

# Thermal Dehydrochlorination of Poly(vinyl Chloride).

## I. Effect of Iron Oxide on the Rate of Dehydrochlorination

YOSHIHIKO UEGAKI and TSUTOMU NAKAGAWA, *Industrial Products Research Institute, Shimomaruko, Otaku, Tokyo, Japan*

### Synopsis

The thermal degradation of poly(vinyl chloride) (PVC) was studied by following the rates of dehydrochlorination at temperatures between 180°C and 280°C in pure nitrogen and air flow. Iron oxide accelerates the elimination of hydrogen chloride from PVC. The accelerating effect depends on the concentration of the oxide, and it has a maximum. This work tried to explain these behaviors. A mechanism of dehydrochlorination is suggested for polymer containing iron oxide.

### INTRODUCTION

A number of studies in the literatures have dealt with the mechanism of degradation and stabilization of PVC. Recently, the effects of metal oxides and metal chlorides as an additive were investigated by several authors.<sup>1-8</sup> Their effects were reported in various ways, but the mechanism of dehydrochlorination of PVC in the presence of these additives was not established.

Dudley et al.<sup>1</sup> observed the thermal degradation of polymers containing chloride under inert gas atmospheres in the presence of iron oxide by using a thermal analytical method, and recognized the accelerating effect of iron chloride on the reaction. The mechanism they proposed shows that labile structures containing chloride ions react during an induction period to yield iron chloride and that at the end of the period iron chloride initiates cationic crosslinking which is followed by rapid elimination of hydrogen chloride. On the contrary, the inhibiting effect of iron chloride was reported by Servaas et al.<sup>5</sup> They explained that the dehydrochlorination reaction proceeds slower than that without additives by trapping chloride anion in the addition of complexing agents such as iron chloride, since chloride anion seems to act as a strong basic catalyst in the reaction.

In the present study, a detailed quantitative examination has been made of the rate of dehydrochlorination of PVC under nitrogen or air flow at temperature between 180°C and 280°C in the presence of iron oxide to clarify the role of the oxide in the reaction. A mechanism of the reaction was also proposed.

### EXPERIMENTAL

**Materials.** The PVC used in these studies has a degree of polymerization of 800. The polymer was washed several times with cooled acetone. All

chemicals were reagent grade and were used without purification. Silica gel of 80/100 mesh was used as supporter.

**Preparation of Catalysts.** Iron oxide was prepared by depositing on the silica gel by addition of ammonia water from an aqueous solution of ferric nitrate, and then calcined at 450°C for a day in the atmosphere as described in the directions.<sup>9</sup> After evacuation at 450°C for a day, it was supplied as a catalyst. Iron chloride catalyst was prepared by the chlorination of the above oxide catalyst in nitrogen flow containing hydrogen chloride at 200°C for 6 hr. Reduced iron oxide catalyst was obtained from the reduction of the iron oxide catalyst in a hydrogen atmosphere at 350°C for 3 hr.

**Preparation of Samples for Degradation.** The catalyst was immersed in a tetrahydrofuran solution containing weighed PVC. Then, the tetrahydrofuran was removed from the catalyst under evacuation for a week at room temperature.

**Experimental Method.** For studies on dehydrochlorination of PVC, a conventional flow system apparatus was used. The glass tube reactor packed with a sample was set in an electric furnace at constant temperature. After the carrier gas passed through, an experiment was begun. The gas outlet of the reactor led into an enclosed flask containing 0.5*N* sodium hydroxide aqueous solution. The hydrogen chloride evolved was followed over the first 3 hr of degradation by measuring chloride ion concentration in the solution. The concentration was analyzed by the argentimetric determination of chloride ions according to Volhard's method.<sup>10</sup> The dehydrochlorination rates were determined from the tangents at some reaction extent in the amount of evolved hydrogen chloride-versus-reaction time curves. The amount of chlorine in PVC was calculated from the initial concentration of PVC and evolved hydrogen chloride, which means the amount of chlorine that is not evolved in the gas phase. The activation energies were also obtained by comparison of the rates at different temperatures corresponding to the same amount of PVC. Infrared spectra of the polymer were measured in KBr pellets by use of a Hitachi EPI-G2 type spectrophotometer. The samples for measurement were obtained by degradation of the polymer films containing iron oxide at 200°C.

