

## Tetrachlorinated Rubber: The Addition of Carbon Tetrachloride to 1,4-Polybutadiene

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### Synopsis

The iron chloride-catalyzed radical chain addition of carbon tetrachloride to 1,4-polybutadiene has been studied. Transparent film forming nonflammable polymers are obtained which contain 50-55% chlorine. Cyclization appears to accompany the addition of carbon tetrachloride as an integral part of the radical reaction.

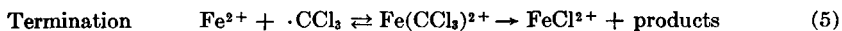
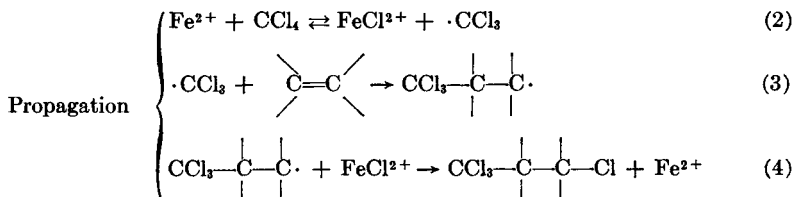
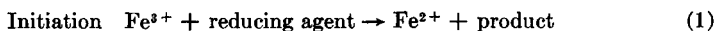
### INTRODUCTION

The reaction of carbon tetrachloride with olefins is among the most studied radical chain processes,<sup>1</sup> but its addition to polybutadiene or polyisoprene has not yet been reported. Although the corresponding adducts are chlorinated polymers of considerable potential interest, the fact that internal olefins react poorly with carbon tetrachloride<sup>2</sup> may account for the scarcity of work on its addition to the above polymers.

The addition of bromotrichloromethane to natural rubber has been described.<sup>3</sup> The resulting adduct was nonflammable and film forming, but unstable and eliminated hydrobromic acid.

It was shown in this laboratory,<sup>4</sup> that iron- and copper chlorides catalysis enables the addition of carbon tetrachloride to almost any olefin. This method was therefore applied to unsaturated polymers.

The proposed chain mechanism is:<sup>4,5</sup>



The present work is concerned with the effect of variables such as temperature, the nature of the solvent, and concentration of the iron chloride catalyst and initiator on the course of the addition of carbon tetrachloride to 1,4-polybutadiene and a butadiene-styrene copolymer. Attention was

paid to loss of unsaturation in excess to that calculated from the chlorine content of the product, which is probably due to cyclization.

### Preliminary Work

Benzoin was used as the initiator throughout this work. The combination of ferric chloride and benzoin steadily supplies ferrous ion during the addition of carbon tetrachloride and gives higher conversions to the addition product than ferrous chloride alone.<sup>4</sup> An initially high concentration of ferrous chloride leads to an enhanced rate of termination [eq. (5)].<sup>5</sup> Anhydrous ferric chloride caused early gelation and discoloration of the reaction product. The hexahydrate was much better in this respect, and also gave much higher rates of addition than copper chloride.

Natural rubber gave adducts with a chlorine content of 40–42%, forming nonflammable films of a poor quality. Extensive degradation occurred during carbon tetrachloride addition, and the product eliminated hydrochloric acid on heating above 100°C. 1,4-Polybutadiene degraded less during reaction and adducts were obtained containing 50–55% chlorine, ("tetrachlorinated rubber" or TCR) that were much more stable thermally.\*

A cosolvent was needed for the homogeneity of the system. Methanol, ethanol, isopropanol, tetrahydrofuran, dimethyl sulfoxide, acetonitrile and diglyme gave either products with a low chlorine content or early gelation. Dimethyl formamide (DMF) and *n*-butanol were finally selected, although the latter reacts with carbon tetrachloride in the presence of iron chloride, producing a small amount of hydrochloric acid.

## EXPERIMENTAL

### Materials

From the American Rubber and Chemical Co. 95% *cis* 1,4-polybutadiene was obtained. Polybutadiene containing 36% *cis*-, 56% *trans*-, and 8% 1,2 units was from the International Synthetic Rubber Co. Ltd. of England. A copolymer of 60% butadiene and 40% styrene (w/w) was supplied by the Diamond Alkali Co. Carbon tetrachloride was a Fluka product (puriss). *n*-Butanol was distilled before use. Dimethylformamide was a BDH Laboratory Reagent. Ferric chloride hexahydrate was a Fisher Certified Reagent. Benzoin was recrystallized from carbon tetrachloride, mp. 137°C.

