Structural and Conformational Changes in Solid-Phase Chlorinated Polyethylene

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ABSTRACT: The structural and conformational changes in solid-phase chlorinated polyethylene samples of different average molecular masses were studied with infrared spectroscopy. Characteristic absorption bands for both chlorinated polyethylene and chlorinated high-molecular-mass polyethylene, containing 1–56% Cl, were identified. The chlorine content in the macromolecular chains, ranging from 1 to 15%, was associated with the presence of single chloromethylene groups and short syndiotactic structural sequences of poly(vinyl chloride) derived from them. Higher degrees of chlorination, ranging from 20 to 56%, resulted in an increase in the relative part of the heterotactic structures with 1,2-, 1,3-, and 1,2,3-modes of mutual location of the chlorine atoms within a fragment. Moreover, solid-phase chlorinated polyethylenes with chlorine concentrations as high as 56% were polymers with a mixed amorphous–crystalline structure. On the basis of the intensity ratio of the absorption at 610 cm^{-1} to the absorption at 660 cm^{-1} for the corresponding characteristic absorption bands, the substitution of the hydrogen atoms for chlorine ones occurred predominantly in the *trans*-methylene groups, which were located within the amorphous and intermediate phases of polyethylene with chlorine concentrations as high as 20%. Consequently, the relative part of the gauche chlorinated methylene groups increased. A trans-to-gauche conformational change was thought to have taken place during the solid-phase chlorination of polyethylene under the influence of the bulky chlorine atoms. These changes were facilitated by the corresponding segmental mobility of the macromolecular chains. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 189–196, 2004

Key words: conformational analysis; infrared spectroscopy; polyethylene (PE); solid-state structure

INTRODUCTION

Chlorination is one of the most widely used methods for polyethylene (PE) modification. It is commonly implemented in solutions, suspensions, the solid state, and so forth. The properties of chlorinated polyethylene (CPE) depend on the structure of the starting material, the methods and conditions of its chlorination, and the chlorine concentration in the product.[1]

The CPE structure has been studied with various instrumental methods, including infrared spectroscopy (IRS). In this connection, publications examining the structural changes accompanying PE chlorination in both solutions and suspensions have been predominant in the literature.[2–8] The chlorine concentration in CPE has changed from 5 to 55%[4,5,7,8] and from 19 to 75%.[2,3,6] The characteristic absorption bands have been interpreted, and the presence of corresponding chlorine-containing structural fragments has been suggested. The possible formation of dichloromethylene groups has also been discussed; according to Nambu,[2] they are not present in PE chlorinated in solution and containing less than 68% Cl. Other authors[4,5,7] came to similar conclusions, claiming that the absence of the corresponding characteristic absorption band [$\nu(CCl_2)$] in CPE containing up to 55% Cl was indicative of a lack of geminal chlorine atoms. According to Chang et al.,[8] however, the number of CCl_2 groups in CPE with a chlorine concentration as high as 50% was too small to be successfully detected by IRS.

Studies on the conformational changes in PE chlorinated in solution and photochlorinated at 20°C in suspensions[6] and chlorinated under heterogeneous conditions as films[9] and monocrystals[10,11] have proved to be interesting. The ratio of TT to TG conformational changes (where T is trans and G is gauche) in CPE has been examined as a function of the degree of chlorination.[6,9] According to Quenum et al.,[6] the growth in the proportion of structural fragments of gauche conformation in the macromolecular chains of PE chlorinated under photochemical conditions resulted from the isomerization of short poly(vinyl chloride) (PVC) syndiotactic TTTT sequences into TTGG ones. Trans-to-gauche conformational changes occurred at room temperature in chlorinated films of low-density polyethylene (LDPE) with chlorine concentrations lower 30%.[9] For the chlorination of the amorphous boundary layer of PE monocrystals under mild conditions, Oyama et al.[10] proposed conforma-

tional models, representing two types of long folds, that could undergo mutual conversion.

There have been a limited number of reports in the literature concerning the study of solid-phase CPE with the IRS method.[12–14] Djagazpanian et al.[12] prepared CPE containing 10–40% Cl through the radiation-induced chlorination of PE in a fluidized-bed reactor. The authors compared the structure of the resulting polymer with that of PE chlorinated in solution and found that, up to a 40% Cl concentration, their product was crystalline. The structure of the solid-phase CPE depended significantly on the chlorination conditions, particularly the temperature.[13,14] Even with a chlorine concentration of 36%, the solid-phase CPE, prepared at a high temperature, was an amorphous product, unlike that obtained at a relatively low temperature.[14]

This work presents a more complete and detailed examination of the structural and conformational changes arising from the heterogeneous chlorination of PEs of various average molecular masses and different chlorine contents. With IRS, LDPE and high-density polyethylene (HDPE) samples of average molecular masses (5000–220,000), chlorinated in both solutions and suspensions, have been predominantly studied.[2,4,6,8] Therefore, it is particularly interesting to analyze the peculiar features of the infrared (IR) spectra of powdered chlorinated HDPE and high-molecular-mass polyethylene (HMMPE) samples and to discuss the effects of the conformational changes in the macromolecular chains with the substitution of hydrogen atoms for chlorine ones.

