

## Vinyl Bromide Polymerization with Alkylboron and Alkyl Halide Catalyst

AKIRA AKIMOTO, *Central Research Laboratory, Toyo Soda Manufacturing Co., Ltd., Shinnanyo-shi, Yamaguchi-ken, Japan*

### Synopsis

Trialkylboron-alkyl halide catalyst systems were found to induce the polymerization of vinyl bromide and other vinyl monomers at low temperatures. Tri-*n*-butylboron is the most effective catalyst. Among alkyl halide, carbon tetrachloride gives the best yield of poly(vinyl bromide). The polymerization process can be controlled by adjusting the reaction conditions of the initiating components. The rate of polymerization varies depending on the diluent.

### INTRODUCTION

Recently, several publications have described the use of alkylboron<sup>1-3</sup> and alkylaluminum<sup>4-6</sup> compounds as radical initiators of the polymerization of vinyl monomers such as vinyl chloride and methyl methacrylate. Generally, a coagent is required; for example, BR<sub>3</sub> peroxide<sup>7</sup> and BR<sub>3</sub> pyridine<sup>8</sup> are known to be effective catalysts for vinyl polymerization.

AlEt<sub>3</sub>-CCl<sub>4</sub><sup>9</sup> and AlEt<sub>3</sub>-Lewis base-CCl<sub>4</sub><sup>10</sup> systems are also known to initiate the free-radical polymerization of vinyl chloride.

The present paper describes binary catalyst systems consisting of BR<sub>3</sub> and alkyl halides. These systems initiate the polymerization of vinyl monomers (especially vinyl bromide) at low temperature.

### EXPERIMENTAL

#### Materials

Vinyl bromide (Toyo Soda Manufacturing Company Ltd.) was distilled from a cylinder and used without further purification, and other vinyl monomers were purified by usual methods.

Boron alkyls were prepared according to the standard method.<sup>11</sup>

Carbon tetrachloride and other alkyl halides were washed with concentrated sulfuric acid, then with water, dried over calcium chloride, and distilled. Solvents were purified by the usual methods and distilled over calcium hydride.

#### Polymerization Procedure

Into a glass tube flushed with nitrogen gas and kept at  $-230^{\circ}\text{C}$ , solvent, alkyl halide, vinyl monomer, and BR<sub>3</sub> were introduced, in that order. The

tube was sealed and shaken while being maintained at the desired temperature in a thermostat.

After a definite time, the polymerization mixture was poured into a large amount of methanol containing a small amount of ammonia (or, for polymerization of vinyl acetate, into a large amount of petroleum ether).

The intrinsic viscosity of the poly(vinyl bromide) and the poly(vinyl chloride) was determined by measurements on their dilute cyclohexanone solutions (N,N-dimethylformamide solution for polyacrylonitrile, benzene solution for others) at 30°C.

## RESULTS AND DISCUSSION

Table I lists the effect of varying the second component with trialkylboron on the polymerization of vinyl bromide. Good activity was observed with  $\text{CCl}_4$  as well as  $\alpha, \alpha'$ -azobisisobutyronitrile (AIBN) at 0°C. Generally, trialkylboron was a good catalyst, but triphenylboron showed little activity.

In Table II are shown the results of the polymerization of some vinyl monomers with  $\text{BBu}_3\text{-CCl}_4$  catalyst. This catalyst is able to initiate polymerization of all vinyl monomers at low temperature. In the polymerization of vinyl chloride, ethyl acrylate, and acrylonitrile, a rapid and uncontrollable reaction started after  $\text{BBu}_3$  was added to the monomer solution at desired temperature.

Figure 1 shows plots of yield and  $[\eta]$  versus time for the polymerization of vinyl bromide with  $\text{BBu}_3\text{-CCl}_4$  catalyst. The rate of polymerization

TABLE I  
Polymerization of Vinyl Bromide with a Trialkylboron-Second Component Catalyst<sup>a</sup>

Polymer no.	$\text{BR}_3$	Second component <sup>b</sup>	Yield, %	$[\eta]$
7	$\text{BEt}_3$	$\text{CCl}_4$	21	0.12
1	$\text{BBu}_3$	$\text{CCl}_4$	38	0.07
45	$\text{BHex}_3$	$\text{CCl}_4$	16	0.09
8	$\text{B}\phi_3$	$\text{CCl}_4$	trace	—
9	$\text{BEt}_3$	AIBN	14	0.10
10	$\text{BBu}_3$	AIBN	19	0.09
46	$\text{BHex}_3$	AIBN	13	0.10
11	$\text{B}\phi_3$	AIBN	trace	—
15	$\text{BEt}_3$	—	3	—
16	$\text{BBu}_3$	—	2	—
48	$\text{BHex}_3$	—	0	—
17	$\text{B}\phi_3$	—	0	—
18	—	AIBN	0	—
20	—	$\text{CCl}_4$	0	—

<sup>a</sup> Vinyl bromide, 5 ml; benzene, 5 ml; 1 mole-% catalyst on monomer; catalyst ratio of second component/ $\text{BR}_3 = 1/1$ , polymerization at 0°C for 3 hr.

