SHORT COMMUNICATIONS

The Catalytic Polymerization of Vinyl Monomers by the Cobalt Cyanide Complex

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In this study of the catalytic activity of the cobalt cyanide complex-hydrogen system, the author found that this complex has the ability to polymerize such vinyl monomers as methyl methacrylate, styrene, acrylonitrile and butadiene.

The polymerization was carried out as follows: 5 ml. of the monomer, 1 ml. of a potassium cyanide solution (3×10^{-1} mol./l.), 1 ml. of a 5% surfactant (non-ionic surfactant "Tween 80" aqueous solution and 2 ml. of water were placed in the main chamber of a Thunberg tube, and the air in the system was replaced with hydrogen. Then 1 ml. of the cobalt(II) chloride solution (5×10^{-2} mol./l.), which had been placed in the side chamber of the tube, was mixed with other components in the main chamber by tilting the side chamber, and the tube was shaken continuously at 25°C.

During the first stage of the reaction, small gel-like polymer particles separate out from the initial white emulsion. As the reaction proceeds, these particles coagulate to larger and harder particles or a mass.

The extent of polymerization on polymethyl methacrylate at various reaction times (in hours) is shown in Fig. 1.

As may be seen in the figure, an induction period was observed in the course of the polymerization of methyl methacrylate. While the surfactant was added to this system, the induction period was not observed (Curve A in the figure) and the reaction rate was accelerated remarkably. The highest yield in the polymerization reactions was 83% in the presence of the surfactant. It was noticed that, in the absence of the surfactant, the polymerization rate was slow (Curve B in the figure). It is recognized also that the intrinsic viscosity of the final product of polymethylmethacrylate was affected by the addition of the surfactant; when the surfactant was added to the polymerization system, the value of 2.75 was obtained for the intrinsic viscosity determined in benzene at 25°C, whereas it was 9.05 when the surfactant was not added.

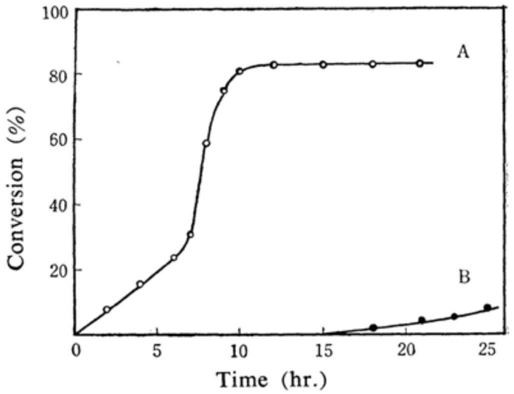

Fig. 1. Process of the polymerization of methyl methacrylate.

Several results obtained for the other monomers are listed in Table I. Generally speaking, it appeared that the use of a surfactant yielded the higher conversion.

TABLE I. POLYMERIZATION* OF VINYL MONOMER BY COBALT CYANIDE COMPLEX POLYMERIZATION CONDITION

Vinyl monomers	Surfactant[a] wt. %	Time hr.	Conversion hr.	Intrinsic viscosity
Methyl methacrylate	1	10	83	2.75[b]
	0	24	12	7.05[b]
Styrene	1	30	90	1.75[b]
Acrylonitril	1	48	25	0.89[c]
Butadiene	1	48	13	—

a) Tween 80 was used as a surfactant.

b) Determined in benzene solution at 25°C.

c) Determined in dimethylformamide solution at 25°C.

* 5 ml. of monomer was polymerized with 5 ml. of cobalt cyanide complex solution (1×10^{-2} ml./l.) as a catalyst under 1 atm. pressure of hydrogen atmosphere at 25°C.

The polymerization rate and yield were depressed when nitrogen gas was used instead of hydrogen gas. When molecular oxygen was present in the reaction systems, the polymerization of these monomers did not occur at all.

From these results, it is deduced that the cobalt cyanide complex-hydrogen system posseses an activity as a polymerization catalyst.

Further details of such catalytic effects of the complex will be published elsewhere.

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