## RESULTS AND DISCUSSION

Typical kinetics of dehydrochlorination of PVC alone and with iron oxide at 200°C are shown in Figure 1. This figure shows apparently the accelerating effect of the oxide on the reaction. There is, however, a fall in the reaction rate with time in the presence of the oxide although PVC alone degrades constantly, and this is shown quantitatively in Table I.

**Variation of Iron Oxide Concentration on Silica Gel.** The rates at different concentrations on silica gel were measured, and the rates at 20% extent of reaction were plotted against the concentrations of iron oxide on silica gel in Figure 2. The rate is linearly proportional to concentration up to at least  $10^{-4}$  Fe<sup>3+</sup> g atom/g silica gel, showing a first-order dependence of the rate on the iron oxide. But when the concentration is higher than about  $2.5 \times 10^{-4}$  Fe<sup>3+</sup> g atom, the rate gradually decreases.

**Variation of PVC Concentration.** The dehydrochlorination rates of PVC in various weights on the iron oxide catalyst ( $10^{-4}$  Fe<sup>3+</sup> g atom/g silica gel) were

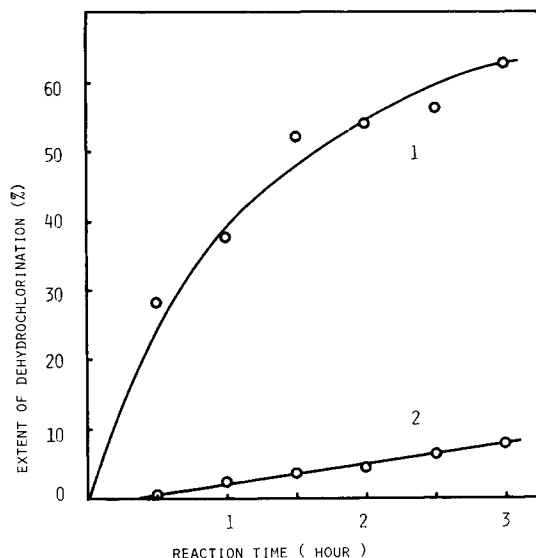


Fig. 1. Dehydrochlorination of PVC in  $N_2$  flow at  $200^\circ C$  alone (2) and with iron oxide (1). Iron oxide:  $1 \times 10^{-4}$   $Fe^{3+}$  g atom/g silica gel; PVC:  $8.0 \times 10^{-4}$  mole monomer units.

investigated to demonstrate the dependence of PVC concentration. As already described, the rate gradually decreases with reaction time and the relation between rate, and the amount of chlorine in PVC is shown in Figure 3. The figure shows that the rates  $r$  increase proportionally with the square of the chlorine  $p$  in PVC. The following equation was obtained:

$$r = cp^2 \quad (1)$$

where

$$p = p_0(1 - a) \quad (2)$$

$p_0$  is the initial concentration of PVC,  $a$  is the extent of reaction, and  $c$  is a coefficient. The tangents  $c$  of the straight lines on Figure 3 decrease with increment in initial concentrations of PVC. The relation between them logarithmically, shown in Figure 4, is linear, with a slope of about  $-\frac{3}{2}$ . Thus, the next equation was obtained:

TABLE I  
Variation in Rate of Dehydrochlorination of PVC in the Presence of Iron Oxide with Extent of Reaction at  $200^\circ C$  in  $N_2$  Flow<sup>a</sup>

Loss of chlorine in polymer, %	Rate of dehydrochlorination, mole evolved HCl $\times 10^4$ /hr
20	4.12
25	3.03
30	2.29
35	1.93
40	1.67
45	1.51
50	1.17

<sup>a</sup>Iron oxide:  $10^{-4}$   $Fe^{3+}$  g atom/g silica gel; PVC:  $8.00 \times 10^{-4}$  mole monomer units.