<sup>b</sup> AIBN =  $\alpha, \alpha'$ -azobisisobutyronitrile.

TABLE II  
 Polymerization of Vinyl Monomer with  $\text{BBu}_3\text{-CCl}_4$  Catalyst System<sup>a</sup>

Polymer no.	Vinyl monomer	Condition of polymerization		Yield, %	[ $\eta$ ]
		°C	hr		
1	Vinyl bromide	0	3	38	0.07
2	Vinyl chloride	40	0.5	48	0.07
3	Vinyl acetate	30	20	65	0.03
4	Methyl methacrylate	30	20	34	1.39
43	Ethyl acrylate	30	0.5	100	—
5	Styrene	30	20	2	—
6	Acrylonitrile	40	0.5	85	1.19

<sup>a</sup> Vinyl monomer, 5 ml; benzene, 5 ml; 1 mole-% catalyst on monomer; catalyst ratio  $\text{CCl}_4/\text{BBu}_3 = 1/1$ .

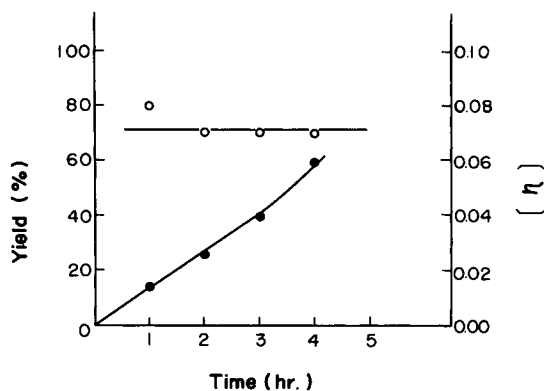


Fig. 1. Plots of time vs. yield (●) and time vs. [ $\eta$ ] (○). Vinyl bromide, 5 ml; benzene, 5 ml; 1 mole-% catalyst on monomer; catalyst ratio  $\text{CCl}_4/\text{BBu}_3 = 1/1$ , at 0°C.

was constant in early stages, and with longer reaction times the rate of polymerization increased. The intrinsic viscosity was observed to be constant as seen in a typical radical polymerization.

Figure 2 shows the yield of polymer and the molecular weight of polymer, respectively, obtained with the  $\text{BBu}_3\text{-CCl}_4$  catalyst at various  $\text{CCl}_4/\text{BBu}_3$  molar ratios. At a constant  $\text{BBu}_3$  content, the polymer yield first rose, then passed through a maximum (a  $\text{CCl}_4/\text{BBu}_3$  ratio of 1/1) with increasing carbon tetrachloride content. The intrinsic viscosity of the polymer decreased with increasing carbon tetrachloride content. These results indicate that a true, effective catalytic site is formed at molar ratio of 1/1 in the binary catalyst system.

Table III shows the results of polymerizing vinyl bromide with  $\text{BBu}_3$  and different alkyl halides. In some alkyl halides, the activity appeared to be a function of bond dissociation energy and steric effect. Thus, in polychloromethane the order of activity per unit chlorine atom was  $\text{CCl}_2\text{H}_2 \geq$

TABLE III  
Effect of Alkyl Halides on Polymerization of  
Vinyl Bromide with Trialkylboron<sup>a</sup>

Polymer no.	Alkyl halide	Yield, %	$[\eta]$
1	CCl <sub>4</sub>	38	0.07
21	CCl <sub>3</sub> H	30	0.11
22	CCl <sub>2</sub> H <sub>2</sub>	27	0.13
23	CBr <sub>3</sub> H	6	0.01
24	CI <sub>3</sub> H	0	—
25	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl	7	0.14
26	<i>iso</i> -C <sub>4</sub> H <sub>9</sub> Cl	22	0.13
27	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Cl	5	0.12
28	<i>tert</i> -C <sub>4</sub> H <sub>9</sub> Cl	6	0.14
29	C <sub>6</sub> H <sub>5</sub> Cl	1	—
30	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	0	—
31	CH <sub>2</sub> =CH—CH <sub>2</sub> Cl	0	—

<sup>a</sup> Vinyl bromide, 5 ml; benzene, 5 ml; 1 mole-% catalyst on monomer; catalyst ratio alkyl halide/BBu<sub>3</sub> = 1/1, polymerization at 0°C for 3 hr.

