Reclamation of Vulcanized Rubbers by Chemical Degradation. IX. Oxidative Degradation of *cis*-1,4-Polyisoprene by Phenylhydrazine-Iron(II) Chloride System

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Degradation of *cis*-1,4-polyisoprene by phenylhydrazine–iron(II) chloride system was investigated in benzene solution at 30 °C in the air. Separate use of the two chemicals was much less effective for degradation. The number of chain scission was found to depend upon only the amount of phenylhydrazine, independent of that of iron(II) chloride, indicating that phenylhydrazine plays the leading part of the phenylhydrazine–iron(II) chloride system in the degradation. When iron(III) chloride was used instead of iron(II) chloride, the degradation became slower, but the number of chain scission was not significantly affected.

Reclaiming processes are well established for natural rubber scrap, and the reclaimed matter can be used in the compounding of new rubber products. However, devulcanization and depolymerization is performed by heating at *ca.* 200 °C, which is not desirable from an economical point of view, for several hours under pressure in the presence of cheap oil and organic chemicals. Moreover, the process is limited to natural rubber scrap. The devulcanization and depolymerization stage should be modified for synthetic rubber scrap. Natural rubber vulcanizates behave well under the present reclaiming conditions, since they soften with heat, but it is difficult to reclaim synthetic rubber vulcanizates. As an example, styrene-butadiene rubber (SBR) vulcanizates, after initial softening by heating, quickly harden on further heating.

The phenylhydrazine–iron(II) chloride system is a good reagent for the reclamation of scrap tire[1] and various types of synthetic rubber vulcanizates[2] during several hours at room temperature. Useful elastomers can be obtained by the vulcanization of these reclaimed product. Devulcanization and depolymerization stage of the new reclaiming procedure was shown to be an oxidative degradation of vulcanized rubbers by the atmospheric oxygen.[3] In the presence of iron(II) chloride, phenylhydrazine rapidly absorbs an equimolar amount of oxygen, evolving an equimolar amount of nitrogen.[4] When *cis*-1,4-polyisoprene was added to the reaction mixture, additional oxygen absorption was observed, the molecular weight of polymer decreasing during the course of additional oxygen absorption. The scission efficiency based on the additionally absorbed oxygen was found to be much higher than that for autoxidation of natural rubber. The high scission efficiency seems to be the source of the strong ability of the phenylhydrazine–iron(II) chloride system as a reagent for the reclamation of vulcanized rubbers. In this work, we have investigated the mechanism of the degradation, with attention focussed on the dependence of the number of chain scission upon the composition of the phenylhydrazine–iron(II) chloride system in the degradation.

Experimental

Materials. *cis*-1,4-Polyisoprene (IR-2200, Japan Synthetic Rubber Co., Ltd.) was masticated at room temperature for 20 min, and dissolved in benzene. The gel was removed by filtration, and the soluble polymer recovered by pouring the filtrate into a large excess of methanol was purified by reprecipitation, followed by drying *in vacuo* at room temperature. Benzene was purified by washing with sulfuric acid. After repeated washing with water, it was dried with calcium chloride, then refluxed over calcium hydride and distilled. Commercial phenylhydrazine, iron(II) chloride, anhydrous iron(III) chloride, methanol, and other chemicals were used without further purification. Thermogravimetric analysis of the iron(II) chloride indicated the presence of 40.8 wt% of water.

Procedure. Viscosity measurements of degraded and undegraded *cis*-1,4-polyisoprene solutions were carried out in benzene at 30°C with an Ubbelohde-type dilution viscometer.

The degradation reaction was carried out in a round-bottomed 100 ml flask equipped with a mechanical stirrer in the air. Phenylhydrazine was added *via* a hypodermic syringe to a mixture of 0.5 g of *cis*-1,4-polyisoprene in 48.0 ml of benzene and a prescribed amount of iron(II) chloride or iron(III) chloride in 2.0 ml of methanol at 30 °C under stirring. Part of the reaction mixture was taken out, and the intrinsic viscosity of the solution was immediately determined at 30 °C using Baker's equation[5]

$$[\eta] = a(\eta_r^{1/a} - 1)/c,$$

parameter *a* for the equation was determined to be 3 prior to experiments on degradation. The dependence of the intrinsic viscosity upon the reaction time was plotted. After the decrease of viscosity became constant, the residue of the reaction mixture was poured into a large excess of methanol, and the polymer was recovered from the solution. The recovered polymer was dried *in vacuo* at room temperature, and the number average molecular weight was determined based on the intrinsic viscosity in benzene solution at 30 °C using the viscosity—molecular weight relationship.[4] The number of chain scission was determined from the decrease in the number average molecular weight during the course of degradation.

