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The Ionic Telomerization of Conjugated Diene Compounds. I. The Cationic Telomerization of Butadiene with Its Hydrochlorides at Low Temperatures

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The telomerization of butadiene with its hydrochlorides (1-chlorobutene-2 and 3-chlorobutene-1) at low temperatures in the presence of cationic catalysts was investigated. The aim of the present investigation is to explore methods to control the molecular weight of the products with various reaction conditions, and to determine the properties and structure of the telomers obtained. The activity of several cationic catalysts at −50—−40°C, and the effects of the conversion and the ratio of chlorobutene to butadiene (RCl/Bu) on the yield and average molecular weights of the telomers were investigated. The products were divided into simple adducts and higher telomers by vacuum distillation. The fraction of the 1 : 1 adduct contained three isomers, one of which was 1-chlorooctadiene-2, 6. The structure and properties of the higher telomers were investigated by the aid of the infrared spectra, the average molecular weight, the iodine value, and elementary analysis. On the basis of the results, the reaction mechanism was discussed.

There is information in the literature about the cationic telomerizations of conjugated dinene compounds with compounds of the allyl halide type. For example, the reactions of isoprene and butadiene with their hydrochlorides in the presence of stannic chloride were investigated by Leets[1] and Petrov[2]; the adducts of a 1 : 1 ratio were thus isolated by vacuum distillation. It was found that the relative amounts of the simple addition products and higher telomers depend primarily on the degree of conversion of the reaction. It was also shown that the addition of allyl and alkyl halides to butadiene and isoprene goes in accordance with Markovnikov's rule and occurs at both the 1, 4 and 1, 2 positions. However, the higher telomers are very complex and have not previously been investigated, and knowledge about the reaction mechanism is lacking.

This paper will be concerned, in particular, with the comparison of the activity of several cationic catalysts in the telomerization of butadiene with its hydrochlorides at low temperatures, and with the effect of the initial ratio of the chlorobutene to butadiene on the degree of conversion of the reaction and on the average molecular weight of the resultant telomers. The structure of telomers will also be discussed.

Experimental

The Synthesis of Chlorobutene.—1-Chlorobutene-2 and 3-chlorobutene-1, which were used as telogens, were prepared according to the method described by Dolnick.[3] The two isomers were separated by the fractional distillation of the obtained products, which consisted of about 65% 1-chlorobutene-2 (b. p. 83—85°C), 32% 3-chlorobutene-1 (b. p. 63—66°C), and a trace of a third product with a lower boiling point. The total yield of chlorobutenes was about 85%. In the present experiments 1-chlorobutene-2 was used as a telogen.

Telomerization.—Butadiene was dried before use by passing it through a column of anhydrous calcium chloride and sodium hydroxide. The purity was found to be above 99.3%. Ethyl bromide was purified by washing it several times with chilled concentrated sulfuric acid and water, drying it on calcium chloride, and distilling it.

A 500-ml. round-bottomed glass flask, equipped with a sealed stirrer, a thermometer, a condenser, and an inlet for gas, was cooled in a dry ice-aceton bath under a nitrogen stream; then it was charged with known amounts of the telogen, butadiene, and ethyl bromide. After the temperature of the solution had reached −50—−55°C, the catalyst, contained in a part of the ethyl bromide, was slowly added. The reaction is exothermic, and the temperature of the solution rises as the reaction proceeds. The rate of the addition of the catalyst solution was adjusted to keep the temperature of the solution under −35°C. After the telomerization, a small amount of pyridine was added to stop the reaction, and then *n*-hexane was added. The precipitated pyridine/catalyst complex was separated, and the solution was washed with a 5% sodium carbonate solution, a 5% hydrochloric acid solution, and then water, and dried on anhydrous calcium chloride. The solvent and the unreacted chlorobutene and butadiene were distilled off under a vacuum by a water jet pump, and the residue was subjected to vacuum distillation.

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[1] K. V. Leets, *Zh. Obshch. Khim.*, **28**, 1823 (1957).