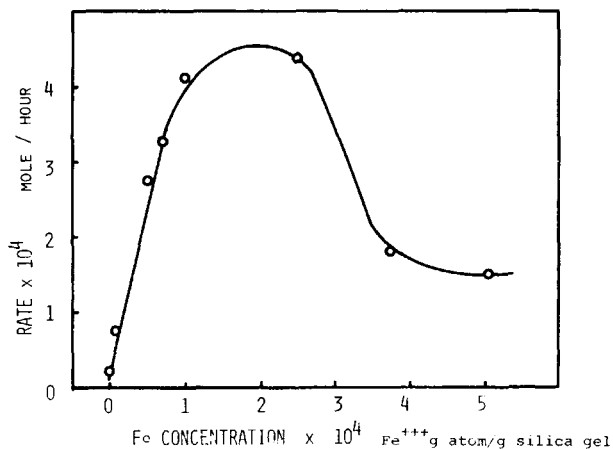


Fig. 2. Rates of dehydrochlorination of PVC in the presence of various concentration of iron oxide in  $\text{N}_2$  flow at  $200^\circ\text{C}$ . PVC:  $8.0 \times 10^{-4}$  mole monomer units.

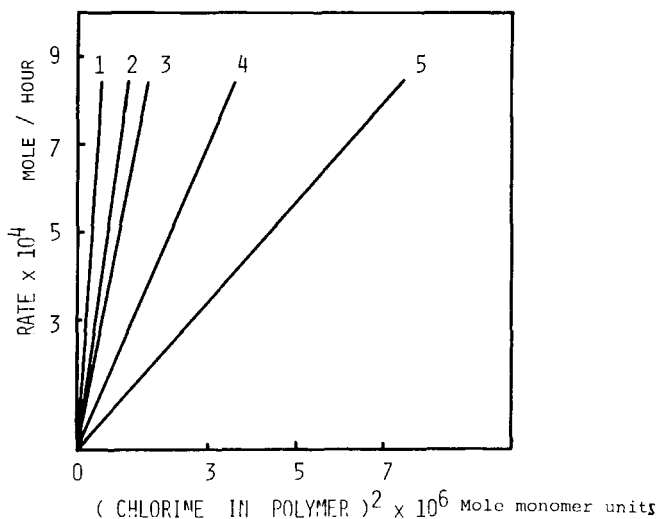


Fig. 3. Relationship between dehydrochlorination rate and chlorine in PVC at  $200^\circ\text{C}$  in  $\text{N}_2$  flow. Initial concentration of PVC: (1) 6.4; (2) 10.4; (3) 16.0; (4) 25.7; (5)  $40.1 \times 10^{-4}$  mole monomer units. Iron oxide:  $10^{-4}$   $\text{Fe}^{3+}$  g atom/g silica gel.

$$c = kp_0^{-3/2} \quad (3)$$

Hence, making use of the eqs. (1), (2), and (3),

$$r = kp_0^{1/2}(1 - a)^2 \quad (4)$$

where  $k$  is constant. On the other hand, a plot of logarithmic rate at 20% reaction extent against logarithmic initial concentration of PVC, shown in Figure 5, is linear, with a slope of about  $1/2$ , and this result well coincides with eq. (4).

Since the dehydrochlorination is a second-order process, the rate constants were calculated from eq. (5):

$$x/p_0(p_0 - x) = kt \quad (5)$$

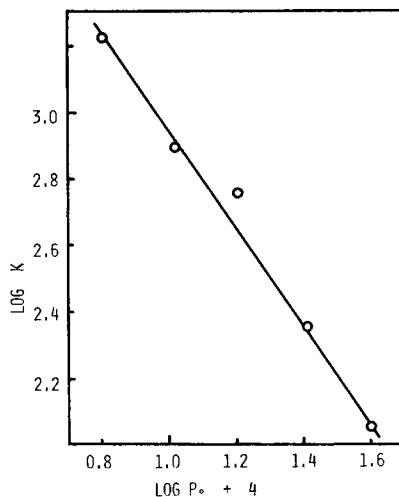


Fig. 4. Relation of rate constant and initial concentration of PVC. Iron oxide:  $1 \times 10^{-4}$  Fe<sup>3+</sup> g atom/g silica gel.