### Procedure

A solution of ferric chloride hydrate and benzoin in 30 g cosolvent and 220 g of a 5% or 1% solution of polymer in carbon tetrachloride was mixed, stirred slowly and refluxed at 78°C by heating in a bath. At regular time

\* Thermal degradation at 180°C was followed by titration of evolved hydrochloric acid.

intervals, 10 ml samples were withdrawn, diluted with 15 ml methylene chloride, filtered through glass wool, and run slowly into 250 ml stirred methanol. The precipitated polymer was separated from supernatant liquor by suction, washed with methanol, kept under methanol during 12 hr, again filtered, washed and dried at 1 mm pressure without heating, until constant weight.

### Analytical

The dried samples were analyzed for chlorine by the Schöniger method.<sup>6</sup> Unsaturation was determined by a modification of the method of Lee, Kolthoff and Johnson.<sup>7</sup> About 40 mg sample was dissolved in 20 ml chloroform (analytical grade).<sup>\*</sup> In carbon tetrachloride 20 ml 0.1 M iodine monochloride was added, and the resulting mixture kept in the dark during 1.5 hr. Iodine was titrated with 0.1 M thiosulfate after addition of 40 ml 0.5 M aqueous acetic acid and 1 g potassium iodide. In this way values for unsaturation (expressed in mole % double bonds per polymer repeat unit) were obtained which compared well with those found by the original method.<sup>7</sup> We adopted this method although we are aware of its limitations.<sup>8</sup> Reasonable trends of loss of unsaturation during the addition of carbon tetrachloride were obtained. This was frequently not the case with NMR spectroscopy, which has been advocated for the determination of residual unsaturation in hydrochlorinated polyisoprene.<sup>8</sup> This may be due to the involved structure of our carbon tetrachloride adducts, units resulting from linear addition of carbon tetrachloride appearing along with cyclic structures, each with its stereoisomers<sup>4,9</sup> (see below).

Relative viscosities of 1% solutions of TCR in toluene were determined at 25°C in an Ostwald viscometer and number average molecular weights in an automatic osmometer (Hallikainen Instruments, Berkeley, California, U.S.A.) in the same solvent at 36°C.

## RESULTS AND DISCUSSION

### Effect of Temperature

Increasing the temperature strongly accelerated the rate of addition of carbon tetrachloride, but the maximum chlorine content remained around 50%. With 2 mole % ferric chloride hexahydrate and benzoin (in butanol) per polymer repeat unit, this was reached after 15 min at 120°C, 30 min at 110°C, 1 hr at 90°C and 2 hr at 78°C.

### Viscosity, Molecular Weight and Degradation

Table I shows the changes in relative viscosity of TCR's during the reaction at 78°C (reflux temperature) under various conditions. Below 40% chlorine, the products are insoluble in toluene, and therefore  $\eta_{rel}$

<sup>\*</sup> Samples containing less than 40% chlorine had to be dissolved immediately after drying. They became insoluble on standing, even under argon.

TABLE I  
Relative Viscosity of TCR after 2 and 7 Hr Reaction

Cosolvent	$\eta_{rel.}$ after	
	2 hr	7 hr
Butanol <sup>a</sup>	1.74	1.52
Butanol <sup>b</sup>	1.84	1.82
DMF <sup>a</sup>	1.89	1.76
DMF <sup>b</sup>	2.69	2.67
DMF <sup>c</sup>	2.13	2.06
DMF <sup>d</sup>	2.20	2.05

<sup>a</sup> Reflux, rapid stirring.

<sup>b</sup> In a sealed ampoule.

<sup>c</sup> Reflux under argon, slow stirring.

<sup>d</sup> Reflux, slow stirring.

refers to samples taken after 2 hr reaction, when the chlorine content was already 45% and increased only slightly afterwards. The viscosity of the TCR's decreased with time, indicating some degradation, probably caused by stirred-in air.

TABLE II  
Relative Viscosities and Degrees of Polymerization of TCR Containing  
49-50% Cl from *cis*-1,4-Polybutadiene (D.P. 2820,  $\eta_{rel.}$ :4.92)

Cosolvent	Reaction	$\eta_{rel.}$	DP
	Temp. °C		
Butanol	78 <sup>a</sup>	1.64	1610
Butanol	78 <sup>a</sup>	1.69	1620
Butanol	110 <sup>b</sup>	1.80	1710
DMF	78 <sup>a</sup>	1.83	1740
DMF	78 <sup>b</sup>	2.71	2260

<sup>a</sup> Under reflux.