[2] A. A. Petrov, X. B. Valiyan, L. I. Vunina-Kriborukoba and T. B. Yakobleba, ibid., **29**, 1576 (1959).

[3] U. S. Pat. 2573695 (1951).

Analysis.—*Molecular Weight.*—The molecular weight of the products was measured in a toluene solution with a Mechrolab vapor-pressure osmometer, model 301A, at 37°C. Squalane was used as the standard material.

Infrared Spectra.—The spectra of the telomers were taken with a Hitachi-Perkin-Elmer double-beam grating spectrophotometer, model 125. The evaluation of the absorption intensity was made by the ordinary base-line method.

Gas Chromatography.—The adducts with a 1 : 1 ratio of butadiene to chlorobutene were analyzed by a Hitachi-Perkin-Elmer F6 gas chromatograph with a flame ionization detector. The separation column was a stainless steel tube packed with Diasolid S (Nihon Chromato Kogyo, Ltd.); the liquid phase was silicon grease (10%).

The Amount of Unsaturation.—The degree of the unsaturation of telomers was determined by the Wijs method in a carbon tetrachloride solution.

Results and Discussion

1) The Activity of Catalysts. — Several cationic catalysts were used in the telomerization of butadiene with 1-chlorobutene-2. The findings on their catalytic activities are shown in Table I. Zinc chloride is partially insoluble in the reaction solution. Table I shows that, under the present reaction conditions, aluminum chloride and ferric chloride have considerable catalytic ability, but the other catalysts investigated gave only a small amount of a product. Stannic chloride in dichloromethane was used as a catalyst at 15—20°C by Petrov[2]; it gave an appreciable amount of the 1 : 1 adduct and higher telomers. However, in the present experiment at low temperatures, stannic chloride in ethyl bromide gives only a very small amount of telomers with higher molecular weights, and scarcely any of the 1 : 1 adduct. All the products are yellow-brownish viscous liquids and contain little of the simple adduct, except for the ferric chloride being used as the catalyst.

TABLE I. TELOMERIZATION OF BUTADIENE WITH 1-CHLOROBUTENE-2 BY CATIONIC CATALYSTS

Catalyst	C/Bu mole	EtBr/Bu vol.	Time min.	Yield %	Av. mol. wt.
$AlCl_3$	0.010	1.5	240	50.4	457
$FeCl_3$	0.015	2.2	240	65.8	527
$SnCl_4$	0.020	1.5	420	2.6	394
$ZnCl_2$	0.029	1.5	1380	1.2	—
BF_3Et_2O	0.058	2.6	240	0.3	—
BF_3Et_2O*	0.106	1.8	240	3.0	1235

RCl/Bu, 1.0 (molar ratio);* RCl/Bu, 0.5 (molar ratio)

On the basis of these results, aluminum chloride and ferric chloride were employed in the following experiments.

2) Conversion and Molecular Weight.—The yield and the molecular weight of the products are plotted against the reaction time in Fig. 1. The reaction nears completion during a short period; therefore, the reaction must be stopped in the early stages if we are obtain lower telomers by the control of the conversion. Under these conditions, the average molecular weight of the telomer is limited to less than about 530; other conditions must be used to obtain the higher telomers.

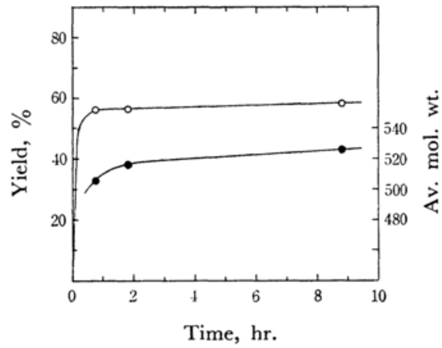


Fig. 1. Changes in yield and average molecular weight of telomer with reaction time.
$RCl/Bu=1.0$ (molar ratio); $AlCl_3/Bu=0.01$ (molar ratio); $EtBr/Bu=1.5$ (volume ratio)
○: Yield ●: Average molecular weight