Results and Discussion

The relation between the intrinsic viscosity of the reaction mixture determined by use of Baker's equation and the reaction time for the degradation of *cis*-1,4-polyisoprene by the phenylhydrazine–Iron(II) chloride system in benzene at 30 °C, is shown in Fig. 1. In the absence of both chemicals, the intrinsic viscosity did not significantly change at 30 °C within 30 min. Curve 1

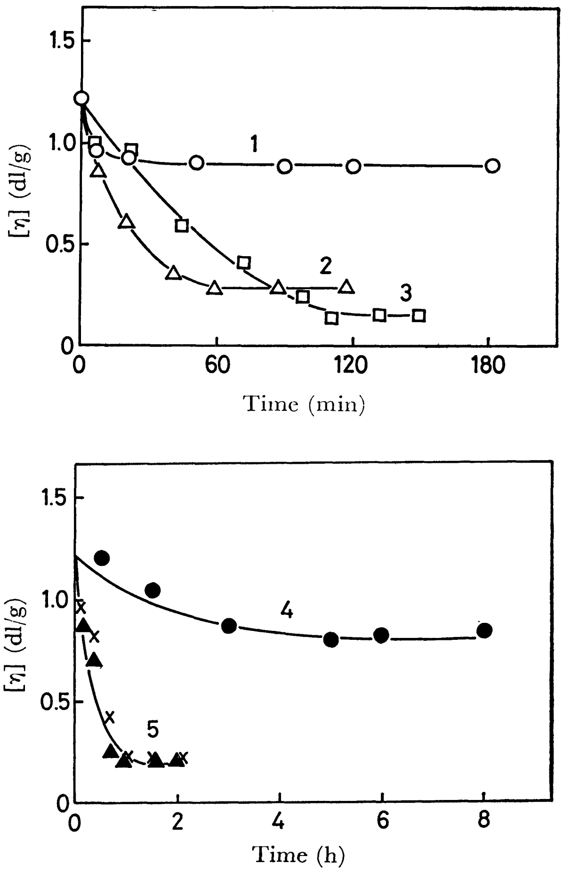

Fig. 1. Time dependence of the intrinsic viscosity of the reaction mixture for the degradation of *cis*-1,4-polyisoprene by the phenylhydrazine–iron(II) chloride system in benzene solution at 30 °C under the atmosphere of air. Conditions: *cis*-1,4-polyisoprene, 0.5 g; benzene, 48.0 ml; methanol, 2.0 ml. (○) iron(II) chloride, 0.10 mmol; phenylhydrazine, 0 mmol. (△) iron(II) chloride, 0.10 mmol; phenylhydrazine, 0.45 mmol. (□) iron(II) chloride, 0.10 mmol; phenylhydrazine, 2.00 mmol. (●) iron(II) chloride 0 mmol; phenylhydrazine, 1.00 mmol. (▲) iron(II) chloride, 0.02 mmol; phenylhydrazine, 1.00 mmol. (×) iron(II) chloride, 0.10 mmol; phenylhydrazine, 1.00 mmol.

was obtained in the presence of iron(II) chloride but in the absence of phenylhydrazine, whereas curves 2 and 3 were obtained in the presence of both compounds. A comparison of the curves indicates that the presence of phenylhydrazine considerably increases the rate of the degradation. Curves 2 and 3 show that degradation was almost complete within 2 h, the number of chain scission increasing with the amount of phenylhydrazine.

Curve 4 was obtained in the presence of phenylhydrazine but in the absence of iron(II) chloride, whereas curve 5 was obtained in the presence of both compounds. We see that separate use of phenylhydrazine and iron(II) chloride is less effective for the degradation of the polymer. This is in line with the fact that separate use of the two compounds is much less effective for the reclamation of scrap tire.

A comparison of curves 4 and 5 indicates that the presence of iron(II) chloride remarkably increases the rate of the degradation. However, curve 5 shows that the number of chain scission is not sensitive to the amount of iron(II) chloride.