EXPERIMENTAL

Materials

HDPE and HMMPE were industrially obtained through the polymerization of ethylene in the presence of Ziegler–Natta catalysts. The main characteristics of HDPE were as follows: the viscosity-average molecular mass (M_η) was 96,500 g mol^{-1}, the melt-flow index was 4.28 g/10 min (determined at 190°C with a weight of 5 kg), the degree of crystallinity was 60.9% (determined by differential scanning calorimetry), and the melting temperature was 128.8°C. The corresponding characteristics of HMMPE were as follows: M_η was 685,000 g mol^{-1}, the melt-flow index was 0.13 g/10 min (determined at 190°C with a weight of 21.6 kg), the degree of crystallinity was 62.2%, and T_m was 133.3°C.

PVC samples, obtained by suspension homopolymerization, were also used, with a Fikentcher constant of 68.1, a number-average molecular mass of 86,000 g mol^{-1}, a bulk mass of 540 kg m^{-3}, and a moisture content of 0.03%. The experimentally determined chlorine content in PVC was 56.48%.

Sample preparation

The chlorination of powdered HDPE and HMMPE was conducted in a fluidized-bed reactor in the presence of a gaseous mixture consisting of chlorine and nitrogen in a volume ratio of 3:7. The experiments were carried out from 20 to 80°C. The combined chlorine content (*G*; mass % Cl) was determined with the Schöeniger method, which was followed by potentiometric titration with a 0.1*N* AgNO₃ solution.

CPE samples, containing 1.27, 3.12, 4.11, 5.08, 6.26, 7.82, 10.14, 15.87, 22.16, 27.62, 37.04, 44.42, or 56.09% Cl, were used for IRS. The chlorine concentrations in the chlorinated high-molecular-mass polyethylene (CHMMPE) samples was as follows: 1.26, 3.31, 4.42, 5.32, 6.67, 7.93, 10.36, 15.68, 21.56, 27.60, 37.00, 44.77, and 53.23%.

Measurements

IR spectra of CPE and CHMMPE were recorded with a Specord 75 IR instrument (Jena, Germany) and a Bruker Vektor 22 Fourier transform infrared instrument (Germany). The spectral region between 1800 and 400 cm^{-1} was scanned. Specimens prepared as KBr pellets and foils were used. The pellets were prepared by the powdery CPE and CHMMPE being pressed with KBr *in vacuo*. The polymer concentration in the samples was 2%, which was calculated with respect to KBr. The foils were prepared via the hot pressing of the powdery CPE and CHMMPE samples between Teflon sheets at 160°C under a pressure of 2.5 MPa and at a 25°C/min cooling rate for the molten samples. The thickness of the foil samples varied from 0.04 to 0.05 mm.

RESULTS AND DISCUSSION

Various absorption bands within the 600–1500-cm^{-1} range were recorded in the IR spectra of CPE prepared via the chlorination of PE under heterogeneous conditions. Some characteristic absorption bands for powdery CPE, analogous to those of powdery CHMMPE, are given in Table I. The interpretation of these spectra was made through a comparison with IR spectra of various chloroalkanes,[15,16] PE,[17,18] PE chlorinated in solutions and suspensions,[2–8] and PVC.[18,19]

Characterization of the C—Cl stretching vibrations for the solid-phase CPE

The absorption bands in the 600–700-cm^{-1} region were characteristic of the stretching vibrations of the C—Cl bond [ν(CCl)].[2,5,6,8] On the basis of corresponding studies of low- and high-molecular-mass reference compounds, the absorption band at 608–615 cm^{-1} was assigned to ν(CCl) for single (isolated) CHCl