3) Telomerization with Two Chlorobutene Isomers and the Polymerization of Chlorobutene.—As has previously been mentioned, two isomeric chlorobutenes are obtained by the addition of hydrogen chloride to butadiene. When it is used as a telogen under the same reaction conditions, 1-chlorobutene-2 gives a little higher yield and average molecular weight of telomers (Table II, Nos. 1 and 2). However, the analysis by gas chromatography shows that the 1 : 1 adducts of butadiene and each of these two chlorobutenes are composed of nearly the same proportions of isomers, and that the higher telomers from each of these two chlorobutenes have nearly the same infrared spectra. These results indicate that the carbonium cation shown below is formed by the interaction between chlorobutene and the catalyst in the initiation process:

$$CH_3-\overbrace{CH\!\!=\!\!=CH\!\!=\!\!=CH_2}^{+}$$

The difference in the yield of telomers may be attributable to the difference in the rate of the initiation reaction.

Experiment No. 3 in Table II shows that the polymerization of 1-chlorobutene-2 by the action of aluminum chloride affords polymers with a low unsaturation. A small amount of dimer was isolated by distillation (21% of total product; b. p. 60—72°C/1 mmHg).

Found: C, 52.81; H, 7.64; Cl, 39.10. Calcd. for $(C_4H_7Cl)_2$: C, 53.05; H, 7.80; Cl, 39.15%.

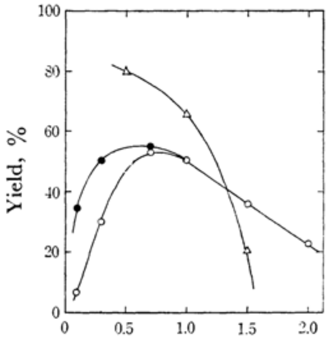
No condensation product was found. Therefore, in the system which contains both butadiene and chlorobutene, the polymerization of chlorobutene and the grafting of a growing carbonium ion onto the preformed telomers are also plausible (see section 8).

TABLE II. TELOMERIZATION OF BUTADIENE WITH TWO CHLOROBUTENE ISOMERS AND POLYMERIZATION OF CHLOROBUTENE

Expt. No.	Telogen	Yield, % Soluble	Yield, % Insoluble	Av. mole wt.	Iodine value
1	1-Cl-But-2	50.4	—	457	201
2	3-Cl-But-1	37.7	—	419	216
3	1-Cl-But-2	60.3	—	466	25
4	—	0.5	38.0	—	—

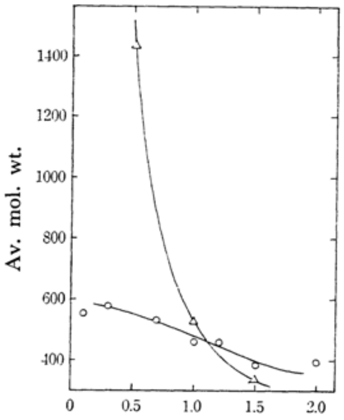
No. 1—3: $AlCl_3/RCl$, 0.01 (molar ratio); RCl/Bu, 1.0 (molar ratio); EtBr/Bu, 1.5 (vol. ratio); Reaction time, 240 min.
No. 3: Reaction in the absence of butadiene.
No. 4: Polymerization of butadiene. $AlCl_3/Bu$, 0.02 (molar ratio); EtBr/Bu, 1.5 (vol. ratio); Reaction time, 100 min.

4) The Effect of the RCl/Bu Ratio.—As Figs. 2 and 3 show, the yield and the average molecular weight of telomers depend on the initial ratio of chlorobutene to butadiene. When aluminum chloride was used as a catalyst, the maximum yield of telomers is obtained at RCl/Bu=0.7. In the region where RCl/Bu is lower than 0.7, the insoluble product is obtained; it increases in amount with the decrease in the RCl/Bu ratio. Moreover, almost all the product obtained from the polymerization of butadiene in the absence of chlorobutene is insoluble in ordinary organic and inorganic solvents (Table II, No. 4). These products are probably caused by branching. As will subsequently be described, the total unsaturation of higher telomers is always low, and it is obviously due to the reactivity of the telomers preformed in side reactions. Grafting and cyclization are suggested, at least as contributory factors.