After the decrease in the intrinsic viscosity of the reaction mixture (Fig. 1) ceased, the degraded polymer was recovered from the reaction mixture. Based on the number average molecular weight of the degraded and undegraded polymer, the number of chain scission was calculated. The number of chain scission versus the amount of phenylhydrazine is plotted in Fig. 2. Curve A was obtained for the degradation by the phenylhydrazine–iron(II) chloride system. Curve B was obtained for the degradation in the presence of phenylhydrazine but in the absence of iron(II) chloride. Fig. 2 indicates that iron(II) chloride considerably increases not only the rate of the degradation but also the number of chain scission. However, the number of chain scission depends upon only the amount of phenylhydrazine, independent of that of iron(II) chloride. This indicates that phenylhydrazine plays the principal part in the phenylhydrazine–iron(II) chloride system for the degradation of the polymer. Iron(II) chloride seems to be a catalyst in the oxidative degradation of the polymer by phenylhydrazine.

Phenylhydrazine is an accelerator for the mastication of rubber.[6,7] Mastication and our new method of reclamation appear to be closely related to each other. Phenylhydrazine was reported to be oxidized on exposure to free oxygen.[8] Iron(II) chloride seems to accelerate the oxidation.[4] Analysis of the products of the reaction of phenylhydrazine with iron(II) chloride under the atmosphere of oxygen and air showed the formation of benzene, phenol, and biphenyl.[4] Thus it seems that the formation of phenyl radical by the oxidation of phenylhydrazine is accelerated by iron(II)

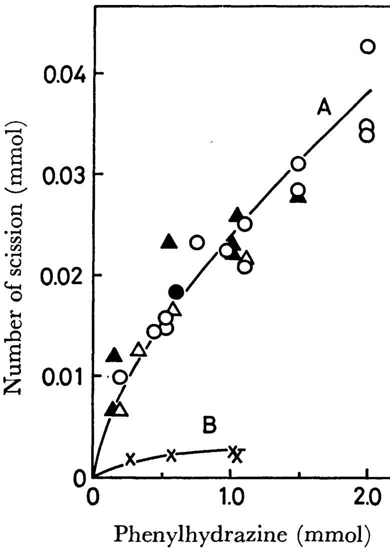

Fig. 2. Plot of the number of chain scission versus the amount of phenylhydrazine for the degradation of *cis*-1,4-polyisoprene by the phenylhydrazine–iron(II) chloride system in benzene solution at 30 °C under the atmosphere of air. Conditions: *cis*-1,4-polyisoprene, 0.5 g; benzene, 48.0 ml; methanol, 2.0 ml; iron(II) chloride, (●) 0.20 mmol, (○) 0.10 mmol, (▲) 0.02 mol, (△) 0.004 mmol, (×) 0 mmol.

chloride. The phenyl radical and related reactive species might attack *cis*-1,4-polyisoprene, causing the degradation of the polymer. Thus the number of the chain scission of the polymer considerably increases with the presence of iron(II) chloride, but not with the amount of iron(II) chloride.

Color change takes place during the course of degradation, showing the change of iron(II) to iron(III). In connection with this the degradation of *cis*-1,4-polyisoprene by the phenylhydrazine–iron(III) chloride system was also studied. The relation between the intrinsic viscosity of the reaction mixture determined by use of Baker's equation and the reaction time for the degradation in benzene at 30 °C, is shown in Fig. 3.

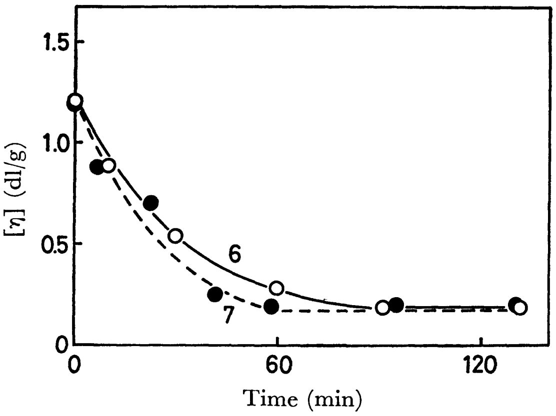

Fig. 3. Time dependence of the intrinsic viscosity of the reaction mixture for the degradation of *cis*-1,4-polyisoprene by the phenylhydrazine–iron(II) chloride system and the phenylhydrazine–iron(III) chloride system in benzene solution at 30 °C under the atmosphere of air. Conditions: *cis*-1,4-polyisoprene, 0.5 g; benzene, 48.0 ml; methanol, 2.0 ml. (●) iron(II) chloride, 0.02 mmol; phenylhydrazine, 1.00 mmol. (○) iron(III) chloride, 0.02 mmol; phenylhydrazine, 1.00 mmol.

