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Polymerization of Methyl Methacrylate with the Chlorocarbonylbis(triphenylphosphine)rhodium(I)-Organic Halides System[1]

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Recently it has been reported that zero-valent transition-metal complexes conjugated with organic halides act as effective radical initiators of methyl methacrylate (MMA).[2,3] Bamford and his co-workers[2] found that metal carbonyls in the presence of organic halides can initiate the free-radical polymerization of MMA and that the polymers thus obtained are more stereospecific than those obtained in the usual free-radical polymerization. In this case, the valency, state of metal appears to play an important role in the free-radical initiation of MMA.

In a previous paper,[4] we reported that some low-valent metal complex, *trans*-$PtHCl\{P(C_2H_5)_3\}_2$ (Pt complex) and the alkyl halide system can serve as radical initiators of MMA and styrene. Chlorocarbonylbis(triphenylphosphine)rhodium(I) (Rh complex) has been known as hydrogenation catalysts of ethylene and acetylene,[5] and in the presence of organic halides they may serve much like the Pt complex in initiating the polymerization of MMA.

This paper will describe the results of the polymerization of MMA with a system composed of the Rh complex and organic halides, and also the results of kinetic studies of the polymerization with the system composed of the Rh complex and carbon tetrachloride.

Experimental

Methyl methacrylate (MMA) was purified by an ordinary method and was stored in a refrigerator until use.

The organic halides were purified by distillation or recrystallization.

Chlorocarbonylbis(triphenylphosphine)rhodium (I) (Rh complex) was synthesized according to the method in the literature[6] and then purified by recrystallization from a benzene solution. It had an mp of 194—196 °C (lit,[6] 195—197 °C).

The other reagents were purified by ordinary methods.

The polymerization was carried out in a sealed glass tube (30 ml) containing a given amount of the Rh complex (18 mg) dissolved in benzene (5 ml); MMA (5 ml) and the required amount of organic halides (solution=3 ml; solid=3 g) were placed in it, and then the air in the tube was replaced with nitrogen before sealing. Polymerization was carried out in a tube in a thermostat maintained at a given temperature. After polymerization, the contents of the tube were poured into a large amount of methanol in order to precipitate the polymer. The conversion was calculated from the weight of the dried polymer thus obtained.

The number-average molecular weight ($\bar{M}_n$) of the resulting polymers was calculated from the intrinsic viscosity, $[\eta]$, in chloroform at 25 °C according to the following equation[7]:

$$[\eta] = 3.4 \times 10^{-5} \bar{M}_n^{0.83}.$$

The rate of polymerization (R_p) was measured by the dilatometric method, using a dilatometer with a capacity of 10 ml as the reaction vessel. The Rh complex was weighed and placed in the reaction vessel, and then benzene was added. After the Rh complex had been solved, the atmosphere of the apparatus was replaced with nitrogen and the reaction vessel was filled with a known amount of MMA and carbon tetrachloride. The dilatometer was placed in a constant-temperature bath, and the rate of contraction in volume was followed up by the use of a cathetometer.

Results and Discussion

Effect of Organic Halides. The results of the polymerization of MMA with the Rh complex in the presence of various kinds of organic halides (carbon tetrachloride, carbon tetrabromide, chloroform, bromoform, iodoform, methylene chloride, hexachloroethane, chlorobenzene, and benzyl chloride) at 60 °C for 7 hr. The initiating activity of the halides was shown only by carbon tetrachloride and carbon tetrabromide, the polymer yields of which were 30.8% ($\bar{M}_n$=6.4×10^4) and 9.0% ($\bar{M}_n$=2.6×10^4) respectively. The nuclear magnetic resonance spectra of poly(methyl methacrylate) obtained with these initi-

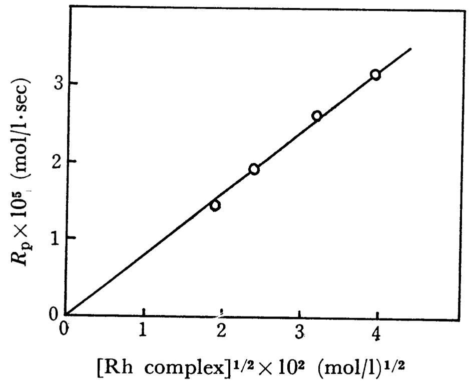

Fig. 1. Relationship between R_p and the concentration of Rh complex: [MMA]=4.65 mol/l, [Carbon tetrachloride]=2.05 mol/l, in benzene at 50 °C.