<sup>b</sup> In a sealed ampoule.

Table II shows the correlation between relative viscosity and molecular weight of TCR samples of 49-50% chlorine content, prepared under various conditions.

There is some degradation during the addition, but the decrease in DP of starting material to product is never more than 1.75:1.

### Effect of Benzoin/Ferric Chloride Ratio

With 20 mole % benzoin as initiator per polymer repeat unit, the concentration of ferric chloride could be changed by a factor of 10 without affecting the rate of carbon tetrachloride addition (Fig. 1, *a*, *b* and *c*). With 2 mole % benzoin, however, an increased concentration of ferric chloride gave an unexpected decrease in the rate of addition (Fig. 1, *a*, *d* and *e*).

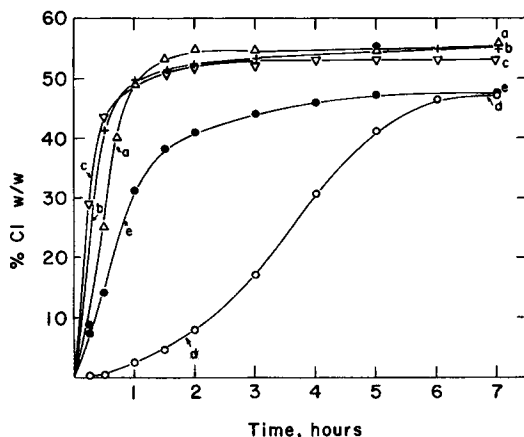
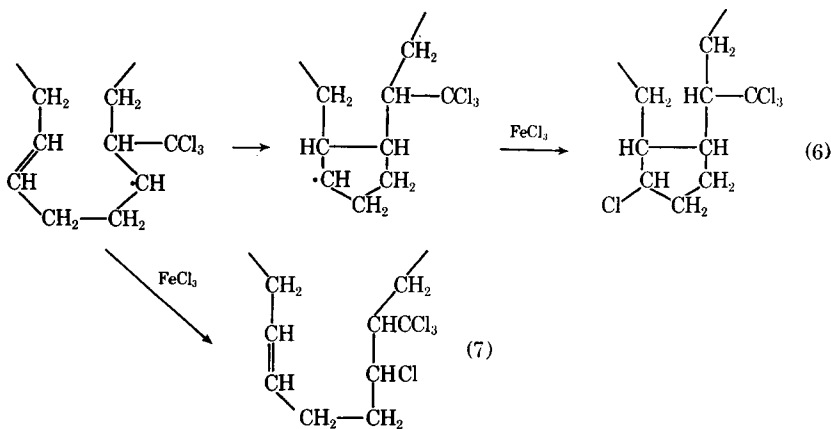


Fig. 1. Addition of carbon tetrachloride to 1,4-polybutadiene. Cosolvent: *n*-butanol: (a) 20 mole %  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 20 mole % benzoin per polymer repeat unit; (b) 6 mole %  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 20 mole % benzoin per polymer repeat unit; (c) 2 mole %  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 20 mole % benzoin per polymer repeat unit; (d) 20 mole %  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 2 mole % benzoin per polymer repeat unit; (e) 0.5 mole %  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 2 mole % benzoin per polymer repeat unit.

### Cyclization

During the reaction with *cis*-1,4-polybutadiene, much more unsaturation disappeared than was calculated from the chlorine content, assuming addition of one mole carbon tetrachloride per double bond. (For a typical case, see Fig. 2.) Polybutadiene having 36% *cis*-, 56% *trans*-, and 8% 1,2-units gave the same result.

If a compound radical obtained from addition of a trichloromethyl radical to a double bond of the polymer attacks a neighbouring double bond, cyclization results [eq. (6)]. The spacing of the double bonds is such, that either five- or six-membered rings are possible. Reaction of the compound radical



