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# THERMAL BEHAVIOR AND CHARACTERIZATION OF SOLID-STATE CHLORINATED POLYETHYLENES

*Stoyanka Stoeva*[1*], *Dimitrinka Tsocheva*[2] *and L. Terlemezyan*[2]

[1]Department of Organic Chemistry, Assen Zlatarov University, 8010 Bourgas, Bulgaria
[2]Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

The melting behavior of solid-state chlorinated polyethylene samples of various average molar mass has been studied by employing the differential scanning calorimetry method. Both the thermal and thermodynamic characteristics of the as-prepared chlorinated powdery polymer samples were found to be essentially different, compared to those of the melt-crystallized ones. The changes in the corresponding values depended mainly on the content of the comonomer units such as chloromethylene and dichloromethylene groups and their distribution along the polymer chains. Therefore, it can be assumed that the order of the polymer crystals arrangement is disturbed in the course of both the chlorination process and the subsequent melt crystallization.

**Keywords:** *chlorinated polyethylenes, DSC, melting behavior*

## Introduction

The modification of polyethylene (PE) by chlorination gives rise to the preparation of products with different properties, depending on the degree of chlorination, the experimental method and the reaction conditions. Commonly, if the chlorination is performed in solution, the chlorine atoms are distributed randomly along the PE chains. Chlorination of PE in suspension and solid-state chlorination conducted below the melting temperature (most frequently, below 100°C) results in the preparation of polymer with block-like structure, characterized by the presence of non-chlorinated as well as low- and highly-chlorinated segments [1]. The interrelationship between the molecular structure of PE, chlorinated in solution or suspension and its thermal characteristics was studied by a number of authors [2–13]. The peak temperature of melting ($T_m$) of these products was found to decrease almost linearly with increasing the fraction of the chlorinated comonomer units [2, 5, 6, 9, 11]. Similar trend was observed with respect to the change of the enthalpy of melting ($\Delta H_m$) and the corresponding degree of crystallinity of the chlorinated products [2, 6, 10].

The melting behavior of heterogeneously chlorinated PE (CPE) samples prepared as powders and films was more complicated [14–17]. Chlorine content up to 7 to 16.4% determined in powdery chlorinated PE or chlorinated superhigh-molecular PE was associated with negligible decrease of $T_m$ [14–16], whereas $\Delta H_m$ did not change [14] or slightly decreased [16]. For as-prepared chlorinated films, a two-step decrease of $T_m$ up to chlorine content of 30% with subsequent increase of this temperature was recorded [17]. According to the authors, the initial decrease of $T_m$ was associated with an increase of the interfacial free energy, similar to that observed for chlorinated PE monocrystals [14, 18].

For melt-crystallized samples of PE chlorinated in suspension, solution and solid state, continuous decrease of $T_m$ and $\Delta H_m$ values was observed. The predominating opinion in this case is that cocrystallization of a certain part of the chlorinated methylene groups (CHCl) with the methylene ($CH_2$) ones takes place [4, 5, 9, 10, 14]. According to Chang *et al.* [9], the trend towards cocrystallization of CHCl with $CH_2$ groups was more clearly pronounced for PE chlorinated in solution, compared to that chlorinated in suspension. In the latter case, the chlorine atoms were located within the amorphous phase of PE predominantly.

Apparently, the melting behavior of CPE depends on the conditions of its preparation and the mode of its thermal treatment. In this work, a systematic study on the thermal behavior of solid-state chlorinated PE with different average molar mass as a function of the chlorine content is performed. Moreover, the changes in some thermodynamic characteristics of chlorinated polyethylenes (CPEs), depending on their microstructure are also studied.

