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Metal-Containing Initiator Systems. III.*1 Polymerization of Styrene by Some Activated Metals in the Presence of Organic Halides

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The polymerization of styrene with systems of various metals and organic halides was investigated at 60°C. It was found that the metals which could be used as hydrogenation catalysts were effective as initiators and that the organic halides with a weak carbon-halogen bond showed a high initiating activity for styrene polymerization. From the kinetic studies of the polymerization of styrene by reduced nickel and chloroform, the rate of polymerization was shown to be proportional to the monomer concentration and to the square-root concentration of both nickel and chloroform in the lower concentration range of chloroform. Some radical inhibitors were also found to inhibit this polymerization. These results indicated that this initiator system could induce the radical polymerization. The apparent overall activation energy for the polymerization by this system was estimated as 11 kcal/mol. The resulting polystyrene was found to be a relatively-low-molecular-weight atactic polymer.

In previous papers,[1,2] it has been reported that some activated metals can serve as radical initiators of vinyl monomers in the presence of some organic

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[*1] Parts I and II of this series are Refs. 1 and 2 respectively.

[1] T. Otsu, M. Yamaguchi, Y. Takemura, Y. Kusuki and S. Aoki, *J. Polymer Sci.*, **B**, **5**, 697 (1967).

[2] T. Otsu, S. Aoki, M. Nishimura, M. Yamaguchi and Y. Kusuki, *ibid.*, **B**, **5**, 835 (1967).

halides. Recently, similar investigations have been published independently by Olivé and Olivé³⁾ and by Iwatsuki *et al.*⁴⁾

The present paper will describe our detailed findings on the polymerization of styrene by systems of various metals and organic halides at 60°C, and on our kinetic studies of the polymerization by a system of reduced nickel and chloroform.

Experimental

Materials. Raney metals were prepared from their commercial aluminum alloys according to the Adkins W-5 method,⁵⁾ followed by successive washings with water, methanol, and benzene.

The Urushibara metals were obtained by adding zinc dust to a metal chloride aqueous solution by the method of Taira⁶⁾; they were used after having been washed with water, methanol, and benzene.

The reduced nickel used was a commercially-obtainable stabilized hydrogenation catalyst (Nikki Chemical Co.) composed of a 50% Ni atom on kieselguhr. Before use, this catalyst was activated by heating it at about 200°C in a stream of hydrogen for an hour. The other hydrogenation catalyst, formate nickel (Nikko Rikagaku Co.), prepared by the thermal decomposition of nickel formate, was a commercial product (50% Ni atom on kieselguhr). The commercial metal powders were also used without further purification.

The organic halides used in this study were purified by distillation or recrystallization. The styrene was purified by the ordinary method and distilled under reduced pressure before use. The other reagents were purified by ordinary methods.

Polymerization Procedure. Into a hard glass tube containing a given amount of the metal, the required amounts of organic halide and monomer were placed. After degassing the contents of this tube by a successive freezing and thawing technique, the tube was sealed off under a vacuum.

Polymerizations were carried out in the dark with shaking in a thermostat maintained at 60°C. After polymerization, the contents of the tube were poured into a large amount of methanol containing concentrated hydrochloric acid in order to precipitate the polymer and dissolve the residual metal initiator. The resulting polymer was then purified by reprecipitating it two or three times using a system of benzene and methanol. The conversion was calculated from the weight of the dried polymer thus obtained.

Analysis of the Polymers. The number-average molecular weight ($\overline{M}_n$) of the polymers was calculated from their intrinsic viscosities, $[\eta]$, determined in benzene at 30°C according to the following equation⁷⁾:

$$[\eta] = 1.74\times10^{-4}\ \overline{M}_n^{0.71}$$

Results and Discussion

Effect of Metals. The effects of various kinds of metals on the polymerization of styrene in the presence of carbon tetrachloride at 60°C in benzene were investigated. The results are shown in Table 1.

TABLE 1. POLYMERIZATION OF STYRENE WITH THE SYSTEMS OF SOME METALS AND CARBON TETRACHLORIDE AT 60°C FOR 18 hr
$[M]=4.14$ mol/*l*, $[CCl_4]=0.49$ mol/*l*
[Metal]$=0.81$ g-atom/*l* in benzene

Metal	Polymer yield, %	Metal	Polymer yield, %
Raney Ni	68.3	Raney Cu	60.7
Urushibara Ni	78.6	Urushibara Cu	70.7
Formate Ni	17.7	Commercial Cu	1.8
Reduced Ni	90.2	Raney Fe	51.2
Commercial Ni	0.5	Urushibara Fe	46.1
Raney Co	76.8	Commercial Fe	1.9
Urushibara Co	76.2	Commercial Zn	0.3
Commercial Co	1.1	None	0.5

As can be seen from Table 1, the systems of Raney and Urushibara metals with carbon tetrachloride were effective as initiators of the styrene polymerization. However, the systems consisting of commericial metal powders were completely inactive with regard to initiation, indicating it is necessary that the metals have a fresh surface.