TABLE I
Characteristic Absorption Bands in the IR Spectra of Powdery CPE

G (mass % Cl)	δ(CH$_2$)	δ(CH$_2$) in α-CHCl	γ$_w$(CH$_2$)	γ$_w$(CH$_2$)	γ$_t$(CH$_2$), γ$_w$(CH$_2$)	δ(CH) in CHCl	γ$_w$(CH) in CHCl	γ$_r$(CH$_2$) in α-CHCl	γ(CCl) S$_{CC}$	γ$_r$(CH$_2$)$_n$ (n ≥ 5)	ν(CCl) S$_{HC}$ TG	S$_{HH}$ TT
					Wave numbers (ṽ, cm^{-1}) and vibration modes							
0	1470, 1462	—	1369 m	1350 w	1300 w	—	—	—	—	731, 718	—	—
1.27	1470, 1462	—	1368 m	1352 w	1303 w	1260 sh	1192 vw	—	—	730, 718	660	610
3.12	1472, 1465	—	1370 m	1350 w	1303 w	1260 vw	1195 vw	—	—	732, 720	660	610
4.11	1471, 1465	—	1370 m	1352 w	1303 w	1263 vw	1192 vw	—	—	730, 718	660	610
5.08	1472, 1462	—	1370 m	1352 sh	1308 w	1263 w	1195 vw	—	—	731, 718	660	610
6.26	1472, 1462	—	1369 m	1353 sh	1310 w	1262 w	1194 vw	—	—	730, 720	660	610
7.82	1471, 1462	1442 sh, 1432 sh	1369 m	1350 sh	1310 w	1263 w	1195 vw	916 sh	790 sh	730, 718	670 sh, 660	610
10.14	1470, 1462	1442 sh, 1432 sh	1369 m	1350 sh	1307 w	1260 m	1195 w	915 w	790 w	730, 718	670 sh, 660	610
15.87	1470, 1460	1440 w, 1430 sh	1369 w	—	1310 sh	1260 m	1195 w	918 w	796 w	730, 718	670 sh, 660	608
22.16	1470, 1462	1442 m, 1432 w	1370 w	—	1310 sh	1266 m	1193 w	920 m	800 m	731, 718	671 sh, 660	608
27.62	1470, 1462	1442 m, 1432 w	1370 w	—	1313 sh	1266 s	1195 m	923 m	800 m	731, 718	672 w, 660	608
37.04	1471, 1462	1440 m, 1430 m	1368 w	—	1310 sh	1265 s	1195 m	925 m	800 m	730, 718	672 w, 660	608
44.42	1471, 1462	1441 s, 1430 s	1370 sh	—	1310 sh	1267 vs	1195 m	930 m	800 m	730, 718	672 w, 660	608
56.09	1470, 1460	1440 vs, 1427vs	1370 sh	—	1310 sh	1267 vs	1195 m	930 s	800 m	730, 718	672 w, 660	616, 608

Relative intensity: vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder.
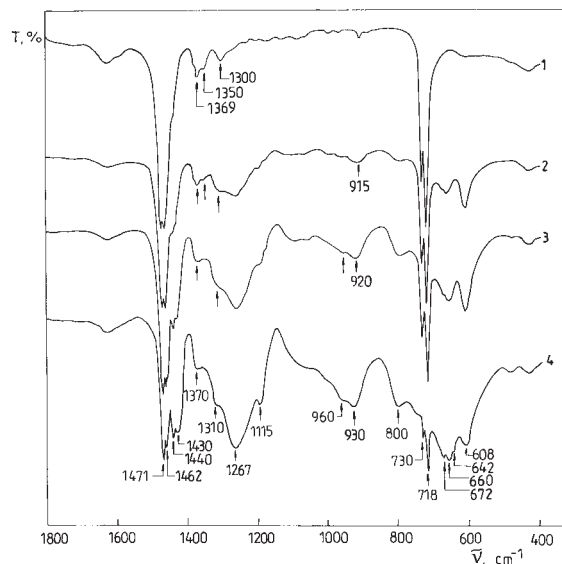

Figure 1 IR spectra of (1) HDPE and (2–4) CPEs containing 10.14, 22.16, and 44.42% Cl (KBr pellets).

groups and the corresponding short syndiotactics structural sequences of the S$_{HH}$ TT conformational mode. The presence of this band proved the existence of a trans planar zigzag mode of chain conformation for the amorphous phases of CPE and CHMMPE. The intensity of the band increased until a 22% Cl concentration was reached; however, at higher degrees of chlorination, it was reduced. No doublet in ν(CCl) at 610 cm^{-1} was detected in the IR spectra of samples with 44% Cl or less (Fig. 1), unlike the samples of suspension PVC and CPE, which contained 53–56% Cl (Fig. 2). The doublet at 610 cm^{-1} was characteristic of
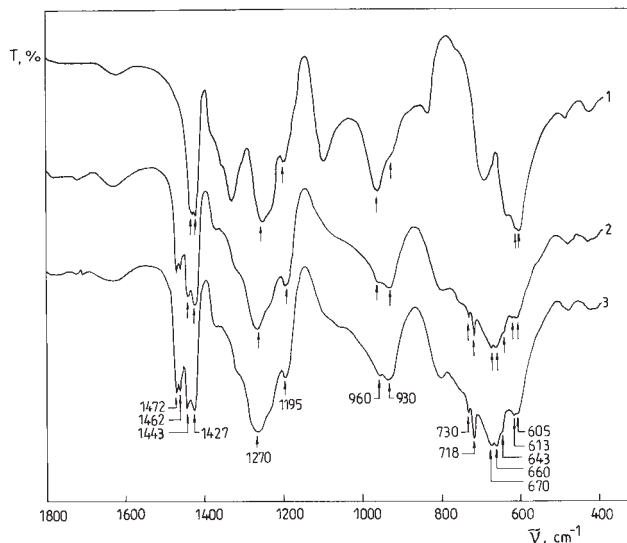