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[*] Author for correspondence: sstoeva2001@yahoo.com

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*Akadémiai Kiadó, Budapest, Hungary*
*Springer, Dordrecht, The Netherlands*

## Experimental

### *Materials*

The parent polymers were a high-density PE of a normal molar mass and a high molar mass PE (HMMPE). These polymers were commercial products of Neftochim, Bulgaria prepared by polymerization of ethylene in the presence of Ziegler-Natta catalysts. The main characteristics of high-density PE were as follows: the average-viscosity molar mass ($\overline{M}_\eta$) was 96.5 kg mol$^{-1}$; the melt flow index was 4.28 g/10 min (determined at 190°C and a load of 5 kg); the degree of crystallinity was 61%, and the peak temperature of melting ($T_m$) was 128.8°C. The corresponding characteristics of HMMPE were as follows: $\overline{M}_\eta$ was 685 kg mol$^{-1}$; the melt flow index was 0.13 g/10 min (determined at 190°C and a load of 5 kg); the degree of crystallinity was 62%; $T_{m1}$ and $T_{m2}$ values were 126.8 and 135.4°C, respectively. The determination of the degree of crystallinity and the peak temperatures of melting was based on the melting curves for the first heating scan at a rate of 5°C min$^{-1}$.

### Sample preparation

The chlorination of powdered high-density PE and HMMPE was conducted in a fluidized-bed reactor in the presence of gaseous mixture of chlorine and nitrogen passed in the volume ratio 3:7 respectively. The experiments were carried out within the temperature interval from 20 to 80°C. The total chlorine content (G, mass% Cl) was determined, according to the Schöeniger method, followed by potentiometric titration with 0.1N $AgNO_3$ solution.

CPE samples, containing 1.27, 3.12, 5.08, 7.82, 10.14, 15.87, 22.16, 27.62, 37.04, 44.42 and 56.09% chlorine were used for DSC analysis. The chlorine content in CHMMPE samples was as follows: 1.26, 3.31, 5.32, 7.93, 10.36, 15.68, 21.56, 27.60, 37.00, 44.77, 53.23 and 55.21%.

### *Methods*

The calorimetric studies were performed on Perkin Elmer DSC 7 differential scanning calorimeter in a temperature range of 40–160°C. The measurements were conducted in argon atmosphere. The heating and cooling rates (β) for all CPE and CHMMPE were 5°C min$^{-1}$. The sample mass was ca. 10 mg in each case. The instrument was calibrated with indium and lead standards for temperature and heat change. An empty aluminum pan was used as a reference sample. The DSC traces were presented as normalized with respect to the sample mass. The real melting temperature ($T_m^r$) of the samples, related to the crystalline structure formed after cooling at the rate of 10°C min$^{-1}$ was determined according to Illers [19]. Heating rates of 2, 5, 10 and 20°C min$^{-1}$ were used. The real initial ($T_i^r$) and final ($T_f^r$) temperatures of the melting interval were also determined, using the experimental values at different scanning rates. These values were obtained from the intersection points of the tangents drawn at the lower and higher temperature sides of the endotherms, respectively, and the tangent to their bases [20, 21]. The heat of fusion was corrected for the chlorine content and expressed in joules per gram of PE according to the following expression [16]:

$$\Delta H_{m(corr)} = \Delta H_{m(obs)}/(1 - 0.972\cdot \text{mass fraction Cl}) \quad (1)$$

The graphically reported values were the average ones for at least two runs at the appropriate chlorine content. The relative error of their determination was less than 3%.

Melting temperatures of chlorinated PE containing up to 30% chlorine, for which CHCl groups only were found [22], were estimated using the Flory's equation for the semicrystalline linear irregular copolymers [23]:

$$1/T_m - 1/T_m^0 = -R/\Delta H_m^0 \ln X_A \quad (2)$$

where $T_m^0$=145.5±0.5°C is the equilibrium melting temperature of an infinite PE crystal [23, 24]; $\Delta H_m^0$=4102 J mol$^{-1}$ $CH_2$ group is the molar enthalpy of melting for the homopolymer (PE), which is actually the melting enthalpy for PE of 100% crystallinity [25]; $R$=8.314 J K$^{-1}$ mol$^{-1}$ is the molar gas constant; $X_A$ is the molar fraction of crystallizable regular units. For CPEs $X_A$=1–$X_B$, where $X_B$ is the molar fraction of non-crystallizable CHCl units.