Curve 6 was obtained for the degradation by the phenylhydrazine–iron(III) chloride system, and curve 7 for the degradation by the phenylhydrazine–iron(II) chloride system. Iron(III) chloride also considerably increases the rate of degradation of the polymer by phenylhydrazine. However, the degradation becomes slower when iron(III) chloride is used instead of iron(II) chloride, as shown in Fig. 3. This is in line with the fact that phenylhydrazine–iron(III) chloride system is less effective than the phenylhydrazine–iron(II) chloride system in the reclamation of scrap tire.1) The number of chain scission versus the amount of phenylhydrazine for the degradation of the polymer by the phenylhydrazine–iron(III) chloride system is plotted in Fig. 4. Curve D was obtained in the absence of iron(III) chloride. We see that iron(III) chloride also considerably increases not only the rate of the degradation but also the number of chain scission. However, the number of chain scission depends only upon the amount of phenylhydrazine and not upon the amount of iron(III) chloride. Phenylhydrazine also seems to play the principal role in the phenylhydrazine–iron(III) chloride system in the degradation of the polymer. A comparison of curve C in Fig. 4 with curve A in Fig. 2 leads us to conclude that the efficiency of the chain scission based on the amount of phenylhydrazine is in the same order of magnitude regardless of whether iron(II) chloride or iron(III) chloride is used. Iron(II) chloride and iron(III) chloride could recycle during the degradation.

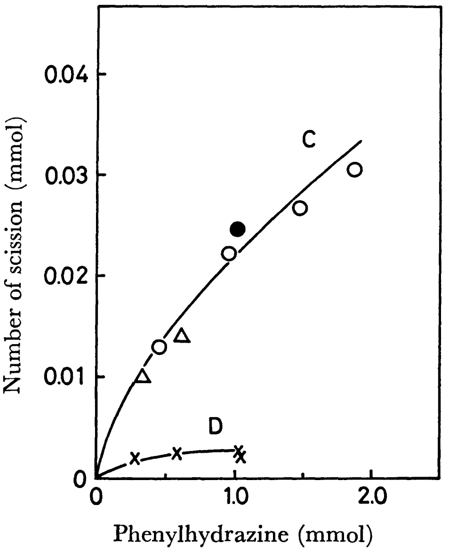

Fig. 4. Plot of the number of chain scission versus the amount of phenylhydrazine for the degradation of *cis*-1,4-polyisoprene by the phenylhydrazine–iron(III) chloride system in benzene solution at 30 °C under the atmosphere of air. Conditions: *cis*-1,4-polyisoprene, 0.5 g; benzene, 48.0 ml; methanol, 2.0 ml; iron(III) chloride, (○) 0.10 mmol, (△) 0.05 mmol, (●) 0.02 mmol, (×) 0 mmol.

The results of the present and previous works suggest a reasonable interpretation of the mechanism of reaction. Experimental evidences are as follows:

1. The infrared spectra of the soluble fractions obtained from various rubber vulcanizates by the treatment with phenlhydrazine–iron(II) chloride system show the presence of carbonyl and hydroxyl groups.2)

2. The treatment of vulcanized *cis*-1,4-polyisoprene by the phenylhydrazine–iron(II) chloride system in the air reduces the effective network chain density of the vulcanizates, giving a soluble fraction of rubber. Treatment in sealed vessels in the absence of oxygen gives no soluble fraction, not decreasing the effective network chain density.3)

3. From the decrease of the effective network chain density and the increase of the soluble fraction, it is concluded that the network chain of the vulcanized rubber undergoes a severance reaction by the phenylhydrazine–iron(II) chloride system in the order: polysulfide linkage>monosulfide linkage>carbon-carbon crosslink.3)

4. Although Chattaway8) indicated that phenylhydrazine is oxidized on exposure to free oxygen, it has been found that iron(II) chloride considerably accelerates oxidation.4)

5. In the presence of iron(II) chloride under air or

oxygen atmosphere, phenylhydrazine rapidly absorbs an equimolar amount of oxygen, evolving an equimolar amount of nitrogen.[4] Gas chromatographic analysis of the reaction mixture shows the presence of benzene, phenol, and biphenyl in 37, 35—60, and 4—8% yields, respectively, based on phenylhydrazine.[4] When *cis*-1,4-polyisoprene is added to the reaction mixture, additional absorption of oxygen is observed, the molecular weight of the polymer decreasing during course of additional oxygen absorption.[4]

6. Under nitrogen atmosphere, the reaction of phenylhydrazine with iron(II) chloride in benzene solution rapidly gives a 2:1 complex, a white solid which is relatively stable under nitrogen but rapidly decomposes in the presence of oxygen; in the air, it is a very effective reagent for the reclamation of vulcanized rubbers.[9]

7. Separate use of phenylhydrazine and iron(II) chloride is much less effective for the degradation of *cis*-1,4-polyisoprene. However, the number of chain scission depends only upon the amount of phenylhydrazine and not upon that of iron(II) chloride.