RCl/Bu, molar ratio

Fig. 2. Effect of the ratio of chlorobutene to butadiene on the yield of telomer.
Reaction time: 4 hr.
○: Catalyst: $AlCl_3$; $AlCl_3/Bu=0.01$ (molar ratio); ●: Insoluble telomor; △: Catalyst: $FeCl_3$; $FeCl_3/Bu=0.015$ (molar ratio)



RCl/Bu, molar ratio

Fig. 3. Effect of the ratio of chlorobutene to butadiene on the average molecular weight of telomer.
Reaction time: 4 hr.
○: Catalyst: $AlCl_3$; $AlCl_3/Bu=0.01$ (molar ratio)
△: Catalyst: $FeCl_3$; $FeCl_3/Bu=0.015$ (molar ratio)

On the other hand, with ferric chloride as a catalyst, the yield of telomers increases monotonously with the decrease in the RCl/Bu ratio; in the low region of this ratio, the product is a very adhesive semisolid, only a small part of which is insoluble.

The increase in the RCl/Bu ratio causes a decrease in the average molecular weight of products when both aluminum chloride and ferric chloride are used as the catalyst. However, the decrease in the average molecular weight is larger when ferric chloride is used than when aluminum chloride is used.

On the basis of these results, it may be concluded that ferric chloride is the most convenient of the catalysts investigated for controlling the molecular weight of telomers in the telomerization of butadiene with 1-chlorobutene-2.

5) Lower Telomers.—The telomerization of butadiene with 1-chlorobutene-2 was carried out to various extents of the reaction. The increasing degree of reaction is accompanied by an increasing total yield of telomers and by a decrease in the yield of lower adducts (Table III). This agrees with the finding of Leets[1] that, in the telomerization of isoprene with prenyl chloride in dichloromethane in the presence of stannic chloride, the yield of monoterpene chloride increases in the early stages of the reaction, but then decreases in the later stages; the increase in the yield of polyterpene chloride follows the opposite pattern. This may be due to the consumption of the preformed 1 : 1 adduct by some side reactions or by its addition to butadiene as a telogen, producing higher adducts.

Table III. Conversion and lower telomers

RCl/Bu mole	EtBr/Bu vol.	Time min.	Conversion %	Lower adducts in telomer, %
1.0	2.20	240	65.8	13.9
1.2	2.22	90	15.9	51.7
1.2	2.23	130	53.9	27.5
1.2	2.23	180	54.4	25.7
1.5	2.30	240	20.5	43.3

Telogen, 1-chlorobutene-2; Catalyst, $FeCl_3$

The fraction with a b. p. of 50—65°C/10 mmHg (I) was again divided into two fractions: 50—58°C/10 mmHg (II) and 58—65°C/10 mmHg (III).

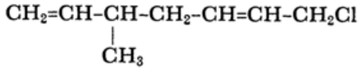
II: Found: C, 64.99; H, 8.81; Cl, 23.43. III: Found: C, 64.10; H, 8.73; Cl, 24.51.

Calcd. for $H(C_4H_6)_2Cl$: C, 66.43; H, 9.06; Cl, 24.51%.

The gas chromatogram of II has two main peaks, which overlap one another, whereas that of III consists of only one peak. The III content in the fraction I is about 61%. The infrared spectrum of the fraction II (Fig. 4, curve 4) exhibits the characteristic stretching (1645 cm⁻¹) and deformation (910 cm⁻¹) bands of a vinyl group, together with the stretching (1665 cm⁻¹) and deformation (965 cm⁻¹) bands of the –CH=CH– grouping. The spectrum of the fraction III (Fig. 4, curve 3) has only the bands of –CH=CH– (965 and 1665 cm⁻¹). The cationic addition of chlorobutene to butadiene is known to abide by Markovnikov's rule; therefore, the structures of the 1 : 1 adducts may be shown as follows:

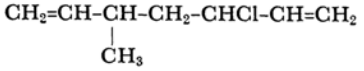
$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2Cl$ (A)