No definite relationship between the initiating activities and the kinds of metals can be observed from Table 1, because the polymerization system was heterogeneous. However, it might be considered that both the oxidation potential of the metals, as was suggested by Olivé *et al.*,³⁾ and their preparation and activation methods, which determined their surface area and purity, were the controlling factors in the initiating activity of these systems.

The resulting polymers were soluble in methyl ethyl ketone at room temperature, indicating that no isotactic polystyrene was obtained and that these systems could not induce the stereospecific polymerization of styrene.

Effect of Organic Halides. Table 2 shows the results of the polymerization of styrene with reduced nickel in the presence of various kinds of organic halides at 60°C.

In Table 2 the initiating activity can be seen to increase as the substitution by halogen atom increases and also as the labile halogen atom is involved. These results suggest that the effectiveness of organic halides in initiation increases with a decrease in the bond-dissociation energy of the carbon-halogen bonds involved in organic halides. The reactivity of the initiating radical

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3) G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **88**, 117 (1965).

4) S. Iwatsuki, H. Kasahara and Y. Yamashita, *ibid.*, **104**, 254 (1967).

5) H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).

6) S. Taira, This Bulletin, **34**, 261 (1961).

7) R. Gregg and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 2373 (1948).

TABLE 2. EFFECT OF ORGANIC HALIDES ON THE POLYMERIZATION OF STYRENE AT 60°C FOR 8 hr
[M]=4.14 mol/*l*, [Halide]=0.2 mol/*l*
[Ni]=0.4 g-atom/*l* in benzene

Organic halide	Polymer yield, %	Degree of polymerization
CH_2Cl_2	6.9	2300
$CHCl_3$	21.7	160
CCl_4	26.5	80
$CHBr_3$	48.6	50
CHI_3	36.0	20
C_2H_5Br	16.8	500
n-C_4H_9Cl	1.4	—
t-C_4H_9Cl	7.7	1500
C_6H_5Cl	1.0	—
$C_6H_5CH_2Cl$	46.8	120
$CH_2{=}CHCH_2Cl$	11.3	700
None	0.6	—

produced from organic halides toward the styrene monomer might also be important.

In Table 2 the degree of polymerization of the resulting polymers can also be observed to decrease in proportion to the increase in the initiating activity of the systems. Since the chain-transfer reactivity of these organic halides has been known to be correlated also with the bond-dissociation energy of their carbon-halogen bonds, such a change in the degree of polymerization might be expected from the reactivities of organic halides in both the initiation and the chain-transfer reaction.

Kinetic Studies of the Polymerization by the System of Reduced Nickel and Chloroform. Figure 1 shows the relationship between the conversion and the polymerization time at 30, 45, 60, and 80°C. In this figure, straight-line relationships can be observed between them at every temperature.

The rates of polymerization (R_p), which were determined from the slopes of the straight lines in Fig. 1, are plotted against the reciprocal polymerization temperatures in Fig. 2. From the slope of the resulting straight line, the apparent activation energy for the overall polymerization by this initiator system was calculated to be 11.1 kcal/mol. Accordingly, the activation energy for initiation was obtained as 9.2 kcal/mol by using the reported rate constants[8] for propagation and termination. This value is quite small compared with that of benzoyl peroxide (29.6 kcal/mol).[9]

Figure 3 shows the relationship between the rate of polymerization and the concentration of reduced nickel at constant concentrations of both the styrene monomer and chloroform. From this figure, the rate can be seen to be proportional to the square-root concentration of reduced nickel, indicating that the radical polymerization occurred.

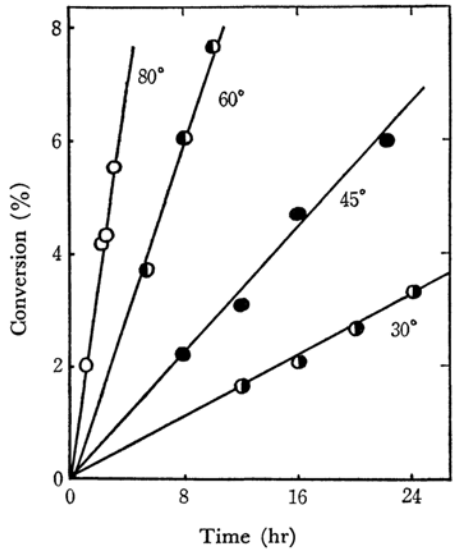

Fig. 1. Time-conversion relations on the polymerization of styrene by the system of reduced nickel and chloroform at 30—80°C: [Ni]=2.5×10^{-2} g-atom/*l*, [$CHCl_3$]=2.5×10^{-2} mol/*l*, [M]=4.35 mol/*l* in benzene.