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[6] D. Evans, J. A. Osborn and G. Wilkinson, "Inorganic Syntheses," Coll. Vol. 11, 99 (1968).

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ator systems showed that its tacticity was similar to that obtained with the conventional radical polymerized poly(methyl methacrylate). No polymer was obtained by the use of the Rh complex alone.

Kinetic Studies of the Polymerization with the System of the Rh complex and Carbon Tetrachloride. Figure 1 shows the relationship between the R_p and the concentration of the Rh complex at constant concentrations of both MMA and carbon tetrachloride.

From this figure, the rate was found to be proportional to the square root of the concentration of the Rh complex. The plots of R_p against the concentration of carbon tetrachloride at constant concentrations of both the Rh complex and MMA are shown in Fig. 2, in which the rate is indicated to be proportional to the square root of the concentration of carbon tetrachloride. The square-root dependence of the concentration of carbon tetrachloride on the rate was observed only in the concentration range lower than 5×10^{-3} mol/l. When the concentration of carbon tetrachloride becomes higher than this, the rate becomes constant and independent of the concentration of carbon tetrachloride.

Figure 3 shows the relationship between the R_p and the concentration of MMA at constant concentrations of both the Rh complex and carbon tetrachloride. From this figure, it is clear that the rate is proportional to the concentration of MMA. This finding indicates that MMA does not participate in the initiation of the radical production.

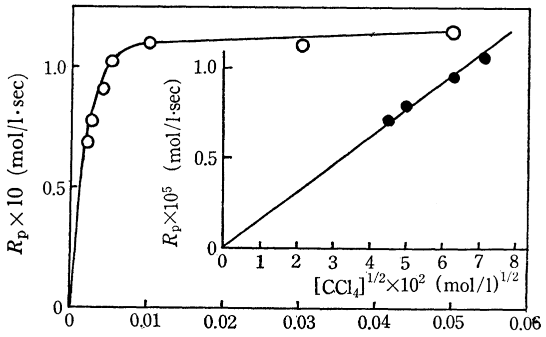

Fig. 2. Relationship between R_p and the concentration of carbon tetrachloride: [MMA]=4.65 mol/l, [Rh complex] $=10^{-3}$ mol/l, in benzene at 50 °C.

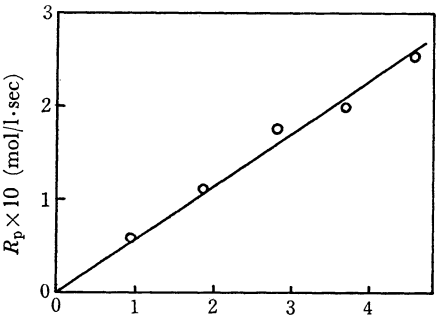

Fig. 3. Relationship between R_p and the concentration of MMA: [Rh complex] $=10^{-3}$ mol/l, [Carbon tetrachloride] $=2.05$ mol/l, in benzene at 50 °C.

Effect of Radical Inhibitor. The effects of several radical inhibitors on the polymerization with the system of the Rh complex and carbon tetrachloride were investigated. α,α-Diphenyl-β-picrylhydrazyl (5×10^{-3} mol/l) and *p*-benzoquinone (5×10^{-3} mol/l) inhibit the polymerization.

Mechanism of MMA Polymerization with the Rh Complex and the Organic Halids System. The results on the polymerization kinetics and on the radical inhibitor, indicate that the polymerization of MMA with the Rh complex and carbon tetrachloride proceeds through a radical mechanism. From the fact that the rate of polymerization is proportional to the square root of the concentration of the Rh complex and of carbon tetrachloride, it can be presumed that free radicals are produced by the reaction of the Rh complex and carbon tetrachloride. These free radical are considered to be trichloromethy radicals, because of the fact that hexachloroethane is found by gas-chromatographic analysis. Trichlorocarbonylbis(triphenylphosphine)rhodium(III) was also found from the infrared spectra in the reaction of the Rh complex and carbon tetrachloride at 60 °C for 3 hr.

Further investigation is required for the elucidation of the mechanism of the Rh complex reaction.