Chlorinated Polyethylene. I. Infrared Study

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(Received June 17, 1974)

ABSTRACT: A qualitative analysis of the infrared spectra of a series of photo-chlorinated (20°C) and thermally (90°C) chlorinated polyethylenes of various chlorine contents by weight (19% up to 73%) was made. In connection with microstructural high-resolution nuclear-magnetic-resonance studies published in our previous paper,^{4–6} new bands were identified between 500 cm⁻¹ and 2000 cm⁻¹. Changes in the molecular structure of the chlorinated polyethylene samples during the chlorination process were discussed.

KEY WORDS Chlorinated Polyethylenes / Poly(vinyl chloride) / Poly(vinylidene chloride) / Band-Assignments / Conformational and Configurational Structures /

The pioneers of infrared study on chlorinated high polymers are Thomson and Torkington;¹ but the first important infrared study of chlorinated polyethylene (CPE), to which many scientists still refer was published in 1960 by Nambu.² This work was carried out with a series of thermal-chlorinated low-density polyethylene samples of various chlorine contents by weight (20% up to 68%).

Since 1970 many microstructural nuclear-magnetic-resonance (NMR) analyses of CPE have been published.^{3–6} NMR is a very efficient tool for this kind of investigation; but infrared analysis is still a fast and routine method which permits conformational and configurational investigations.

This report confirms some band-attributions made by Nambu² and gives other new ones.

EXPERIMENTAL

The parent-polymers are a branched low-density polyethylene sample (LDPE), and a linear high-density one (HDPE). Their characteristics, the chlorination conditions, and the techniques of characterization have been published elsewhere^{4–7}. A Perkin-Elmer model 421 infrared spectrophotometer was used for the measurements. The films used as experimental samples were obtained by evaporation of the 1,2-dichlorobenzene solution of CPE samples from the sur-

face of a heated glass plate¹. The solvent was removed from the film by heating the glass plate covered with the polymer solution in a furnace at 80°C, during a period of from 3 hr up to 24 hr depending on the thickness of the films. This treatment, which was necessary in order to have a coherent film, was followed by a 48-hr immersion of the cooled glass plate in methyl alcohol (MeOH) at room temperature. The film was then vacuum dried at 45°C for 8 to 15 days depending on its thickness, after immersion in warm (60°C) MeOH. This warm MeOH medium was periodically changed. At the end of this treatment (48 hr) the film was again vacuum dried at 45°C for 8 to 15 days.

A comparative differential thermal analysis of the films and the powder of the CPE samples⁸ showed that the structure of the chlorinated products is not affected by these various treatments. The spectra of the films are solvent-band-free.

The infrared spectra of a poly(vinyl chloride) (PVC), a head-to-tail poly(vinylidene chloride) (H-T-PVDC), and poly(vinyl chloride) (CPVC) chlorinated to saturation level (73%) were also measured; the samples were pressed into KBr disks containing 3% of the product.

RESULTS

Figure 1 shows the infrared spectrum of the

initial low-density polyethylene. The spectra of a PVC, a H-T-PVDC, and a 73-% Cl_2 CPVC samples are represented in Figure 2. Different CPE samples spectra (chlorine content: 10, 41, 59, and 73-% Cl_2 by weight) in the 500–2000- cm^{-1} region

Figure 1. Infrared spectrum (600–2000 cm^{-1}) of a low-density polyethylene (branched polymer).

Figure 2. Infrared spectra (500–2000 cm^{-1}): 1, poly(vinyl chloride) (PVC); 2, head-to-tail poly(vinylidene chloride) (H-T-PVDC); 3, chlorinated (73%) poly(vinyl chloride) (CPVC).