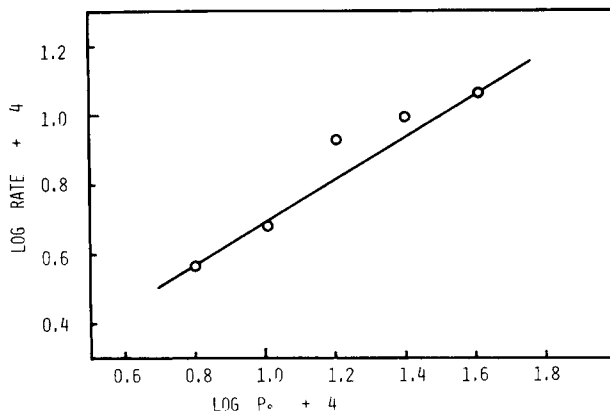


Fig. 5. Relation of rate and initial concentration of PVC at 20% reaction extent. Iron oxide:  $1 \times 10^{-4}$  Fe<sup>3+</sup> g atom/g silica gel.

where  $x$  is the evolved hydrogen chloride,  $p_0$  is the initial concentration of PVC,  $k$  is the rate constant, and  $t$  is the reaction time after an induction period. The results are tabulated in Table II with the activation energies obtained from the rate constants at different temperatures. In the nitrogen atmosphere, the values are reported to be as great as ours, for example, 34 kcal/mole by Arlman,<sup>11</sup> 39 kcal/mole by Hartman,<sup>12</sup> and 33 kcal/mole by Talamani.<sup>13</sup> Yoshinaga et al.<sup>14</sup> reported that the activation energy obtained from induction period of ignition was 16.6 kcal/mole for PVC containing 5% antimony oxide and 12 kcal/mole for PVC alone. But in an atmosphere of antimony chloride vapor, it was 22.9 to 17.0 kcal/mole, which varied with the amount of the chloride. Their results are not easily comparable with ours because of quite different experimental conditions.

**Dehydrochlorination of PVC with Various Iron Compounds.** In order to clarify a role of iron oxide in the dehydrochlorination of PVC, experiments

TABLE II  
Second-Order Rate Constants and Activation Energies for  
Dehydrochlorination of PVC in N<sub>2</sub> Flow<sup>a</sup>

Catalysts temperature, °C	Rate constants × 10 <sup>-3</sup> , mole <sup>-1</sup> hr <sup>-1</sup>					E <sub>a</sub> , kcal/mole
	182	200	227	253	271	
Silica gel	—	0.03	0.25	0.91	3.82	34.5
Iron oxide	0.07	0.19	—	2.50	4.40	24.0
Iron chloride	0.22	0.33	0.82	1.27	—	16.9

<sup>a</sup>Iron oxide: 1 × 10<sup>-5</sup> Fe<sup>3+</sup> g atom/g silica gel; iron chloride: 1 × 10<sup>-4</sup> Fe<sup>3+</sup> g atom/g silica gel.

were tried with various iron compounds. These were iron oxide, iron chloride, and reduced iron oxide. The results obtained at 200°C are shown in Figure 6. The rate is thus deduced as follows: iron chloride (air), iron oxide (air), iron oxide (N<sub>2</sub>), iron chloride (N<sub>2</sub>), reduced iron oxide (N<sub>2</sub>), silica gel (air), silica gel (N<sub>2</sub>). Parentheses show the atmosphere of the experimental conditions. These results prove that both iron and oxygen have a role in the dehydrochlorination of PVC.

