

## Studies on Chlorinated Polyethylenes. I. Infrared Spectra of Chlorinated Polyethylenes

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### INTRODUCTION

The structural changes in polyethylenes caused by chlorination are believed to result in a number of changes in the various properties of the chlorinated products.

Recently the molecular structures of chlorine-containing high polymers, for instance polyvinyl chloride<sup>1</sup> and polyvinylidene chloride,<sup>2</sup> have been elucidated by the analysis of their infrared spectra. Also the molecular structure of afterchlorinated polyvinyl chloride and the behavior of chlorine in the chlorination process have been discussed by Fuchs and Louis.<sup>3</sup> According to their report, the infrared spectra of the afterchlorinated polyvinyl chlorides are clearly distinguished from those of

polyvinylidene chlorides, and a new chemical unit, CHCICHCl, appears in the main chain of the chlorinated polyvinyl chloride.

In the present report an analysis of the infrared spectra of a series of chlorinated polyethylenes having various chlorine contents is given, and the changes in molecular structure during the chlorination are discussed. In a report on the infrared spectra of compounds of high molecular weight, Thompson and Torkington have described briefly the same problem.<sup>4</sup>

### EXPERIMENTAL

The series of chlorinated polyethylene samples used in the present study was obtained by the

TABLE I  
Infrared Absorption Bands of Chlorinated Polyethylenes

S-1 (20.1% Cl)		S-2 (45.0% Cl)		S-3 (58.3% Cl)		S-4 (61.7% Cl)		S-5 (68.1% Cl)	
Frequency, cm. <sup>-1</sup>	Relative intensity <sup>a</sup>	Frequency, cm. <sup>-1</sup>	Relative intensity <sup>a</sup>	Frequency, cm. <sup>-1</sup>	Relative intensity <sup>a</sup>	Frequency, cm. <sup>-1</sup>	Relative intensity <sup>a</sup>	Frequency, cm. <sup>-1</sup>	Relative intensity <sup>a</sup>
607	s	612	s	616	w	616	sh		
654	s	654	s	654	s	660	s	674	s
715	s								
		727	sh	736	sh	735	sh	736	wsh
763	sh	775	m	794	w	794	vwsh	794	vwsh
								818	sh
						880	sh	883	sh
913	w	918	w	918	m	924	m	930	m
1062	vw	1062	w	1064	w	1062	w	1066	w
1122	vvw	1112	vwsh	1091	vwsh				
1197	sh	1197	w	1197	w	1197	w	1197	w
						1241	vwsh	1241	sh
1270	m	1267	vs	1267	vs	1265	vs	1275	vs
1307	vw	1307	wsh	1316	wsh	1316	wsh	1325	sh
				1366	vvw	1362	vw	1343	vwsh
1380	m	1378	m	1379	w	1379	w	1365	vw
						1428	vwsh	1383	w
1444	sh	1451	vs	1444	vs	1440	vs	1427	vs
1465	vs	1463	w					1440	sh

<sup>a</sup> v: very, w: weak, m: medium, s: strong, sh: shoulder.