$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CHCl\text{-}CH{=}CH_2$ (B)



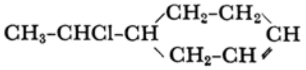
$$CH_2{=}CH\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2Cl$$

(C)



$$CH_2{=}CH\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}\text{-}CH_2\text{-}CHCl\text{-}CH{=}CH_2$$

(D)



(E)

From the results mentioned above, the fraction III is determined to be A. The fraction II is considered, from the infrared spectrum, probably to be a mixture of B and C. The iodine values of II and III are 325 and 315 respectively, values which correspond to 92.8 and 90.0% of the theoretical value based on the assumption that two C–C double bonds are present in each molecule. Consequently, the amount of cyclic product (E) must be small.

6) The Infrared Spectra of Higher Telomers.—The infrared spectra of higher telomers, obtained from telomerizations under various conditions, were taken and the amounts of *trans*-1, 4, *cis*-1, 4 and 1, 2 linkages were determined by the method described by Richardson⁴⁾ and by Golub⁵⁾. The *trans*-1, 4 linkage predominates, accounting for 80—85% of the total observed unsaturation. The contents of 1, 2 and *cis*-1, 4 linkages are determined to be 9—15% and 2—10% respectively. The structures of telomers vary with the RCl/Bu ratio, the conversion, the structure of chlorobutenes, and the catalysts, but the differences are small and no definite trend can be discerned.

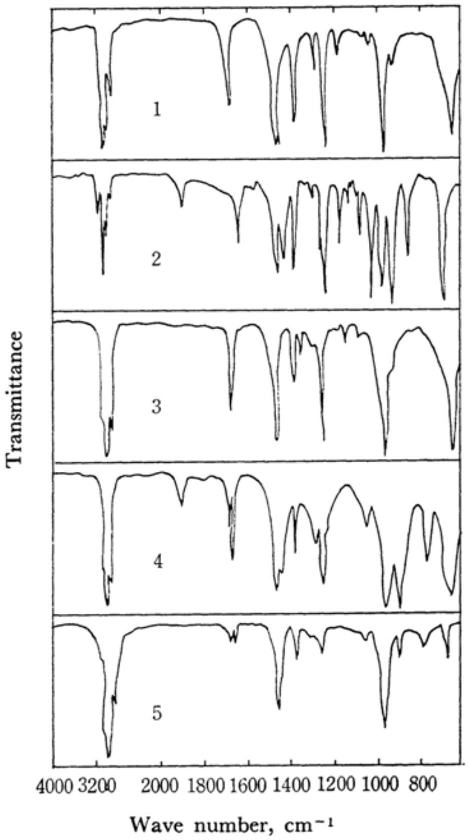


Fig. 4. Infrared spectra of telogens and telomers.
1: 1-Chlorobutene-2 2: 3-Chlorobutene-1
3: Fraction III 4: Fraction II
5: Higher telomer

7) The Unsaturation of Telomers.—The amount of the unsaturation of higher telomers was determined by the Wijs method in a carbon tetrachloride solution. According to Kemp,⁶⁾ the iodine value of polybutadiene depends on the

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4) W. S. Richardson, *J. Polymer Sci.*, **13**, 229 (1954).
5) M. A. Golub, ibid., **25**, 373 (1957).
6) A. R. Kemp and H. Peters, *Ind. Eng. Chem., Anal. Ed.*, **15**, 453 (1943).

Table IV. Amount of unsaturation in telomers

Expt. No.	RCl/Bu mole	Catalyst	Conversion %	Av. mol. wt.	Iodine value	Unsaturation %
1	0.3	$AlCl_3$	50.6	577	251	57.2
2	0.7	$AlCl_3$	55.2	530	201	45.9
3	1.0	$AlCl_3$	50.4	457	201	46.5
4	1.0	$AlCl_3$	12.8	346	222	52.7
5	1.5	$AlCl_3$	36.0	384	195	45.7
6	2.0	$AlCl_3$	22.7	396	179	42.0
7	0.5	$FeCl_3$	79.8	1436*	147	32.1
8	1.0	$FeCl_3$	65.8	527	194	44.3
9	1.5	$FeCl_3$	20.5	340	253	60.4
10	0.5	BF_3Et_2O	4.1	1235*	289	63.0

* Eighty cubic centimeters of carbon tetrachloride were used becauce of the low solubility of the telomers in carbon tetrachloride - acetic acid solution.

