids (for example CH_3COOH and HCOOH). Therefore we may find more general combinations of acids and metals or their lower valencial salts. These kinds of metals or salts have hitherto been generally known as anti-catalysts of polymerization. The polymerization of methyl methacrylate by hydrazine and platinum[2], or formic acid and palladium[3], were reported by Paravano as experimental researches. According to the results of the present experiments, the degree of polymerization is not yet so high, but we think that this new method of polymerization is interesting both from scientific and technical points of view.

Summary

(1) It has been that the polymerization of

(2) G. Paravano, *J. Am. Chem. Soc.*, **72**, 3855 (1950).
(3) G. Paravano, ibid., **72**, 5546 (1950).

methyl methacrylate happens catalytically with Cu or Cu_2Cl_2 and acids at room temperature. Polymerization products were obtained as fine powder easily separable from the reaction mixture.

(2) It has been pointed out that the polymerization is initiated by free radicals of hydrogen.

(3) Calculating from the degree of polymerization of the produced polymers and consumed Cu_2Cl_2, the efficiency of the produced $H^{\cdot}$ for the polymerization is not so good.

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