Figure 3. Infrared spectra (500–2000 cm^{-1}) of chlorinated low-density polyethylene (CPE) samples of various chlorine contents by weight: 1, 10-% Cl_2 (thermal-chlorinated LDPE); 2, 41-% Cl_2 (thermal-chlorinated LDPE); 3, 59-% Cl_2 (thermal-chlorinated LDPE); 4, 73-% Cl_2 (photochlorinated LDPE).

are shown in Figure 3. Figures 4 and 5 show the 500–800- cm^{-1} region and Figures 8 and 9 the 1100–1500- cm^{-1} region of several CPE; these regions are the most interesting for analysis. In Table II the absorbances of some bands are listed. The arrows near some frequencies indicate the band-shifting as the chlorination proceeds.

DISCUSSION

The discussion will concern the CPE samples made from the branched low-density polyethylene. Nevertheless, plots of CPE samples made from the linear high-density polyethylene are

also shown in Figures 6 and 13 since they are useful in understanding Part II¹³ of this series.

Assignments of the Infrared Bands

The 500—800-cm⁻¹ Region. The 610—615-cm⁻¹ band in the PVC spectrum is attributed to the C—Cl stretching mode of the CHCl units in PVC syndiotactic sequences.⁹ Krimm, *et al.*,¹⁰⁻¹² have called this frequency the S_{HH} resonance mode. This band is strong in the spectra of the low-chlorine-content CPE samples and disappears as the photochlorination degree increases beyond 60% (Table II). At saturation level (73-% Cl₂), when the parent polymer is a branched LDPE, the 615-cm⁻¹ band appears again if the minimum chlorination time⁴ necessary to obtain 73-% Cl₂ is overrun (Figure 13).

Figure 4. Infrared spectra (500—800 cm⁻¹) of photochlorinated low-density polyethylene samples of various chlorine contents by weight: 1, 19.5-% Cl₂; 2, 46-% Cl₂; 3, 49-% Cl₂; 4, 55-% Cl₂; 5, 60.6-% Cl₂; 6, 68.4-% Cl₂.

The PVC spectrum shows a band at 690 cm⁻¹ attributed to the C—Cl stretching mode of CHCl units in PVC isotactic sequences;⁹ this frequency has been termed the S_{HC} resonance mode by Krimm, *et al.*¹⁰⁻¹² In the CPE samples spectra (Figures 4 and 5) a band appears at 660 cm⁻¹ which shifts to 685 cm⁻¹ and broadens as the chlorination degree proceeds beyond the 55—60-% interval. In agreement with Nambu², we assign the 660-cm⁻¹ band to the C—Cl stretching mode of CHCl units of vinyl triads surrounded by polyethylene sequences:

By the 55—60-% chlorine-content interval the polyethylene sequences are completely changed into vinyl ones.¹³ When the chlorination proceeds beyond 60% a large number of vinyl

Figure 5. Infrared spectra (500—800 cm⁻¹) of thermal-chlorinated low-density polyethylene samples of various chlorine contents by weight: 1, 24-% Cl₂; 2, 33-% Cl₂; 3, 38-% Cl₂; 4, 54.5-% Cl₂; 5, 61.5-% Cl₂; 6, 62.8-% Cl₂.

sequences are changed into $-\text{CH}_2-\text{CHCl}-\text{CHCl}-$ and $-\text{CHCl}-\text{CHCl}-\text{CHCl}-$ structures, which can be considered as responsible for the shift of the 660-cm^{-1} band to 685-cm^{-1} ; the broadening of this 685-cm^{-1} band is the consequence of the formation of numerous CHCl units¹². Adilov and coworkers¹⁴ assigned the 660-cm^{-1} band to the $\text{C}-\text{Cl}$ stretching mode of the CCl_2 units. We think that this is an incorrect attribution because the $-\text{CCl}_2-$ units are not so numerous as the CHCl units,¹³ in addition, the CPE spectra does not show, as the H-T-PVCD spectrum does, any significant band at $520\text{--}530\text{-cm}^{-1}$ which could be attributed to the $\text{C}-\text{Cl}$ stretching mode of the CCl_2 units.¹⁵

The CH_2 -rocking mode of the initial polymer is found at $720\text{--}730\text{-cm}^{-1}$.¹⁶ In the CPE spectra this band disappears progressively as the chlorination proceeds but it is still present until 55-% chlorine content, which indicates the presence of at least two unchlorinated polyethylene monomeric units $(4\text{ CH}_2)^{1,16}$.