Figure 2 IR spectra of (1) a PVC suspension with 56.48% Cl, (2) CPE with 56.09% Cl, and (3) CHMMPE with 53.23% Cl (KBr pellets).

a uniform distribution of chlorine atoms along the macromolecular chains of syndiotactic PVC;[18] therefore, its absence up to 44% Cl proved the nonuniform mode of chlorination of PE in the solid phase, particularly in a fluidized-bed reactor. However, the gradual increase in the molar part of the chlorinated pentads of the CH_2—$CHCl$—CH_2—$CHCl$—CH_2 type caused the emergence of a slightly pronounced doublet at 610 cm^{-1} in the IR spectra of CPE and CHMMPE samples containing 53–56% Cl.[20]

The absorption band at 660–685 cm^{-1} was assigned to S_{HC} TG or gauche–trans (GT) types of conformation for chlorinated chains with predominant chlorine atoms of an isotactic (i) configuration.[15,18,19,21] Powdery samples of CPE and CHMMPE showed such a band at 660 cm^{-1}, and the latter did not change its position with a higher degree of chlorination. The same was observed for PE chlorinated in solution.[6] Samples with chlorine concentrations of 7.82–56.09% in CPE and of 6.67–53.23% Cl in CHMMPE indicated rather weak absorptions at 670–672 cm^{-1} (Table I). The latter were assumed to characterize the formation of longer structural sequences of the CH_2—$CHCl$—CH_2—$CHCl$ type, analogously to the band at 677 cm^{-1} in the IR spectrum of PVC.[18] Moreover, within the concentration interval of 22–56% Cl, a shoulder at 642 cm^{-1} was detected, which, in agreement with Bikson et al.,[21] was assigned to structures with vicinal chlorine atoms. The existence of such structures was proved by ^{13}C-NMR spectroscopy of samples of solid-phase CPE containing 10–56% Cl.[20]

After the hot pressing of the powdery CPE and CHMMPE samples, some of the absorption bands for ν(CCl) shifted toward higher frequencies, that is, from 610 to 615–622 cm^{-1} and from 660 to 667–670 cm^{-1}. This was probably determined by changes in the structures of the starting CPE samples subjected to melting and crystallization under nonequilibrium conditions. According to Klaeboe[22] the applied high pressure facilitated the formation of conformers with the smallest molar volume. This led to an enhancement of the heterotactic mode of chlorination in the chains for the CPE and CHMMPE samples prepared as foils.

Like for PE chlorinated in solutions and suspensions,[2,4,5,7] no absorption bands for ν(CCl$_2$) at 525–530 cm^{-1} were detected in the IR spectra of CPE and CHMMPE, with 1–56% Cl, prepared in a fluidized-bed reactor. The absence of this band was obviously associated with the fact that the molar part of the CCl$_2$ groups for polymers with 36–56% Cl concentrations was rather small, as determined previously with ^{13}C-NMR analysis.[20] In fact, according to Chang et al.,[8] the only groups detectable by IRS for samples of relatively low chlorine concentrations were single CHCl ones.

With chlorine concentrations exceeding 8–10%, absorption bands at 790–800 cm^{-1} were detected in the IR spectra of the CPE samples prepared as foils and

powders from the starting materials (Figs. 1 and 2 and Table I). Different interpretations concerning the nature of these bands are available in the literature.[2,6,16,19] The most acceptable one belongs to Krimm and coworkers,[16,19] according to whom the band could be assigned to C—Cl stretching vibrations for chlorinated CH$_2$ sequences with an S_{CC} conformation. Shipman et al.[15] claimed that an S_{CC} conformation could become detectable for secondary monochloroalkanes if certain structural and electronic effects stabilized it. Such a conformational type could be considered nontypical for some reference compounds. However, with the solid-phase CPEs, it was observed over a certain degree of chlorination. For the CPE samples, the border value of the degree of substitution corresponded to approximately 7.82% Cl or higher, whereas, for CHMMPE, a weak band was observed at 6.67% Cl. The formation of structures of the S_{CC} conformation type at lower chlorine concentrations for CHMMPE was probably due to the decreased limitations set by the ordered regions with respect to the rotations around the simple C—C bonds for the chlorinated CH$_2$ sequences in the amorphous polymer phase.