8. When iron(III) chloride is used instead of iron(II) chloride, the degradation becomes slower, the number of chain scission not being significantly affected.

9. Color change takes place during the course of degradation, showing the change of iron(II) to iron(III).

We postulate the following mechanism for the reclamation of vulcanized rubbers by the phenylhydrazine–iron(II) chloride system. Devulcanization and the depolymerization stage of the new reclaiming procedure is an oxidative degradation of vulcanized rubber by atmospheric oxygen. The function of the phenylhydrazine–iron(II) chloride system is essentially the acceleration of autoxidation of vulcanized rubber.

$$2\mathrm{PhNHNH_2} + \mathrm{FeCl_2} \longrightarrow \underset{\mathbf{1}}{[2\mathrm{PhNHNH_2}\cdot\mathrm{FeCl_2}]}, \qquad (1)$$

$$\mathbf{1} \xrightarrow{\mathrm{O_2}} \underset{\mathbf{2}}{\mathrm{Ph}\cdot} + \underset{\mathbf{3}}{\mathrm{PhOOH}} + \underset{\mathbf{4}}{\mathrm{HOO}\cdot} + \mathrm{N_2}, \qquad (2)$$

$$\mathbf{2} \longrightarrow \begin{cases} \xrightarrow{\mathrm{RH}} \mathrm{R}\cdot + \mathrm{PhH} & (3) \\ \xrightarrow{\mathbf{2}} \mathrm{PhPh} & (4) \\ \xrightarrow{\mathrm{O_2}} \mathrm{PhOO}\cdot \xrightarrow{\mathrm{RH}} \mathrm{R}\cdot + \mathbf{3}, & (5) \end{cases}$$

$$\mathbf{3} \xrightarrow{\mathrm{Fe^{2+}}} \underset{\mathbf{5}}{\mathrm{PhO}\cdot} + \mathrm{Fe^{3+}} + \mathrm{OH^-}, \qquad (6)$$

$$\mathbf{4} \xrightarrow{\mathrm{RH}} \mathrm{R}\cdot + \mathrm{H_2O_2}, \qquad (7)$$

$$\mathbf{5} \xrightarrow{\mathrm{RH}} \mathrm{R}\cdot + \mathrm{PhOH} \qquad (8)$$

$$\mathrm{R}\cdot \xrightarrow{\mathrm{O_2}} \mathrm{ROO}\cdot \xrightarrow{\mathrm{RH}} \mathrm{ROOH} + \mathrm{R}\cdot, \qquad (9)^{10)}$$

$$\mathrm{Fe^{3+}} \xrightarrow{\mathrm{ROOH}} \mathrm{Fe^{2+}} + \mathrm{ROO}\cdot + \mathrm{H^+}, \qquad (10)$$

$$\mathrm{Fe^{3+}} \xrightarrow{\mathrm{PhOOH}} \mathrm{Fe^{2+}} + \mathrm{PhOO}\cdot + \mathrm{H^+}, \qquad (11)$$

$$\mathrm{R}\cdot \xrightarrow{\mathrm{O_2}} \mathrm{ROO}\cdot \longrightarrow \mathrm{R'CHO} + \mathrm{HOR''}, \qquad (12)^{10)}$$

Where RH represents rubber molecule. In the reclamation of sulfur vulcanizate, the severance of crosslink predominates scission of the main chain.[3] In such a case, we should take into consideration the following mechanism[11] proposed for the severance of monosulfide linkage of the vulcanizate.

$$\mathrm{RSR} \xrightarrow{\mathbf{3}} \mathrm{RSOR} + \mathrm{PhOH}, \qquad (13)^{11)}$$

$$\mathrm{RSR} \xrightarrow{\mathrm{H_2O_2}} \mathrm{RSOR} + \mathrm{H_2O}, \qquad (14)$$

$$\mathrm{RSOR} \longrightarrow \mathrm{R'SOH} + \mathrm{R''H}, \qquad (15)^{11)}$$

where RSR represents the crosslinked part of sulfur vulcanizate. Equations 12 and 15 respectively denote the degradation of main chain and the severance of sulfur crosslink of vulcanized rubber.

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