From the 49–55-% chlorine interval (Figures 4 and 5) a band appears at $740\text{--}750\text{-cm}^{-1}$ which

could be assigned to the $\text{C}-\text{Cl}$ bending mode of the $-\text{CHCl}-$ units in structures such a $-\text{CH}_2-\text{CHCl}-\text{CHCl}-$ or $-\text{CHCl}-\text{CHCl}-\text{CHCl}-$. This assignment is consistent with the following considerations:

This band becomes a strong one when the $-\text{CH}_2-\text{CHCl}-\text{CHCl}-$ and $-\text{CHCl}-\text{CHCl}-\text{CHCl}-$ structures appear in large numbers, as proved by NMR studies.^{6,13}

The plot of A_{615}/A_{685} against A_{615}/A_{745} (for absorbance) (Figure 6) for CPE samples at the saturation level (73%)⁴ is a straight line, which indicates that the 745-cm^{-1} and 685-cm^{-1} bands deal with the same structures.

We assign the weak band which appears at 785-cm^{-1} and shifts to 800-cm^{-1} when the chlorination proceeds to a vibrational mode of CHCl . Figure 7 shows that this band and the $1195\text{--}1200\text{-cm}^{-1}$ band have the same variation. A band ($1195\text{--}1200\text{-cm}^{-1}$) which is not present in

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Table I. The infrared bands' assignment

Frequency, cm ⁻¹	Resonance mode	Atoms concerned	Units concerned	Structures concerned in the CPE chains
610—615	Stretching	C—Cl	—CHCl—	PVC Syndiotactic sequences
690	Stretching	C—Cl	—CHCl—	PVC Isotactic sequences
685	Stretching	C—Cl	—CHCl—	(CH ₂ —CHCl—CHCl) (CHCl—CHCl—CHCl) and PVC isotactic sequences
720—730	Rocking		—CH ₂ —	(CH ₂) _n (n ≥ 4)
740—750	Bending	C—Cl	—CHCl—	(CH ₂ —CHCl—CHCl) (CHCl—CHCl—CHCl)
785—800	Bending		—CHCl—	(CH ₂ —CHCl—CHCl) (CHCl—CHCl—CHCl)
825—850	Rocking		—CH ₂ —	—CHCl—CH ₂ —CCl ₂ —
1195—1200	Deformation		—CHCl—	(CHCl—CHCl—CHCl) (CH ₂ —CHCl—CHCl) and PVC sequences
1375—1380	Deformation		—CH ₃ —	—CH ₂ —CH—CH ₂ — and —CH ₂ —C(=O)—O—CH ₃ ¹³
1440—1430→1428	Bending		—CH ₂ —	PVC Syndiotactic sequences
1450—1445→1434	Bending		—CH ₂ —	PVC Isotactic sequences
1470	Bending		—CH ₂ —	—CHCl—(CH ₂) _x —CHCl—
1465	Bending		—CH ₂ —	—CHCl—(CH ₂) _y —CHCl—
1460	Bending		—CH ₂ —	—CHCl—(CH ₂) _z —CHCl— with x > y > z

Table II. Absorbances of some infrared bands tabulated in Table I

cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	
1470	1450	1440				615	720	615	785	
1465 ↓ ^a	1445 ↓	1430 ↓	1195	615	660 ↓	615	725	750	790	Cl ₂ , % ^b
4460	1434	1428	1200		685 ↓	660	750	750	800	

Thermal chlorination of the branched polyethylene (LDPE) at 90°C in 1,1,2,2-tetrachloroethane (TCE)