Specifics of the CH_2 and CH bending vibrations for solid-phase CPE

The various CH$_2$ and CH bending vibrations were identified in the 700–1500-cm^{-1} region (Table I). Some of these were present in the IR spectra of both the starting PE and HMMPE and the corresponding chlorinated products, whereas others were characteristic of CPE and CHMMPE with certain degrees of chlorination.

The most pronounced splits in the IR spectra of PE and HMMPE were those corresponding to the absorptions at 725 and 1460 cm^{-1}, which were assigned to the rocking vibrations of long CH$_2$ groups containing structural sequences [$\gamma_r(CH_2)_n$] at $n \geq 5$ and to the CH$_2$ bending vibrations [$\delta(CH_2)$; Figs. 1 and 2 and Table I]. The band at 718–720 cm^{-1} is known to be associated with the vibration of long trans CH$_2$ structural sequences in both the amorphous and crystalline phases of PE.[18,21] The band at 730 cm^{-1} is characteristic of $\gamma_r(CH_2)_n$ at $n \geq 5$ for the crystalline phase of PE and is sometimes called a crystallinity band.[18] The doublets at 1462 and 1470 cm^{-1} can be assigned to $\delta(CH_2)$ for the amorphous and crystalline phases of PE, respectively. As expected, the corresponding IR spectra (Figs. 1 and 2) indicated that the total CH$_2$ and (CH$_2)_n$ groups content decreased as the degree of chlorination became higher. The plot of the graph, indicating the light absorption at 718–720 cm^{-1} ($A_{718–720}$) versus the chlorine content (Fig. 3), showed that, within 1–10% Cl, the change in the CH$_2$ group concentration was more pronounced than that for the samples with 10–56% Cl. The steeper branch of this
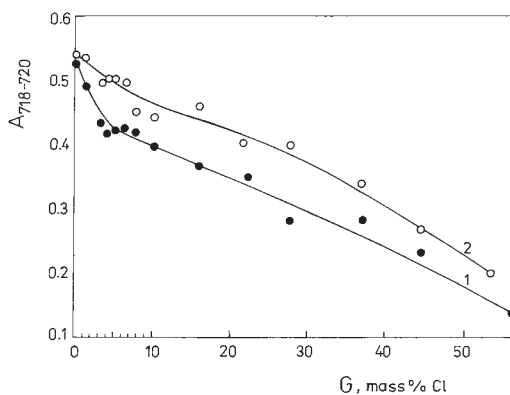
Figure 3 Dependence of $A_{718-720}$ for methylene groups on G for powdered samples of (1) CPE and (2) CHMMPE.

graph corresponded to the initial (faster) stage of chlorination within the amorphous phase of the starting polymers.[23] After that, both the amorphous and crystalline phases of PE and HMMPE were subjected to chlorination, which led to a reduction in the intensity of the characteristic crystalline band at 730 cm^{-1} (Figs. 1 and 2). Even at a low intensity, this band was also fairly detectable in the IR spectra of CPE and CHMMPE with high chlorine concentrations (53–56%). This proved the presence of at least two types of nonchlorinated monomer units in these polymer products and the preservation of the crystalline structure. This result fully agreed with the determined value for the residual degree of crystallinity (19% for CPE containing 56.09% Cl).[24] The doublet, indicated by the bands at 718–732 and 1460–1472 cm^{-1} within the concentration range studied (1–56% Cl), showed also that the solid-phase CPE had a nonuniform structure. Obviously, the chlorinated samples of the starting polymers contained nonchlorinated CH$_2$ structural sequences as well as chlorinated ones, located within the corresponding amorphous regions. Moreover, as shown in Figure 3, the concentration of the nonchlorinated CH$_2$ groups in CHMMPE was higher than that of CPE with the same chlorine content. This was probably due to the longer macromolecular chains of HMMPE, which were responsible for its more pronounced interphase irregularity.

The so-called conformational bands of PE were also recorded within the 1300–1370 cm^{-1} interval.[18] These absorption bands were present in the spectra of the starting polymers and chlorinated products and were characteristic for the twisting (γ_t) and wagging (γ_w) vibrations of the CH$_2$ groups located within the amorphous phase.[17,18,21] The increase in the chlorine content resulted in a reduction of their intensities, and this proved the active mode of chlorination within the amorphous regions of PE and HMMPE. Moreover, the rather weak band at 1350–1353 cm^{-1}, characteristic for γ_w(CH$_2$) with GG and GTG conformational modes of

the CH$_2$ groups,[21] was recorded for chlorinated samples containing up to 10–15% Cl.