**Infrared Spectra Measurement.** Infrared spectra of the polymer samples were taken before and after the reaction. Figure 7 demonstrates the differences between PVC degradation alone and those with iron oxide at 200°C for 2 hr in

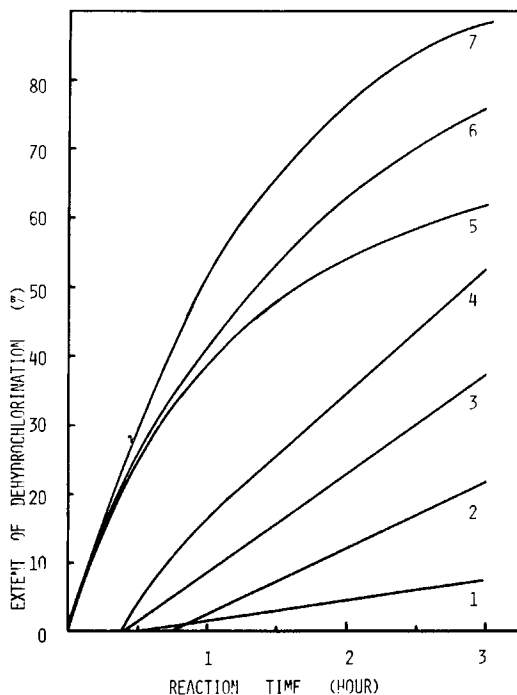


Fig. 6. Dehydrochlorination of PVC on various iron compounds at 200°C in N<sub>2</sub> or air flow: (1) silica gel (N<sub>2</sub>); (2) silica gel (air); (3) reduced iron oxide (N<sub>2</sub>); (4) iron chloride (N<sub>2</sub>); (5) iron oxide (N<sub>2</sub>); (6) iron oxide (air); (7) iron chloride (air). Fe: 1 × 10<sup>-4</sup> Fe<sup>3+</sup> g atom/g silica gel; PVC: 8.0 × 10<sup>-4</sup> mole monomer units.

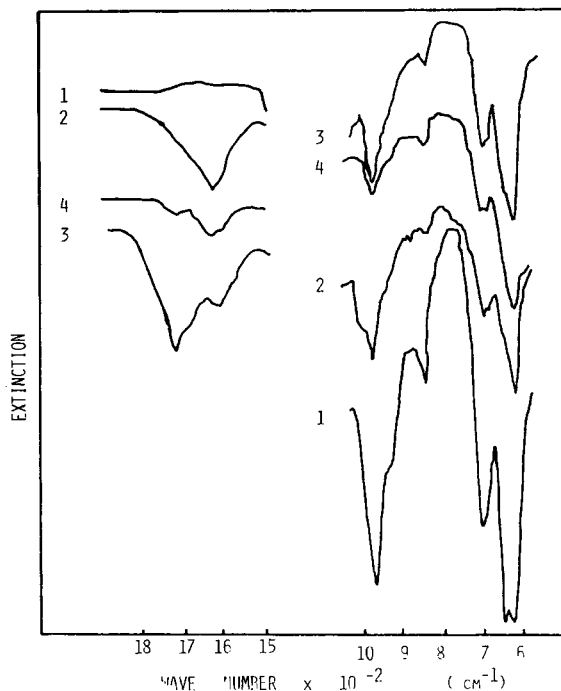
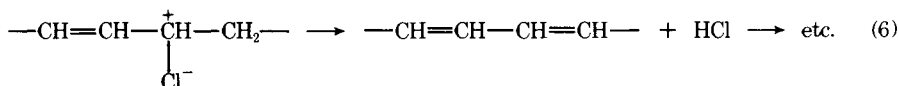


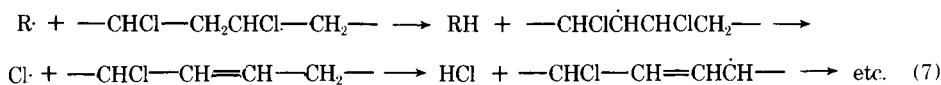
Fig. 7. Infrared spectra of PVC before (1) and after (2, 3, 4) heating at 200°C in N<sub>2</sub> or air flow: (1) PVC with iron oxide; (2) PVC (N<sub>2</sub>); (3) PVC (air); (4) PVC with iron oxide (N<sub>2</sub>).

nitrogen atmosphere. The most obvious difference between the two samples is the appearance of the strong absorption bands between 1840 and 1520 cm<sup>-1</sup>, identified as carbonyl and vinyl absorption bands.<sup>15</sup> The carbonyl band has its highest absorption at 1720 cm<sup>-1</sup>, indicating a ketonic group, which is also generated on the oxidation of PVC alone (see curve 3 in Fig. 7). Yoshinaga et al. obtained the same results on the degradation of PVC in the presence of antimony oxide in nitrogen atmosphere. These results suggest that the role of oxygen in the oxide on the dehydrochlorination process of PVC resembles that in the oxidation of PVC. Namely, carbonyl groups formed in PVC by oxygen in the oxide may induce a radical reaction during the dehydrochlorination.