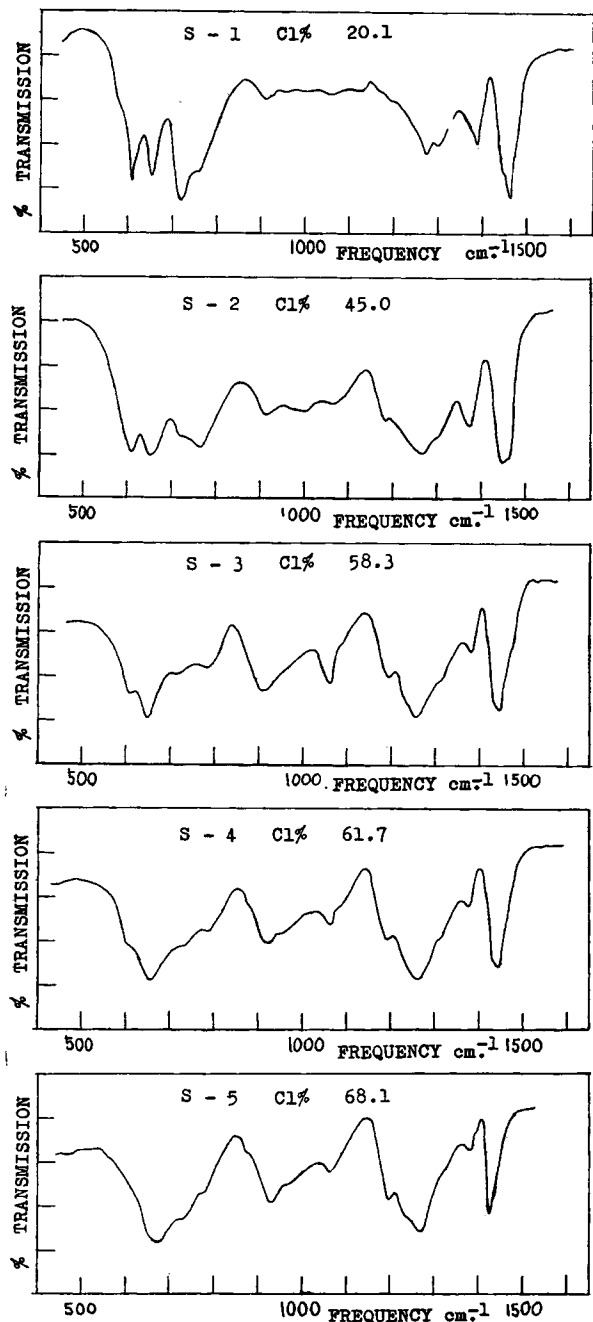


Fig. 1. Infrared spectra of chlorinated polyethylenes.

chlorination of polyethylene having relatively low molecular weight (product of Allied Chemicals No. 615; average molecular weight 5000) in carbon tetrachloride solution at 70°C. with a constant flow rate of chlorine gas, the degree of chlorination being controlled by the length of the reaction period.

After the predetermined reaction period, the reaction mixture was poured into a large volume of methanol to precipitate the products. The details

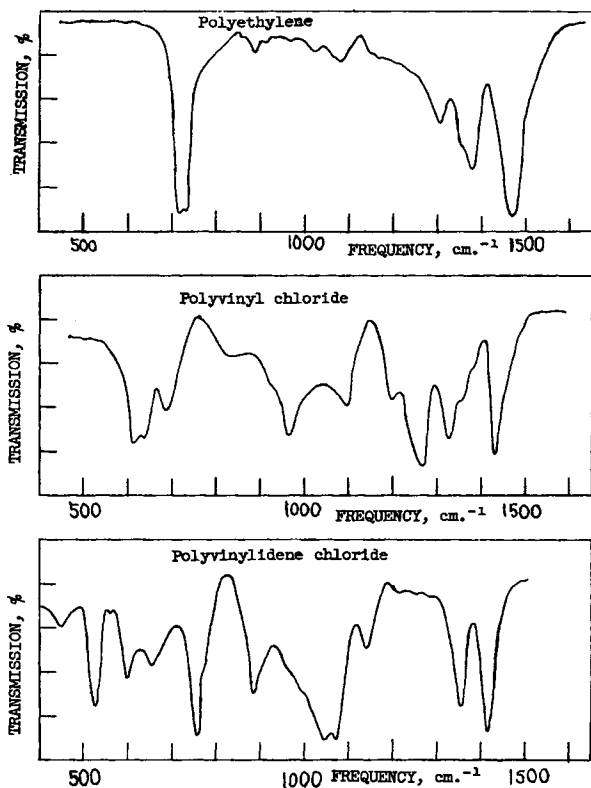


Fig. 2. Infrared spectra of polyethylene, polyvinyl chloride, and polyvinylidene chloride.

of the chlorination process will be reported elsewhere.

Samples containing more than 58 wt.-% chlorine were obtained in powdered form, and infrared spectra of these samples in the form of a KBr disk were then obtained. The other samples, containing not more than 45% chlorine, were too viscous to be pressed into a KBr disk; these were dissolved in carbon bisulfide, the resulting viscous solution being spread on a KBr plate. The thin films of the sample remaining after evaporation of the solvent were used for the measurement.

A Perkin-Elmer Model 13 infrared spectrophotometer was used for the measurement. The infrared spectra of the original polyethylene, of polyvinyl chloride, and of polyvinylidene chloride were also measured for the purpose of comparing them with those of the chlorinated polyethylenes.

## RESULTS

Figure 1 shows the infrared spectra of the several chlorinated polyethylenes; the chlorine contents are also given.