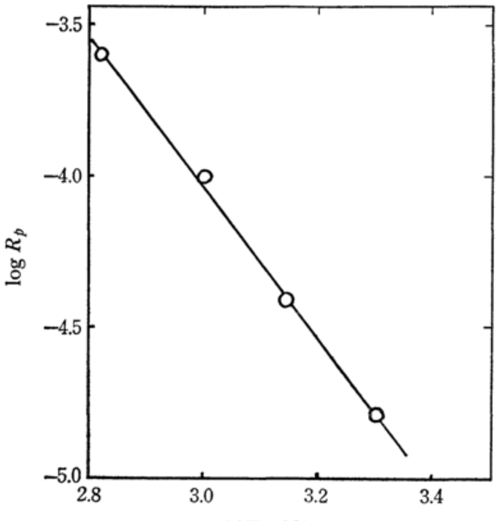

Fig. 2. Arrehnius plot between R_p and $1/T$.

The relationship between the rate of polymerization and the concentration of chloroform is shown in Fig. 4, from which the square-root dependence of the concentration of chloroform on the rate was observed only in the concentration range lower than 5×10^{-3} mol/*l*. In the concentration range above this, the rate was constant independently of the concentration of chloroform. This result

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[8] A. V. Tobolsky and B. Baysal, *J. Polymer Sci.*, **11**, 471 (1953).

[9] C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

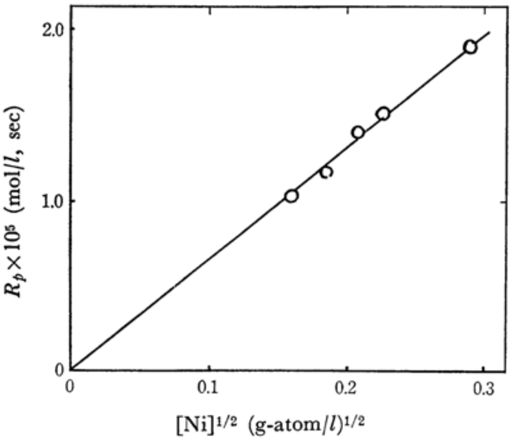

Fig. 3. Relationship between R_p and the concentration of reduced nickel: $[CHCl_3]=2.5\times10^{-2}$ mol/l, $[M]=4.35$ mol/l in benzene at 60°C.

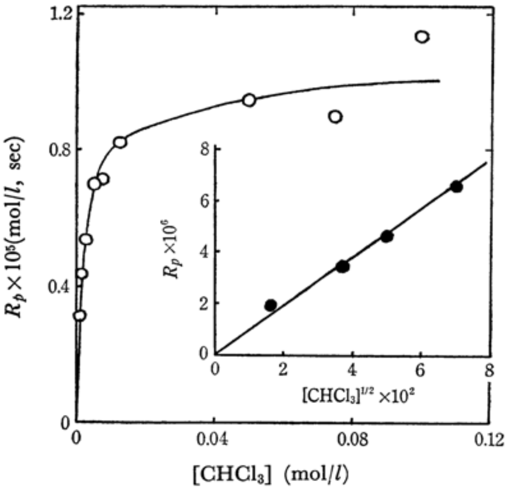

Fig. 4. Relationship between R_p and the concentration of chloroform: $[Ni]=2.5\times10^{-2}$ g-atom/l, $[M]=4.35$ mol/l in benzene at 60°C.

suggests that the initiating radical is produced *via* a complex formation between reduced nickel and chloroform, as was pointed out by Olivé and Olivé³⁾ and by Iwatsuki *et al.*⁴⁾

Figure 5 shows the plot of the polymerization rate against the concentration of the styrene monomer. It was clear that the rate was directly proportional to the monomer concentration. This result also indicates that the monomer did not participate in intiating radical production.

Effect of Radical Inhibitor. The effect of some radical inhibitors on the polymerization by a system of reduced nickel and carbon tetrachloride was also investigated. The results are shown in Table 3.