To explain the effect of iron oxide on the dehydrochlorination of PVC, a mechanism should be considered. In the literature, two main mechanisms have been suggested for the reaction: a free-radical one<sup>16</sup> and an ionic one.<sup>17</sup> In the latter case, the reaction is initiated through allyl activation of adjacent chlorine as shown in the sequences of eq. (6):



A free-radical mechanism takes place as shown in eq. (7):

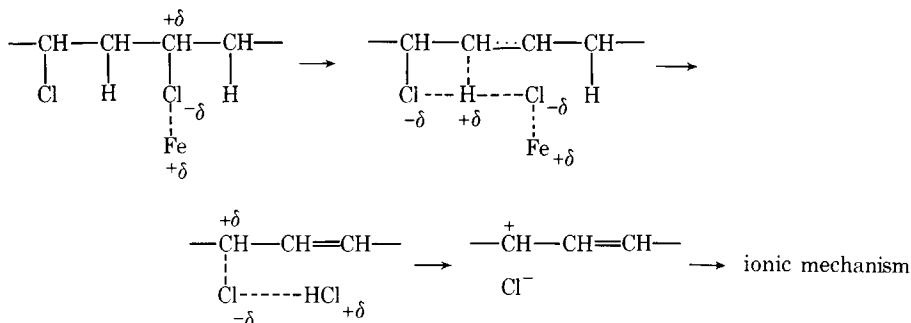


The initiating radical comes from a catalyst residue or is the result of oxidation.

The accelerating effect of oxygen and hydrogen chloride on the degradation of PVC has been explained on the basis of the above mechanism: oxygen eliminates tertiary hydrogen, and hydrogen chloride removes chloride atom. In order to stabilize PVC, on the other hand, it has been considered to remove evolved hydrogen chloride, to feed generating radicals immediately, or to prevent the growth of conjugated double bonds.<sup>18</sup> Therefore, the accelerating effect of the iron oxide must have somewhat of a role in the initiation process of the PVC degradation.

Mochida et al.<sup>19</sup> recently reported that solid acids catalyze the elimination reaction of haloethanes, and they suggested the following mechanism. The elimination reaction on solid acids takes place through an ionic mechanism consisting of abstraction of a chloride anion and a proton. As primary carbonium ions formed are unstable, they immediately decompose into olefins. Therefore, in the elimination of chlorine from PVC, iron oxide must also act in the same role as a solid acid.

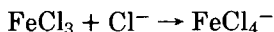
As mentioned regarding the degradation of PVC in the presence of many other metal oxides by Abu-Isa,<sup>20</sup> an iron atom in the oxide will attack an electronegative chloride atom in PVC and abstract it as a chloride anion. The reaction may proceed through an ionic mechanism as follows:



Furthermore, evolved hydrogen chloride reacts with iron oxide to form iron chloride which has been well known as one of Friedel-Crafts catalysts being useful for the introduction of alkyl groups into the carbon atom, including unsaturated bonds.<sup>21</sup> In our work, as shown in Figure 6, iron chloride accelerates the reaction and will probably act as Friedel-Crafts catalyst. These explanations were also made by Kelen et al.<sup>22</sup> and Dudley et al.<sup>1</sup> on the degradation of PVC in the presence of calcium oxide and zinc oxide, respectively.

In conclusion, it is reasonable to propose that iron oxide may electrically attract chloride atom to be easily eliminated from the polymer and that the reaction may proceed through an ionic mechanism.