The infrared spectra of the original polyethylene, polyvinyl chloride, and polyvinylidene chloride are

represented in Figure 2. The changes of several important infrared maximum absorption bands and shoulders caused by the chlorination are listed in Table I.

## DISCUSSION

### A. General Features of the Infrared Spectrum

The infrared spectra represented in Figures 1 and 2 are discussed as follows.

**The Region from 500 to 700  $\text{cm}^{-1}$ .** As a rule, the CCl-stretching mode appears in the region of 500–700  $\text{cm}^{-1}$ . A strong band assigned to the  $\text{CCl}_2$ -stretching mode appears at 527  $\text{cm}^{-1}$  in the spectrum of polyvinylidene chloride.<sup>2</sup> The chlorinated polyethylene containing more chlorine than polyvinyl chloride does not have any band in the region below 600  $\text{cm}^{-1}$ . The infrared spectra of the chlorinated polyethylenes are more closely analogous to those of polyvinyl chlorides than of polyvinylidene chlorides in the region of the CCl-stretching mode.

The  $\text{CH}_2$ -rocking mode of polyethylene is found at about 720  $\text{cm}^{-1}$  in the spectrum of sample S-1, which contains about 20% chlorine, but this band disappears rather quickly as the chlorination proceeds.

**The Region from 800 to 1100  $\text{cm}^{-1}$ .** The carbon-carbon skeletal mode generally appears in this region. The carbon-carbon skeletal mode of polyethylene appears weakly, but a few new bands which are not observed in the spectrum of polyethylene appear now in the spectra of the chlorinated polyethylenes. Two such bands, namely, those at about 920 and 1060  $\text{cm}^{-1}$ , become stronger as the chlorination proceeds. Although a characteristic doublet is found at 1046 and 1071  $\text{cm}^{-1}$  in the spectrum of polyvinylidene chloride,<sup>2</sup> no such doublet could be found in the spectra of the chlorinated polyethylenes. Polyvinyl chloride<sup>1</sup> has two carbon-carbon skeletal modes at 960 and 1090  $\text{cm}^{-1}$ . The bands at about 920 and 1060  $\text{cm}^{-1}$  in the spectra of the chlorinated polyethylenes resemble those at 960 and 1090  $\text{cm}^{-1}$  in the spectrum of polyvinyl chloride in their frequencies and their shapes.

**The Region from 1100 to 1300  $\text{cm}^{-1}$ .** A weak band appearing at about 1197  $\text{cm}^{-1}$  in the spectra of the chlorinated polyethylenes could not be found in the spectrum of the original polyethylene. This band probably corresponds to the weak band at 1196  $\text{cm}^{-1}$  in the spectrum of polyvinyl chloride.

The CH-deformation mode appears strongly at 1255  $\text{cm}^{-1}$  in the spectrum of polyvinyl chloride;<sup>1</sup> this strong band is not found in this region of the spectrum of polyvinylidene chloride.<sup>2</sup> A similar strong band appears at about 1270  $\text{cm}^{-1}$  in the spectra of the chlorinated polyethylenes. The band is not so strong in the spectrum of sample S-1 which contains only about 20% chlorine, but it becomes very strong as the chlorine content of the sample rises above 45%.

Generally, the infrared spectra of the chlorinated polyethylenes strongly resemble those of polyvinyl chlorides in the region of from 1100 to 1300  $\text{cm}^{-1}$ . This observation suggests that polyethylene is chlorinated in the form of  $-\text{CHCl}-$  and that hardly any  $-\text{CCl}_2$  units are formed.

**Behavior of the  $\text{CH}_3$  Deformation Mode of Polyethylene.** The  $\text{CH}_3$  deformation mode appears at about 1380  $\text{cm}^{-1}$  in the spectrum of the original polyethylene.<sup>5</sup> In the spectra of the chlorinated polyethylenes this band becomes weaker as the chlorine content increases, but it is still present in the spectra of the products containing more chlorine than polyvinyl chloride, that is, methyl groups are still found in the molecule.

**Behavior of the  $\text{CH}_2$ -Bending Mode of Polyethylene.** The  $\text{CH}_2$ -bending mode appears at about 1470  $\text{cm}^{-1}$  in the spectrum of polyethylene,<sup>5</sup> at about 1428  $\text{cm}^{-1}$  in the spectrum of polyvinyl chloride, and at about 1407  $\text{cm}^{-1}$  in the spectrum of polyvinylidene chloride. Thus the  $\text{CH}_2$ -bending mode shifts to lower frequency as the  $\text{CH}_2-\text{CH}_2$  unit is changed to the  $\text{CH}_2-\text{CHCl}$  and to the  $\text{CH}_2-\text{CCl}_2$  units.