The third group of absorption bands within the 700–1500 cm^{-1} interval was associated with the bending vibrations of CH$_2$ and CH groups, which emerged over a certain degree of chlorination. These were the absorption bands at 915–930, 1195, 1260–1270, 1430, and 1440 cm^{-1}. Initially, the band at 915–930 cm^{-1} appeared as a shoulder in the band, which was characteristic for the terminal vinyl group at 910 cm^{-1}; however, at a higher degree of chlorination, its intensity increased continuously. Moreover, the IR spectra of the samples containing over 16% Cl also indicated a weak band at 960 cm^{-1}. According to Dechant et al.[18] and Krimm et al.,[19] the band at 957–960 cm^{-1} could be assigned to γ_r(CH$_2$) for the crystalline phase of PVC, whereas the band at 925 cm^{-1} was characteristic of its amorphous phase. Commonly, the absorption band at 925 cm^{-1} in the IR spectra of PE chlorinated under various conditions has not been discussed[4,5] or has been assigned to C—C skeletal vibrations, the intensity of which is similar to that of the 960- and 1090 cm^{-1} bands for PVC.[2,12] Because the 720–1050 cm^{-1} region is indicative for the γ_r(CH$_2$) vibration mode of PE,[18] the absorption band at 915–930 cm^{-1} could be assigned to γ_r(CH$_2$) vibrations of CH$_2$ groups located at the α position with respect to the CHCl groups in the amorphous phase of CPE and CHMMPE. For CHMMPE, it was recorded at 6.67% Cl, and for CPE, it was recorded at 7.82% Cl. This was in good agreement with the band at 670–672 cm^{-1} observed earlier that characterized the formation of PVC-type structural sequences. The increase in the intensity of this band and its shift toward higher wave numbers with an increase in the chlorine content suggested the presence of longer chlorinated segments of the PVC type. The corresponding scissor bending vibrations of the CH$_2$ groups for the formed structural sequences of the PVC type appeared at 1430 and 1440 cm^{-1} (Figs. 1 and 2 and Table I). The band at 1432–1437 cm^{-1} was assigned to δ(CH$_2$) for PVC-type structures with a predominantly syndiotactic configuration[6,18] in the solid-phase CPE and HMMPE. On the other hand, the band at 1442–1440 cm^{-1} could be assigned to PVC-type structures of an isotactic configuration.[12,18,19] Its intensity in the interval from 22 to 44% Cl was higher than that of the band at 1432–1430 cm^{-1}. This indicated the predominant formation of chlorinated structures of an isotactic configuration. These two bands for samples of CPE and CHMMPE, containing 56.09 and 53.23% Cl, respectively, were stronger that the characteristic δ(CH$_2$) bands at 1460 and 1470 cm^{-1} for PE and HMMPE (Fig. 2). The latter was due to the large molar part of the chlorinated structures of various kinds in the solid-phase CPE.[20]

The absorption bands at 1195 and 1260–1268 cm^{-1} were recorded in the spectra of CPE and HMMPE of
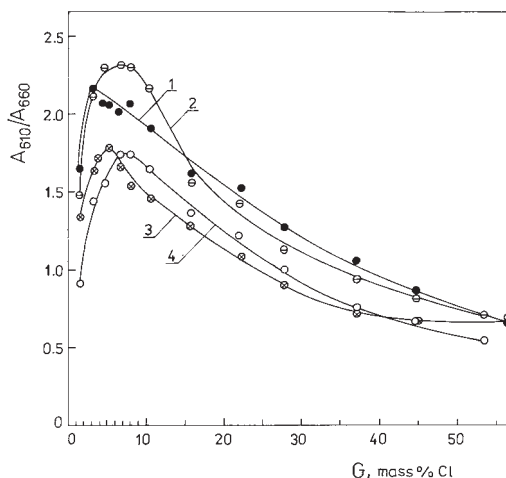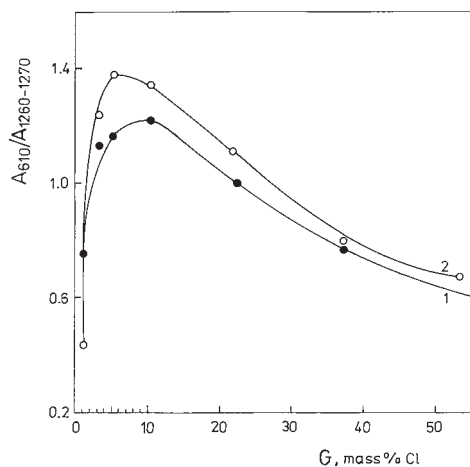
Figure 4 Dependence of A_{610}/A_{660} for chloromethylene groups on G for powdered samples of (1) CPE and (2) CHMMPE and for foils of (3) CPE and (4) CHMMPE.