A quite different behavior of iron oxide on the reaction is seen in the variation of its concentration as shown in Figure 2. The oxide accelerates the reaction at less than  $2 \times 10^{-4}$  Fe<sup>3+</sup> g atom/g silica gel that is, 4 Fe<sup>3+</sup>/Cl in PVC = 1, but the rate becomes slower with higher concentration. This behavior may be explained to take account of the formation of iron chloride. An iron atom can combine with three chloride atoms as in the following Friedel-Crafts reaction:





Therefore, in the case of the larger amount of iron than of chlorine in the polymer, most eliminated chlorine may be fed faster by iron than hydrogen chloride will appear in the gas phase by an unzipping reaction. But hydrogen chloride is eliminated by oxygen in the oxide and appears in the gas phase at a smaller rate. On the other hand, when the amount of iron is smaller than that of chlorine, after a short induction period hydrogen chloride appears in the gas phase at a higher rate than in the case of PVC alone.

The role of metal oxide in the dehydrochlorination of PVC must be well proven if the same experiments over many other metal oxides are compared to the results of the Friedel-Crafts reaction. This work is currently in progress in this laboratory.

## CONCLUSIONS

Dehydrochlorination rate of PVC depends on a half-order of the initial concentration of PVC and a first order of iron oxide in the smaller concentration than that of PVC. The mechanism of the dehydrochlorination of PVC containing iron oxide can be proposed as follows: the initial step takes place mainly via an ionic mechanism by iron and somewhat via a radical mechanism by oxygen in the oxide, and propagates like an unzipping reaction.

## References

1. M. A. Dudley and D. A. Smith, *S. C. I. Monograph No. 26*, Society of Chemical Industry, London, 1967, p. 49.
2. P. Dunn and B. C. Ennis, *J. Appl. Polym. Sci.*, **14**, 355 (1970).
3. G. A. Rasuvaev, L. S. Troiskaya, and B. B. Troiskii, *J. Polym. Sci. A-1*, **9**, 2673 (1971).
4. G. Briggs and N. F. Wood, *J. Appl. Polym. Sci.*, **15**, 25 (1971).
5. S. van der Ven and W. F. de Wit, *Angew. Makromol. Chem.*, **8**, 143 (1969).
6. R. Nagatomi and Y. Saeki, *Kogyo Kagaku Zasshi*, **65**, 393 (1962).
7. A. Reiche, A. Gimm, and G. Mücke, *Kunststoffe*, **52**, 398 (1962).
8. S. Okazaki, *Enbi To Porima*, **12**, 17 (1972).
9. Catalysis Society of Japan, Ed., *Shokubai Kagaku Koza*, Vol. 5, Chijin Shokan & Co., Ltd., Tokyo, 1967, p. 88.
10. I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, Macmillan, London, 1936, p. 545.
11. E. J. Arlman, *J. Polym. Sci.*, **12**, 547 (1954).
12. A. Hartman, *Kolloid-Z.*, **139**, 146 (1954); *ibid.*, **149**, 67 (1956).
13. G. Talamani and G. Pezzin, Symposium über Makromoleküle, IUPAC, Wiesbaden, Oct. 1959, Sec. 4, A, p. 1.
14. S. Yoshinaga, M. Matsumoto, and T. Nagaishi, *Nippon Kagaku Kaishi*, 175 (1973).
15. E. O. Krafts, T. B. Zavarova, G. T. Fedoseeva, and E. S. Minsker, *Vysokomol. Soedin.*, **13**, 899 (1971).
16. J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **70**, 2767 (1948).
17. B. Baum and L. H. Wartman, *J. Polym. Sci.*, **28**, 537 (1958).
18. M. B. Neiman, *Starenie i Stabilizatsiya Polimerob*, Nauka, Moscow, 1964, p. 134.
19. I. Mochida, J. Take, Y. Saito, Y. Yoneda, and T. Seiyama, *J. Catalysis*, **18**, 33 (1970).
20. I. A. Abu-Isa, *J. Polym. Sci. A-1*, **10**, 881 (1972).
21. *Encyclopaedia Chimica*, Vol. 8, Kyoritsu Shuppan, Tokyo, 1963, p. 8.

Received August 5, 1975

Revised March 19, 1976