1.327	0.783	0.674	0.189	0.497	0.452	1.1	0.699	0.715	0.235	24
1.092	0.930	0.812	0.288	0.671	0.671	1	0.935	1.595	0.369	33
0.989	0.892	0.778	0.335	0.636	0.662	0.960	0.444	0.430	1.360	38
0.662	0.832	0.739	0.338	0.596	0.815	0.804	0.474	1.260	0.379	54.5
0.753	0.893	0.783	0.361	0.639	0.850	0.753	0.498	1.280	0.417	61.5
0.411	0.712	0.672	0.418	0.551	0.625	0.625	0.540	1.020	0.384	62.8

Photochlorination of the branched polyethylene (LDPE) at 20°C in 1,1,2,2-tetrachloroethane (TCE)

1.425	0.757	0.580	0.204	0.358	0.384	0.935	1.240	0.290	0.195	19.5
0.763	0.448	0.359	0.183	0.328	0.448	0.730	0.395	0.827	0.191	46
1.697	0.676	0.629	0.280	0.463	0.689	0.675	0.494	0.938	0.285	49
0.790	0.441	0.427	0.216	0.348	0.541	0.660	0.337	1.030	0.219	55
0.454	0.316	0.276	0.198	0.272	0.468	0.582	0.311	0.875	0.183	60.6
0	0.577	0.287	0.462	0	0.898	0	0.696	0	0.484	67.5
0	0.240	0.541	0.524	0	0.962	0	0.825	0	0.638	68.4
0	0.237	0.431	0.500	0	0.980	0	0.800	0	0.645	73 ^c

^a The arrows near some frequencies indicate the band-shifting when the chlorination procedures.

^b Chlorine content by weight.

^c After 4 hr of photochlorination.

the initial polyethylene spectrum is found in the PVC one; Fredriksen and Crow¹⁷ attributed it to the $-\text{CH}-$ deformation mode of CHCl .

The 800–1000- cm^{-1} Region. In the spectrum of the 63-% photochlorinated CPE sample (Figure 4) a band appears at 825 cm^{-1} and shifts to 850

Figure 8. Infrared spectra ($1100\text{--}1500\text{ cm}^{-1}$) of photochlorinated low-density polyethylene samples of various chlorine contents by weight: 1, 19.5-% Cl_2 ; 2, 46-% Cl_2 ; 3, 49-% Cl_2 ; 4, 55-% Cl_2 ; 5, 60.6-% Cl_2 ; 6, 68.4-% Cl_2 .

Figure 9. Infrared spectra ($1100\text{--}1500\text{ cm}^{-1}$) of thermal chlorinated low density polyethylene samples of various chlorine contents by weight: 1, 24-% Cl_2 ; 2, 33-% Cl_2 ; 3, 38-% Cl_2 ; 4, 54.5-% Cl_2 ; 5, 61.5-% Cl_2 ; 6, 62.8-% Cl_2 .

cm^{-1} for the saturated (73%) CPE sample (Figure 3). We assign it to the $-\text{CH}_2-$ rocking mode of the $-\text{CHCl}-\text{CH}_2-\text{CCl}_2-$ structure. NMR analyses^{6,13} show that these structures are numerous in the 60–73% chlorine interval. A similar band has been attributed by Murayama and Amagi¹⁸ to the $-\text{CH}_2-$ rocking mode of head-to-head poly(vinylidene chloride) (H-H-PVCD).

The 1100–1500- cm^{-1} Region. In agreement with Nambu² we assign the band which appears at 1470 cm^{-1} or 1465 cm^{-1} or 1460 cm^{-1} in the CPE samples spectra to polyethylene sequences of various length. The absorbance values listed in Table II show that the polyethylene sequences disappear faster in the photochlorination process than in the thermal one.

Satoh and Enomoto¹⁹ made spectroscopic studies of vinylidene chloride–vinyl chloride copolymers and attributed the 1448- cm^{-1} band to the $-\text{CH}_2-$ bending mode of head-to-head PVC and the 1445- cm^{-1} band to the CH_2 bending mode of H-H-PVCD. Such bands are present at 1450–1445 cm^{-1} and 1440–1430 cm^{-1} in the CPE samples spectra and shift respectively to 1434 cm^{-1} and 1428 cm^{-1} when the PVC sequences lengthen in the CPE chains.^{6,13} By comparison with PVC^{9–12} we assign the 1440–1430→1428- cm^{-1} band and the 1450–1445→1434- cm^{-1} band respectively to the vinyl syndiotactic and isotactic structures present in the CPE chains.