Figure 5 Dependence of $A_{610}/A_{1260-1270}$ on G for powdered samples of (1) CPE and (2) CHMMPE.

rather low chlorine concentrations (Table I). The band at 1192–1195 cm^{-1} was analogous to the observed one in the IR spectrum of PVC at 1203 cm^{-1} and was assigned to the wagging C—H vibrations in the CHCl groups.[18] Up to 10% Cl, this band appeared as a shoulder in the 1260–1267 cm^{-1} absorption region because single CHCl groups were surrounded by non-reacted methylene structural sequences. Eventually, its intensity increased because of the formation of various PVC-type structures, such as head-to-tail (CH$_2$CHClCH$_2$CHCl) and head-to-head (CH$_2$CHCl-CHClCH$_2$). According to Quenum et al.,[6] the band at 1192–1195 cm^{-1} was also characteristic of a structure of the CHClCHClCHCl type. The CH bending vibrations for the chlorinated structures mentioned previously were observed at 1260–1270 cm^{-1}.[2,18,19,21] This band was particularly strong for the samples with 22–56% Cl because of the higher concentration of the CHCl groups in chlorinated structural fragments of various types.

Conformational changes accompanying the solid-phase chlorination of PE

The changes in the structures of PE and HMMPE during their chlorination in a fluidized-bed reactor were examined on the basis of the intensity ratio (r) of the absorption at 610 cm^{-1} (A_{610}) to the absorption at 660 cm^{-1} (A_{660}). The latter was used to calculate the relative part of the trans and gauche conformations for both solution CPE and PE prepared by photochemically induced chlorination in suspension[6] as well as heterogeneously CPE films containing over 9% Cl.[9]

The dependence of parameter r on the chlorine content in powdery samples of CPE and CHMMPE (curves 1 and 2) and corresponding foil samples

(curves 3 and 4) is shown in Figure 4. All the curves showed maximums in the region within 3–10% Cl. The calculated r values exceeded unity for samples with 22–25% Cl. This suggested that the solid-phase chlorination of PE and HMMPE up to about 22% Cl was mainly associated with the formation of single CHCl groups and their short syndiotactic structural sequences of a predominantly S_{HH} TT conformational mode.

The conformational differences emerging during chlorination were estimated by the concentration dependence of the $A_{610}/A_{1260-1270}$ and $A_{660}/A_{1260-1270}$ parameters,[5] which are shown in Figures 5 and 6, respectively. Apparently, during the first stage of chlorination (1–10% Cl added), both the trans and gauche CHCl groups were formed. Up to 20% Cl, the trans CH$_2$ groups were predominantly chlorinated. This corresponded to the studies of Bikson et al.[21] and Cheng et al.,[25] according to which CH$_2$ sequences of a trans conformation were predominant in both the amorphous and intermediate phases of PE. The higher values of the $A_{610}/A_{1260-1270}$ ratio for CHMMPE, com-
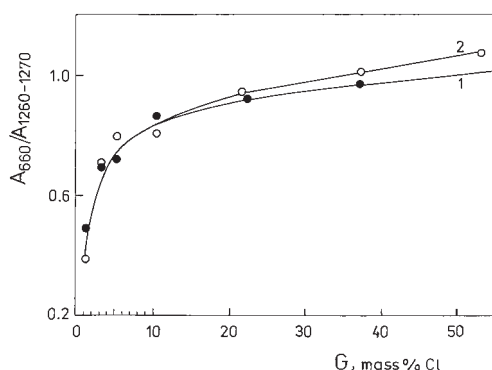
Figure 6 Dependence of $A_{660}/A_{1260-1270}$ on G for powdered samples of (1) CPE and (2) CHMMPE.

pared with those of CPE (Fig. 5), proved the predominance of the trans CH_2 groups in the interphase regions of the former.

An increase in the chlorine content beyond 10% led to a steady reduction of the A_{610}/A_{660} absorption ratio (Fig. 4). For the powdery samples, both the steadily increasing relative part of the CHCl groups of an S_{HC} TG (GT) conformation (Fig. 6) and the formation of vicinal CHCl groups during the chlorination affected these results. It was established previously[20] that the molar part of the vicinal CHCl groups increased as the content of chlorine added to PE exceeded 10%. The study indicated the presence of these groups for chlorine concentrations of about 20% or higher, and this was proved by the recorded absorption bands at 642 and 1195 cm^{-1}. On the other hand, for the region of 22–56% Cl, pronounced chlorination of the CH_2 structural sequences, located within the crystalline phase of PE, was detected, which resulted in a steady reduction in its degree of crystallinity.[24] The CH_2 groups in the crystalline phase of PE are known to possess a planar trans zigzag conformation.[18,26] Within the interval of 22–56% Cl, the relative part of the trans CHCl groups was reduced, whereas that of the gauche CHCl groups increased (Figs. 5 and 6). Therefore, it could be assumed that the trans-to-gauche conformational changes took place during the solid-phase chlorination of PE and HMMPE.