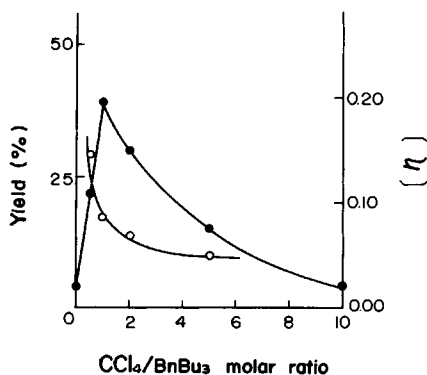


Fig. 2. Effect of CCl<sub>4</sub>/BBu<sub>3</sub> molar ratio on the yield (●) and  $[\eta]$  (○). Vinyl bromide, 5 ml; benzene, 5 ml; 1 mole-% catalyst on monomer, polymerization at 0°C for 3 hr.

CCl<sub>3</sub>H  $\geq$  CCl<sub>4</sub>; and in some alkyl and aryl halides, the order of activity was *iso*-C<sub>4</sub>H<sub>9</sub>Cl > *n*-C<sub>4</sub>H<sub>9</sub>Cl, *sec*-C<sub>4</sub>H<sub>9</sub>Cl, *tert*-C<sub>4</sub>H<sub>9</sub>Cl > C<sub>6</sub>H<sub>5</sub>Cl. Moreover, in bromoform and iodoform it was low and inert. The polymerization of vinyl bromide does not occur in benzyl chloride and allyl chloride.

It was suggested that the formation of alkyl radical by the reaction between BBu<sub>3</sub> with alkyl halide affects the polymerization of vinyl bromide seriously.

Temperature had the expected effects on polymerization. A decrease in temperature decreased the yield of polymer. However, molecular weight of the polymer had a maximum at a temperature of about -20°C (Table IV).<sup>12</sup>

Table V presents the results of the polymerization of vinyl bromide with BBu<sub>3</sub>-CCl<sub>4</sub> catalyst in some diluents. Expected yields of polymer were

TABLE IV  
Polymerization of Vinyl Bromide at Various Temperatures<sup>a</sup>

Polymer no.	Polymerization temp., °C	Yield, %	[ $\eta$ ]
33	+10	48	0.06
1	0	38	0.07
34	-10	12	0.15
35	-20	9	0.23
36	-30	7	0.20
44	-78	2	0.15

<sup>a</sup> Vinyl bromide, 5 ml; benzene, 5 ml; 1 mole-% catalyst on monomer; catalyst ratio  $\text{CCl}_4/\text{BBu}_3 = 1/1$ , polymerization for 3 hr.

TABLE V  
Polymerization of Vinyl Bromide in Various Diluents<sup>a</sup>

Polymer no.	Diluent	Yield, %	[ $\eta$ ]
1	Benzene	38	0.07
39	<i>n</i> -Hexane	36	0.07
37	Tetrahydrofuran	6	—
41	Dioxane	7	—
38	Ethyl acetate	10	—
40	Dimethyl sulfoxide	16	0.07
42	N,N-Dimethylformamide	24	0.08

<sup>a</sup> Vinyl bromide, 5 ml; diluent, 5 ml; 1 mole-% catalyst on monomer; catalyst ratio  $\text{CCl}_4/\text{BBu}_3 = 1/1$ , polymerization at 0°C for 3 hr.

obtained in *n*-hexane. Dimethyl sulfoxide and N,N-dimethylformamide gave a moderate amount of polymer, while tetrahydrofuran, dioxane and ethyl acetate were poor diluents for polymerization of vinyl bromide.

It is well known that  $\text{BEt}_3$ -THF complex with carbon tetrachloride does not initiate the polymerization of vinyl chloride,<sup>10</sup> and  $\text{AlEt}_3$  forms an complex with these diluents easily. It seems likely that the formation of a stable boron complex reduces the polymerization rate of vinyl bromide.

The difference of the activity between  $\text{BR}_3$  and  $\text{AlR}_3$  on the polymerization of vinyl monomer could be explained on the basis of the ionic character of center metal atom.

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