It was impossible to identify a band at 1422 cm^{-1} and 1405–1410 cm^{-1} which could be assigned respectively to the CH_2 bending mode of $-\text{CHCl}-\text{CH}_2-\text{CCl}_2-$ and $-\text{CCl}_2-\text{CH}_2-\text{CCl}_2-$ structures.¹⁹

The CH_3 deformation mode of the initial polyethylene is found at about 1375–1380 cm^{-1} .^{3,16} This band is still present in the spectra of all the CPE samples. Nambu² drew the conclusion that methyl groups are still found in CPE; but did not give any precise statement about the origin of these methyl groups. Dynamic mechanical properties of CPE samples²⁰ show that the temperature of the β -relaxation of the initial polyethylene, related to $-\text{CH}_2-\text{CH}-\text{CH}_2-$

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structure by Robinson,²¹ stands almost at the same position for thermally chlorinated (up to 40% chlorine content) CPE samples made from

a branched polyethylene. Therefore one can draw the conclusion that with thermal chlorination, during the first chlorination-step, some branchings of the parent-polymer and particularly methyl groups remained unchlorinated. But in the case of photochlorinated and thermal CPE samples of high chlorine content by weight, there is a connection between the recovering method of the CPE samples from the chlorination medium and the 1375–1380- cm^{-1} band. Indeed, after the predetermined reaction period the reaction mixture is poured into a large volume of MeOH to precipitate the chlorinated product (1 volume of reaction mixture against 3 volumes of MeOH); the acylchloride structures present in the CPE chains react with MeOH produce acetate structures¹³ whose methyl groups give the 1375–1380- cm^{-1} band and whose carbonyl groups are responsible for the 1740–1760- cm^{-1} band.

Spectra Nos. 1 and 2 in Figure 10 compare a 73% Cl_2 (CPE sample) degree of polymerization $\overline{\text{DP}}_n=627$ with its fraction of the lowest number-average molecular weight ($\overline{\text{DP}}_n=67$).¹³ Spectrum No. 2 shows that the 1375–1380- cm^{-1} band and the 1740–1760- cm^{-1} band are stronger than the corresponding ones in the spectrum No. 1, which indicates that the carbonyl groups are localized

Figure 10. Infrared spectra (600–2000 cm^{-1}): 1, chlorinated low-density polyethylene (73% Cl_2) $\overline{\text{DP}}_n$, 627; 2, chlorinated low-density polyethylene (69% Cl_2) $\overline{\text{DP}}_n$, 67.

at the ends of the chlorinated chains. The strong $1600\text{--}1640\text{-cm}^{-1}$ band which appears in spectrum No. 2 of Figure 10 indicates the presence of some $\text{C}=\text{C}$ bonds at the end of the CPE chains.

Configurational and Conformational Changes in CPE

Shimanouchi and Tasumi²² demonstrated that the PVC syndiotactic sequences are energetically stable when the $\text{C}-\text{C}$ -bond internal rotation arrangement are *trans* (*T*). This arrangement avoids close contact between 2 successive chlorine atoms. But the PVC isotactic sequences are energetically stable if 2 successive $\text{C}-\text{C}$ bonds (2 successive monomeric units) are *T* and *gauche* (*G*) or *G* and *T*. The conformational structures linked to each kind of PVC configurational structure are represented in Figures 11a and b.

The *TT* syndiotactic conformation has been related to the 615-cm^{-1} band or to the S_{HH} resonance mode and the *TG* or *GT* isotactic conformation to 690-cm^{-1} band or to the S_{HC} resonance mode by some authors^{11,12} who stated that the ratio A_{615}/A_{690} can be used to calculate the

Figure 11. (a) Conformations of a PVC syndiotactic diad.