Table V. Structural factors of telomers

Expt.* No.	α	β	Av. No. *a*	*b*	*c*	% *a*	*b*	*c*
1	4.97	1.85	7.34	0.85	2.63	67.8	7.9	24.3
2	3.05	2.60	5.33	1.60	2.14	58.8	17.6	23.6
3	2.65	2.52	4.16	1.52	1.54	57.6	21.1	21.3
5	2.46	2.23	3.26	1.23	1.32	56.1	21.2	22.7
7	2.91	7.43	14.19	6.43	6.88	51.6	23.4	25.0
8	2.22	3.44	4.20	2.44	1.18	53.7	31.2	15.1
9	2.77	1.79	3.17	0.79	0.78	66.9	16.7	16.4

* Numbers are in common with Table IV.

reaction time and on the amount of excess iodine chloride. Therefore, the effects of the amount of iodine chloride and the reaction time on the iodine value of the telomer with a molecular weight of about 550 were studied; it was concluded that, in the presence of about a 60% excess of idoine chloride, the addition of iodine chloride to the C–C double bond in telomers nears completion after 3 hr. The results are shown in Table IV. The theoretical unsaturation is always low, and it may be taken as evidence of the occurrence of some side reactions. As will be shown below, various side reactions may possibly occur, particularly grafting and cyclization which involve the loss of unsaturation.

When aluminum chloride is used as a catalyst, the theoretical unsaturation of telomers decreases somewhat with the increase in the RCl/Bu ratio. However, in case of ferric chloride, an appreciable increase in the theoretical unsaturation is observed.

The amount of the residual unsaturation also depends on the conversion. It increases with the decrease in the conversion. This is considered to be due to the predominance of the side reactions as a result of the decrease in the butadiene concentration and the increase in the telomer concentration at the later stage of the reaction.

8) The Mechanism of the Reaction.—The reaction mechanism of the cationic telomerization of butadiene with chlorobutene is known to be as follows:

Initiation:

$$\left.\begin{array}{l} CH_3\text{-}CH{=}CH\text{-}CH_2Cl \\ CH_3\text{-}CHCl\text{-}CH{=}CH_2 \end{array}\right\} + AlCl_3 \longrightarrow$$

$$CH_3\text{-}\overbrace{CH{\cdots}CH{\cdots}CH}^{+}{}_2 + AlCl_4^- \qquad (1)$$

Propagation:

$$CH_3\text{-}\overbrace{CH{\cdots}CH{\cdots}CH}^{+}{}_2 + (n-1)CH_2{=}CH\text{-}CH{=}CH_2$$

$$\longrightarrow H(C_4H_6)_{n-1}CH_2\text{-}\overbrace{CH{\cdots}CH{\cdots}CH}^{+}{}_2 \qquad (2)$$

Transfer reaction:

$$H(C_4H_6)_{n-1}CH_2\text{-}\overbrace{CH{\cdots}CH{\cdots}CH}^{+}{}_2$$

$$+ CH_3\text{-}CH{=}CH\text{-}CH_2Cl \longrightarrow$$

$$H(C_4H_6)_nCl + CH_3\text{-}\overbrace{CH{\cdots}CH{\cdots}CH}^{+}{}_2 \qquad (3)$$

Termination:

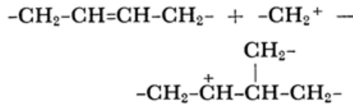
$$H(C_4H_6)_{n-1}CH_2\text{-}\overbrace{CH{\cdots}CH{\cdots}CH}^{+}{}_2 + AlCl_4^-$$

$$\longrightarrow H(C_4H_6)Cl + AlCl_3 \qquad (4)$$

The finding that the proportion of the 1, 4-1, 4 adduct in the mixture of the 1 : 1 adduct is about 61% suggests that the probability of finding the positive charge on the terminal carbon atom of a growing carbonium ion is about 78%. This is compatible with the value in the butadiene polymerization.[7]