In Table 3, *p*-benzoquinone, diphenylpicrylhydrazyl (DPPH), and oxygen can be seen to inhibit this polymerization. Accordingly, it is obvious that this initiator system induced the radical polymerization of styrene. However, the hydroquinone does not act as a radical inhibitor.

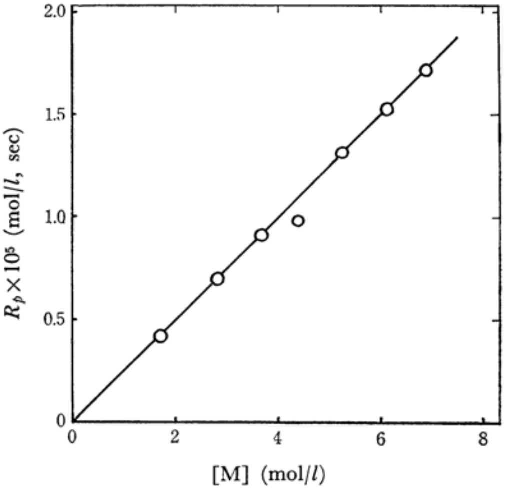

Fig. 5. Relationship between R_p and monomer concentration: $[Ni]=2.5\times10^{-2}$ g-am/l, $[CHCl_3]=2.5\times10^{-2}$ mol/l in benzene at 60°C.

TABLE 3. EFFECT OF RADICAL INHIBITOR ON THE POLYMERIZATION OF STYRENE WITH THE SYSTEM OF REDUCED NICKEL AND CARBON TETRACHLORIDE

$[M]=4.14$ mol/l, $[CCl_4]=0.2$ mol/l
$[Ni]=0.4$ g-atom/l in benzene, at 60°C, for 10 hr

Inhibitor (g)	Polymer yield (%)
None	20.2
Air	6.5
Hydroquinone (0.05)	16.7
p-Benzoquinone (0.05)	4.0
DPPH (0.05)	0.4

Mechanism of Styrene Polymerization by These Systems. From the results of the polymerization kinetics and of the radical inhibitor, it is clear that the polymerization of styrene by these systems proceeds via a radical mechanism. This conclusion is also supported by the results of copolymerization with methyl methacrylate by a system of reduced nickel and carbon tetrachloride at 60°C.¹⁰⁾

As was pointed out Olivé and Olivé³⁾ and by Iwatsuki *et al.*,⁴⁾ the initiation by these systems may be considered to occur in the following way: a complex between the metal (Me) and the organic halide (RX) is formed, and then a one-electron transfer from the metal to the carbon-halogen bond in the halide to give the initiating radical occurs:

$$\text{R-X} + \text{Me} \rightleftharpoons [\text{complex}] \rightarrow \text{R}\cdot + \text{Me}^+ + \text{X}^-$$

This mechanism is also confirmed by the fact

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10) T. Otsu and M. Yamaguchi, *J. Polymer Sci.*, **A1**, **6**, 3075 (1968).

that hexachloroethane and nickel chloride were found in a reaction mixture of reduced nickel and carbon tetrachloride.[10]

If the step of the one-electron transfer is rate-determining, the ease of the initiating radical production may be dependent on both the oxidation potential of the metal and the bond-dissociation energy of the carbon-halogen bond in the halide. However, no definite correlation was obtained between the initiator activity and the kind of metal, as may be seen in Table 1. This result is understandable if it is assumed that the surface area and the purity of the metal are more signicant than its oxidation potential in the formation of the complex with the halide rather.

The probable structure of the complex in the transition state may be written as follows:

$$\underset{\text{I}}{[\mathrm{R}:\mathrm{X}\ \mathrm{Me}} \rightarrow \underset{\text{II}}{\mathrm{R}\cdot\mathrm{X}^{-}:\mathrm{Me}^{+}]}$$

in which the I structure is the structure near the reactant system and the II structure is that after the one-electron transfer has occurred. The importance of a similar transition-state structure has been discussed by Kochi *et al.*[11] for the reduction of alkyl halides with the chromium(II) ion.

From Table 2, the degrees of polymerization of some polystyrenes can be seen to be lower than that to be expected from the chain-transfer constant and the concentration of the organic halides used. In connection with this observation, we found recently that the systems of reduced nickel and methylchlorosilanes could induce the cationic polymerization of styrene.[12] This point will be clarified in a later paper.

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11) J. Kochi and D. Davis, *J. Am. Chem. Soc.*, **85**, 5264 (1964).

12) T. Otsu, S. Aoki, M. Nishimura, M. Yamaguchi and Y. Kusuki, *J. Polymers Sci.*, **A1**, in press.