(b) Conformations of a PVC isotactic diad.

Figure 12. Conformational changes in the polymeric chains: 1, photochlorinated polyethylene samples from a branched parent-polymer (LDPE); 2, thermal-chlorinated polyethylene samples from a branched parent-polymer (LDPE).

relative proportion between the *T* and *G* conformations.

A plot of $A_{615}/A_{660-685}$ against chlorine contents in weight (Figure 12) for the photochlorinated and thermal chlorinated CPE samples leads to the following conclusions:

S_{HC} resonance mode prevail from the beginning of the chlorination reaction, *i.e.*, PVC isotactic sequences are more numerous in the CPE chains than syndiotactic ones. From the 55–60% chlorine content interval up to 73%, in the photochlorination process, $-\text{CHCl}-\text{CHCl}-\text{CH}_2-$ or $-\text{CHCl}-\text{CHCl}-\text{CHCl}-$ and $-\text{CHCl}-\text{CH}_2-\text{CCl}_2-$ structures arise from the chlorination of the isotactic portions of the PVC heterotactic tetrads and *GG* portions of PVC syndiotactic sequences *TTGG*.¹³ As can be seen in Figure 12, the appearance of these new structures enhanced the *G*-conformation proportion in the CPE chains. From the 55–60% chlorine content interval up to the 73% level one must

Figure 13. Conformational changes in the polymeric chains of polyethylene samples chlorinated beyond the minimum chlorination time necessary to obtain the saturation level (73-% Cl₂): △, HDPE (linear polyethylene); ▲, LDPE (branched polyethylene).

speak of S_{HC} and S_{HCl} resonance modes for the 685-cm⁻¹ band.

When the scheduled chlorination time necessary to reach the maximum chlorine content by weight is overrun⁴ the amount of *T*-conformation begin to increase again in the chains of the 73-% CPE samples issued from a branched polyethylene. This evolution is related to an important mechanism¹³ (Figure 13).

Quantitative Structural Analysis

Crowo and Fredriksen¹⁷ published an original method for calculating the ratio of number of CH₂ units/number of CHCl units (nb CH₂/nb CHCl) for CPVC samples. They used the absorbance of the CH₂ bending mode at 1428 cm⁻¹ and the CH-deformation mode at 1195 cm⁻¹. For a PVC sample the ratio of these absorbances (A_{1428}/A_{1195}) gives a number $\langle X \rangle$ which is related to a nb CH₂/nb CHCl=1. Thus the calculated A_{1428}/A_{1195} of a CPVC sample permits one to evaluate its ratio, nb CH₂/nb CHCl. But as the ratio, A_{1428}/A_{1195} , of a PVC is dependent on its tacticity²³¹ this method is adequate only if the reference PVC sample is the parent-polymer of the analysed CPVC samples and under the assumption that tacticity does not rule the chlorination

mechanism. Nevertheless, one can use it for routing calculation; for precise investigation the method based on NMR analysis is more accurate.^{4-6,13}

CONCLUSION

In connection with NMR investigations published elsewhere⁴⁻⁶ new bands have been identified in the CPE infrared spectrum. At the highest chlorine content by weight (73%), CPE and CPVC have nearly the same spectrum, which is different from the PVDC one. Although NMR proves that —CCl₂— units are present in CPE chains, it is impossible to identify their C—Cl stretching frequency.

In the case of overrunning the minimum scheduled chlorination time to reach the 73-% chlorine level, one cannot use the A_{1428}/A_{1434} ratio to calculate the syndiotacticity-index¹³ of the CPE because it is impossible to identify the 1434-cm⁻¹ band.

Infrared analysis is an important tool for showing the influence of tacticity on the polyethylene chlorination mechanism. In another paper¹³ we will discuss the photochlorination and thermal chlorination mechanisms of low-density polyethylene and high-density polyethylene samples in connection with this infrared analysis.

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