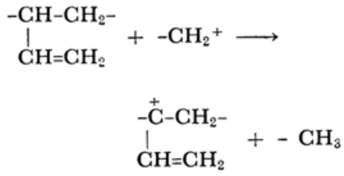
Several side reactions are also possible; they are shown as follows:

Grafting:



$$-CH_2-CH=CH-CH_2- + -CH_2^+ \longrightarrow -CH_2-\overset{+}{C}H-\overset{CH_2-}{\overset{|}{C}H}-CH_2- \quad (5)$$

Hydride-ion transfer from the telomer:

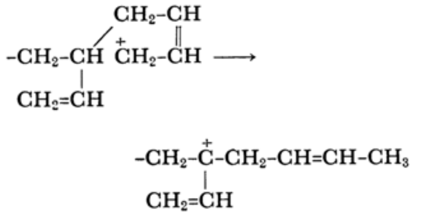


$$\underset{CH=CH_2}{\underset{|}{-CH}}-CH_2- + -CH_2^+ \longrightarrow \underset{CH=CH_2}{\underset{|}{-\overset{+}{C}}}-CH_2- + -CH_3 \quad (6)$$

Proton transfer to the telomer:

$$-CH_2-CH=CH-CH_2- + -CH_2-CH=CH-CH_2^+ \longrightarrow -CH_2-\overset{+}{C}H-CH_2-CH_2- + -CH=CH-CH=CH_2 \quad (7)$$

Intramolecular tranfser reactions:



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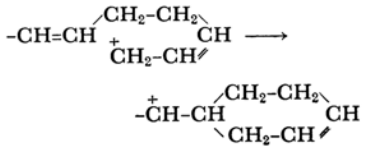

(9)

Reactions 5 and 9 cause a decrease in the average iodine value of telomer mixtutes. Reactions 5, 6 and 7 give telomers with more than one chlorine atom, but reactions 6 and 7 have no effect on the average chlorine contents in the telomer mixtures.

The telomers which are formed by reactions 1—4 can be represented by the general formula, $H(C_4H_6)_nCl$. However, the low amount of unsaturation, the formation of insoluble telomers, and the high chlorine contents in higher telomers suggest the presence of side reactions. Thus, telomers represented by the general formula $[H(C_4H_6)_\alpha Cl]_\beta$ are obtained. The values of α and β were calculated from the results of the elementary analysis and the average molecular weights (Table V).

If a telomer is formed by a times of propagation (Eq. 2), b times of grafting (Eq. 5), and c times of cyclization (Eq. 9), and if the reaction is initiated exclusively by Eq. 1, the following relations must hold:

$$\begin{aligned} \alpha\beta &= a + b + 1 \\ \beta &= b + 1 \\ F &= a - c + 1 \end{aligned} \quad \text{(i)}$$

where F represents the average number of the residual C–C double bonds in a telomer and can be obtained from the iodine value determination. Equation i can then be rewritten as follows:

$$\begin{aligned} a &= \beta(\alpha - 1) \\ b &= \beta - 1 \\ c &= \beta(\alpha - 1) + 1 - F \end{aligned} \quad \text{(ii)}$$

The calculated values of a, b and c are given in Table V. When aluminum chloride is used as the catalyst, the increase in the RCl/Bu ratio causes an increase in the proportion of grafting, with a decrease in the contribution of propagation. On the other hand, when ferric chloride is used as the catalyst, the proportion of propagation increases with the RCl/Bu ratio. The cyclization occurs almost independently of the RCl/Bu ratio. The high occurrence of cylization in Exp. 7 may be related to a very high conversion of the reaction.

Knowledge about reactions 6, 7 and 8 is lacking; there is no direct evidence for any of these reactions.

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[7] P. H. Plesch ed., "The Chemistry of Cationci Polymerization," Pergamon Press Ltd., London (1963), p. 356.