A similar shift is now observed within the series in the spectra of the chlorinated polyethylenes. A strong band remains at 1465  $\text{cm}^{-1}$  with a shoulder at 1444  $\text{cm}^{-1}$  in the spectrum of sample S-1. While this band at 1465  $\text{cm}^{-1}$  is still present in the spectrum of sample S-2, a new band appears in addition at 1440  $\text{cm}^{-1}$ . In the spectrum of sample S-3, which contains more chlorine than polyvinyl chloride, the band at 1465  $\text{cm}^{-1}$  disappears, the band at 1440  $\text{cm}^{-1}$  becomes stronger, and a shoulder appears at 1430  $\text{cm}^{-1}$ . This shoulder is stronger in the spectrum of sample S-4, and a strong band appears at the same position in the spectrum of sample S-5. On the other hand, the band at 1440  $\text{cm}^{-1}$  becomes a faint shoulder in the last spectrum.

The above-mentioned transitions in the appearance of the infrared spectra are summarized in Table II.

TABLE II

Sample	Chlorine content, %	Band peaks and shoulders		
		1428 cm. <sup>-1</sup>	1440 cm. <sup>-1</sup>	1465 cm. <sup>-1</sup>
Polyethylene	0	—	—	strong peak (1470)
Chlorinated polyethylenes				
S-1	20.1	—	shoulder	strong peak
S-2	45.0	—	peak	peak
S-3	58.3	shoulder	peak	—
S-4	61.7	shoulder	peak	—
S-5	68.1	peak	faint shoulder	—
Polyvinyl chloride	56.7	peak	—	—

These observations would be explained on the following assumption: the band at 1465 cm.<sup>-1</sup> would be assigned to the bending mode of polyethylene (CH<sub>2</sub>—CH<sub>2</sub>), the band at 1428 cm.<sup>-1</sup> to that of polyvinyl chloride (CH<sub>2</sub>—CHCl), the band at 1440 cm.<sup>-1</sup> to the total of these two bending modes.

According to the above observation and assumption, the chlorination of the main carbon chain of polyethylene seems to occur as follows. At the first stage of the chlorination some of the CH<sub>2</sub>—CH<sub>2</sub> units which are in the relatively amorphous part are chlorinated, the CH<sub>2</sub>—CHCl unit being formed as in sample S-1. As the chlorination proceeds, the other CH<sub>2</sub>—CH<sub>2</sub> units are gradually changed to CH<sub>2</sub>—CHCl units as in sample S-2 (45% Cl), until the chlorine content reaches that of polyvinyl chloride. After the chlorine content exceeds 56.7% (that of polyvinyl chloride) as in sample S-3, the chlorine introduced is added so as to form the CHCl—CHCl unit. The chlorinated product containing 68% chlorine (sample S-5) is composed mostly of CH<sub>2</sub>—CHCl and CHCl—CHCl units, with very few unchanged CH<sub>2</sub>—CH<sub>2</sub> units; CH<sub>2</sub>—CCl<sub>2</sub> units could not be found.

## B. Discussion on the Region of the CCl-Stretching Mode

The infrared spectral changes of the chlorinated polyethylenes in the region of the CCl-stretching modes are discussed in some detail in order to elucidate the mechanism of addition of chlorine atoms to the carbon-carbon main chain.

Mizushima and Shimanouchi have correlated the CCl-stretching frequencies of various chlorine-containing molecules with their structures.<sup>7</sup> Their classification system is shown in part in Table III.

According to this correlation, bands appearing at about 730 and from 760 to 790 cm.<sup>-1</sup> are assigned to P<sub>X</sub> (X being carbon). These bands correspond

TABLE III  
C—Cl-Stretching Frequencies in Various Structures

C—Cl bond	Stretching frequency, cm. <sup>-1</sup> (atom <i>trans</i> to Cl)	
	Chlorine or Carbon	Hydrogen
Primary	700–760 (P <sub>X</sub> )	650–690 (P <sub>H</sub> )
Secondary	670–700 (S <sub>X</sub> )	600–640 (S <sub>H</sub> )
Tertiary	610–640 (T <sub>X</sub> )	550–580 (T <sub>H</sub> )

to the stretching mode of the C—Cl of the (3) (2) (1)  
—CH<sub>2</sub>—CH<sub>2</sub>—CHCl at the chain end, the C—Cl being in the *trans* position with respect to the third carbon atom, from the chain end, C(3). The band at 715 cm.<sup>-1</sup> in the spectrum of sample S-1, which contains a relatively small amount of chlorine, should be assigned to the CH<sub>2</sub>-rocking mode of the unchlorinated polyethylene portion of the molecule and therefore should be excluded from the present discussion.