The following considerations are discussed to prove the conformational and configurational changes characterizing the chlorinated polymer chains:

1. The substitution of hydrogen atoms (0.12 nm) for chlorine ones (0.18 nm) caused significant stresses in the macromolecules, and in most cases, the latter could not preserve their planar conformation.[26]
2. The distortions of the macromolecules, influenced by the bulky chlorine atoms, led to S_{HC} conformations, rather than $S_{HH'}$ ones.[19]
3. The chloromethylene groups in the structural sequences of the $CHCl(CH_2)_n CHCl$ type ($n \leq 9$) affected the conformation of the CH_2 groups located between them.[27]

Even with nonchlorinated HDPE, Cheng et al.[25] found that exchanges involving the trans and gauche conformations within its amorphous phase were possible. The implementation of the trans-to-gauche conformational changes during the chlorination of the powdery PE and HMMPE samples was also facilitated by the fact that the experimental temperatures (20–80°C) were significantly higher than the corresponding glass-transition ones. Thus, the increased segmental mobility of their macromolecules led to an increased number of PVC-type isotactic structures of TG conformation. This was proved by the increasing intensity of the absorption band at 1440–1442 cm^{-1}. Moreover, the absorption bands at 790–800 cm^{-1} recorded in the IR spectra of CPE and CHMMPE indicated the formation of structures with an S_{CC} conformation. Therefore, the heterogeneous chlorination of PEs of different average molecular masses was accompanied by the formation of structures of S_{HH}, S_{HC}, and S_{CC} conformations until the chlorine concentration reached 56%.

The foil samples were characterized by lower A_{610}/A_{660} ratios in comparison with those of the powdery samples (Fig. 4, curves 3 and 4). The observed change was associated with the conditions of their processing, that is, melting and crystallization under higher pressure. The increases in the temperature and pressure resulted in the emergence of less favorable conformations.[18,22] This resulted in an observed reduction in the intensity of the absorption band at 615–622 cm^{-1} (S_{HH} TT conformation) and an increase in the intensity of the band at 667–670 cm^{-1} [S_{HC} TG(GT) conformation] in the IR spectra of the foils. Therefore, the high-temperature processing of the samples at increased pressure caused changes in the arrangement of the macromolecules, which were accompanied by an increased relative part of the chlorinated structural sequences with the gauche type of conformation.

CONCLUSIONS

The specifics of the structure of solid-phase CPEs of different molecular masses as a function of the degree of chlorination were studied. At the same chlorine concentration, the absorption bands in the IR spectra of CPE and CHMMPE were identical. For the 600–1000 cm^{-1} region, some of these bands were recorded at lower degrees of chlorination of HMMPE than PE. This could be ascribed to the different structural organizations of the interphase layers of these polymers.

The spectra of the chlorinated samples with up to 10% Cl added resembled to a higher degree those of the PE and HMMPE starting materials than that of PVC. The IR spectra of the samples containing 10–56% Cl showed combinations of certain characteristic absorption bands observed for PE and PVC. The band at 720–730 cm^{-1} was rather indicative because its doublet mode, observed for all the chlorinated samples, proved the preservation of their crystalline–amorphous structure within the concentration range studied.

The solid-phase chlorination of PE and HMMPE up to various degrees of chlorination led to the preparation of macromolecular blends with a nonuniform distribution of the chlorine atoms along the polymer chains. Single trans-chlorinated CH_2 groups and short syndiotactic structural sequences of the PVC type were predominantly formed during the initial stage of the process, and their relative part was higher for

CHMMPE than for CPE. Higher degrees of chlorination (20–56% Cl) resulted in an increase among the heterotactic (s + i) PVC-type structural sequences, in which structures with S_{HH}, S_{HC}, and S_{CC} conformations were observed.

The conformational changes accompanying the chlorination of powdery PE and HMMPE were estimated from the concentration dependence of the A_{610}/A_{660} absorption ratio in the IR spectra of the corresponding samples. Its high values at low degrees of chlorination (4–15% Cl) were considered an evidence for the predominant part of the chlorinated sequences of the S_{HH} TT conformational type. The conformation of the macromolecules within the interval of 20–56% Cl was affected by the mode of substitution of hydrogen atoms for chlorine ones. This caused a new structural organization to emerge for the amorphous phase of CPE and CHMMPE, which was associated with an increase in the relative part of the chlorinated CH_2 groups of the gauche conformation. It was, therefore, assumed that the heterogeneous chlorination of PE was accompanied by trans-to-gauche conformational changes under the influence of the bulky chlorine atoms and the corresponding segmental mobility of the macromolecules.

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