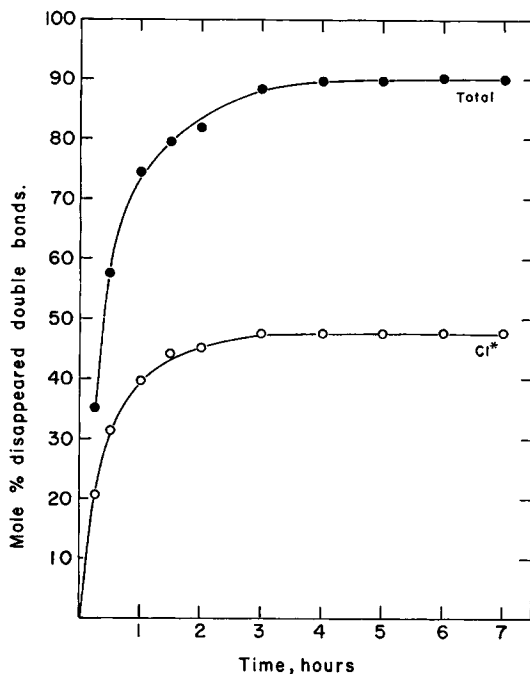


Fig. 2. Addition of carbon tetrachloride to 1,4-polybutadiene. Cosolvent: *n*-butanol: (2 mole %  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 20 mole % benzoin per polymer repeat unit). Cl\*: calculated from chlorine content.

with ferric chloride leads to linear addition [eq. (7)]. (If this were the only reaction, there should be no difference between disappearance of unsaturation as calculated from chlorine content and found by titration.)

In order to change the competitive power of ferric chloride, we varied its ratio with respect to polybutadiene by a factor of 40. As calculated from chlorine content 0.5 mole % ferric chloride per polymer repeat unit gave 37% reacted double bonds, and 84% by titration (47% unaccounted-for), whereas 20 mole % ferric chloride gave 51% reacted double bonds from chlorine content and 89% by titration (38% unaccounted-for). Polybutadiene solutions of 5% and 1% gave similar results.

Reaction of carbon tetrachloride with a butadiene copolymer in which the 1-5 sequence of double bonds was interrupted by the incorporation of 35 mole % styrene gave 49% reacted double bonds as calculated from chlorine content and 78% by titration (29% unaccounted-for).

The above results indicate that inefficient loss of unsaturation is mainly caused by cyclization. The parallel rise in unaccounted-for double bonds and in consumed double bonds as calculated from chlorine content (Fig. 2) points in the same direction.

This admittedly indirect evidence for cyclization is in accord with the results of Brace, who studied the addition of carbon tetrachloride to 1,6-heptadiene under iron chloride catalysis.<sup>9</sup> He found 63% addition through

cyclization and only 20% linear addition. Cyclization is the intramolecular analog of telomer formation in addition of carbon tetrachloride to a monoolefin such as 1-butene. Yet, in the latter case only 1:1 adduct is formed under the same conditions.<sup>4</sup> Cyclization would thus appear to be heavily favored in the case of polyolefins, probably as the result of a higher activation entropy for intramolecular addition of a compound radical to a suitably placed double bond, as compared with intermolecular reaction with ferric chloride.

Our addition products contained some residual double bonds (7–20% of the initial) which remained even after a prolonged reaction. They are perhaps "buried" in the cyclic adduct as a result of poor steric accessibility, and may be trapped already at the early stages of the reaction, when cyclization is at its maximum. A higher concentration of initiator gave a lower residual unsaturation. A short treatment of the product (dissolved in methylene chloride) with chlorine gave a completely saturated product.

In order to assess the possibility of an acid-catalyzed cyclization, polybutadiene was refluxed in trichloroethylene as an inert solvent in the presence of ferric chloride hydrate and benzoin dissolved in DMF or *n*-butanol. The starting material was recovered without loss of unsaturation. In this system, radicals are not generated, but the combination of ferric chloride hydrate and benzoin introduces acidity. Our result indicates therefore that acid-catalyzed cyclization does not occur. (Golub and Heller<sup>8</sup> showed that even during the addition of hydrochloric acid to polyisoprene, cyclization is only a minor part of the reaction).

#### Initiation by azo-bis-Isobutyronitrile (AIBN)

Table III shows that AIBN is an efficient initiator only in the presence of ferric chloride. This indicates the analogy between benzoin and AIBN

TABLE III  
Reactions Catalyzed by azo-bis-Isobutyronitrile (AIBN)  
(110 g 5% Polybutadiene-Solution in Carbon Tetrachloride, 7 hr Reflux)

AIBN mole %*	FeCl <sub>3</sub> ·6H <sub>2</sub> O mole %*	Cosolvent (10 g)	Cl found (% w/w)
2	—	—	1.7
2	2	Butanol	49.5
2	2	DMF	42.5

\* Per polymer repeat unit.

in our catalytic system. The radicals formed by thermal decomposition of the latter reduce ferric chloride,<sup>10</sup> thus initiating the chain reaction.

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