The band which appears strongly at 610 cm.<sup>-1</sup> in the spectrum of sample S-1 and becomes weaker as the chlorine content increases is assigned to S<sub>H</sub>. This corresponds to the secondary C—Cl stretch-

ing mode of —CH<sub>2</sub>—CHCl—CH<sub>2</sub>—, one of the two hydrogen atoms on the methylene group

adjacent to the CHCl group (H) being in the *trans* position with respect to the C—Cl bond. The band which appears at about 650 cm.<sup>-1</sup> shifts to about 670 cm.<sup>-1</sup> as the chlorination proceeds, while the band at about 650 cm.<sup>-1</sup> is assigned to the mode of the deformed configuration of carbon chain, i.e., S<sub>X</sub> (X being carbon); therefore, the C—Cl being in the *trans* position with respect to the third carbon atom from that which bears the Cl, the band at 670 cm.<sup>-1</sup> is assigned to the other S<sub>X</sub>, since the newly substituted chlorine atom

being in the *trans* position with respect to the already substituted chlorine atom, as in the previous case of  $P_X$ . Therefore it is suggested that the regular normal carbon chain of polyethylene assumes a configuration with the carbon atom in the *trans* position with respect to the substituted chlorine atom for a while, and, as the chlorination proceeds, the new chlorine atom occupies the *trans* position with respect to the already substituted chlorine atom, thus forming a *trans*-CHCl—CHCl unit. The shape of the spectrum above  $700\text{ cm.}^{-1}$  could not be resolved in the infrared spectrum of highly chlorinated polyethylene because the band at  $670\text{ cm.}^{-1}$  becomes stronger and wider, obscuring all other bands at that region.

The author wishes to thank Prof. A. Kotera of Tokyo University of Education and Prof. T. Shimanouchi of Tokyo University for helpful discussion.

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### Synopsis

The infrared absorption spectra of chlorinated polyethylenes with various amounts of combined chlorine have been investigated, and some data on the mechanism of addition of chlorine to the polyethylene molecule has been studied. When polyethylene is chlorinated in carbon tetrachloride solution at  $70^\circ\text{C}$ . by chlorine gas,  $\text{CH}_2\text{—CHCl}$  and the  $\text{CHCl—CHCl}$  units are formed in the main carbon chain, but formation of the  $\text{—CCl}_2$  units could not be detected by the present infrared spectral study.

### Résumé

On a étudié les spectres d'absorption infrarouge des polyéthylènes chlorés possédant différentes quantités de chlore combiné, et on a obtenu une information au sujet de la façon dont l'atome de chlore s'attache à la molécule de polyéthylène. Lorsque le polyéthylène est chloré en solution dans le tétrachlorure de carbone à  $70^\circ\text{C}$  par le chlore gazeux, les unités  $\text{CH}_2\text{—CHCl}$  et  $\text{CHCl—CHCl}$  sont formées dans la chaîne carbonée principale, mais la formation de l'unité  $\text{—CCl}_2\text{—}$  ne pourrait pas être observée par la présente étude spectrale infrarouge.

### Zusammenfassung

Die Infrarot-Absorptionsspektren von chlorierten Polyäthylenen mit verschiedenem Gehalt an gebundenem Chlor wurden untersucht und es wurde eine Angabe über die Art der Anbringung des Chloratoms an dem Polyäthylenmolekül erhalten. Bei der Chlorierung von Polyäthylen in Tetrachlorkohlenstofflösung bei  $70^\circ\text{C}$  durch Chlorgas werden in der Hauptkette  $\text{CH}_2\text{—CHCl}$ - und  $\text{CHCl—CHCl}$ -Gruppen gebildet, es konnte aber in der vorliegenden Infrarotuntersuchung keine Bildung von  $\text{—CCl}_2\text{—}$ Gruppen beobachtet werden.

Received January 18, 1960