The parameter of the intrachain cooperativity of melting (ν) was estimated, according to the following expression [20, 21]:

$$\nu = 2R(T_m^r)^2/\Delta H_m^0 \Delta T^r \quad (3)$$

where $T_m^r$ is the real peak temperature of melting; $\Delta T^r = T_f^r - T_i^r$ and $T_i^r$ is the same as $T_{onset}^r$. The parameter ν reflects the minimum unit sequences in the chain, that proceed entirely from the crystal to the melt in the state of statistical spheres. It was presented as the number of $CH_2$ groups N($CH_2$) or as the length of the chain sequences, expressed in Å.

The parameter of thermodynamical stiffness of the macromolecule or the so-called steric coefficient (σ) was determined on the basis of the following empirical equation [26]:

$$\Delta S_c = R\ln z' + C_{z'}/\sigma^2 \quad (4)$$

where $\Delta S_c$ is the conformational entropy; $z'$ is the statistical sum of the contributions of the *trans* and *gauche* isomers in the chain. The parameter $C_{z'}$ is associated with the difference between energies of the *trans* and *gauche* isomers. The values of the parameter σ depend mainly on short-range interactions, concerning four consecutive bonds in the main polymer chain. It was found that, for most polymers, $R\ln z'=1.5\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and $C_{z'}=18\ \mathrm{J\ K^{-1}\ mol^{-1}}$ [26]. As a result, the empirical Eq. (4) can be expressed as: $\Delta S_c=1.5+18/\sigma^2$. Therefore, for known $\Delta S_c$ values, the parameter σ can be calculated. $\Delta S_c$ was determined on the basis of the following empirical equation [21]:

$$\Delta S_c=(0.75\pm0.1)\Delta S_u \tag{5}$$

where $\Delta S_u$ is the overall melting entropy, expressed by the ratio:

$$\Delta S_u=\Delta H_{m(corr)}/T_m^r \tag{6}$$

$\Delta H_{m(corr)}$ is the corrected enthalpy of melting of the sample. The calculated values of σ are not the absolute ones and can only be compared with each other.

## Results and discussion

Some typical melting endotherms for the first and the second heating scans of CPE and CHMMPE are shown in Figs 1 and 2, respectively. In the temperature range studied, a monomodal peaks of the first melting of as-prepared CPE samples were observed on the curves (Fig. 1). The CHMMPE samples showed broad bimodal first melting peaks up to 22% Cl content at all scanning rates, on analogy with the parent polymer (Fig. 2). At higher chlorine content monomodal endotherms of decreased area were observed, with broader melting range.

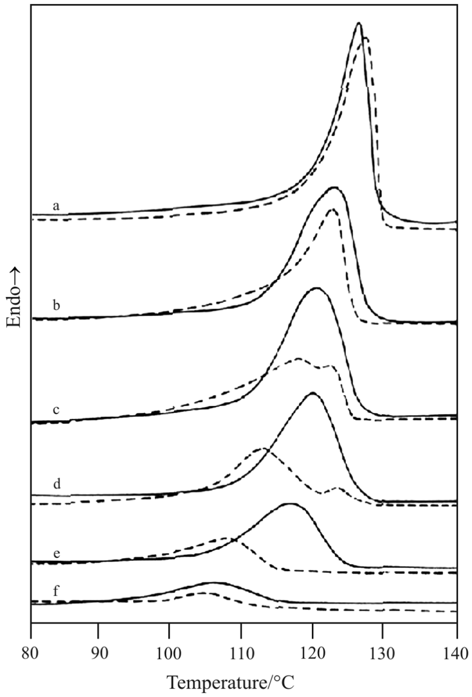

**Fig. 1** Normalized DSC curves for the first (—) and second (- - -) heating scans of a – high-density PE and heterogeneously chlorinated PE, containing b – 5.08% Cl, c – 10.14% Cl, d – 22.16% Cl, e – 37.04% Cl and f – 56.09% Cl; the heating rate is 5°C min$^{-1}$

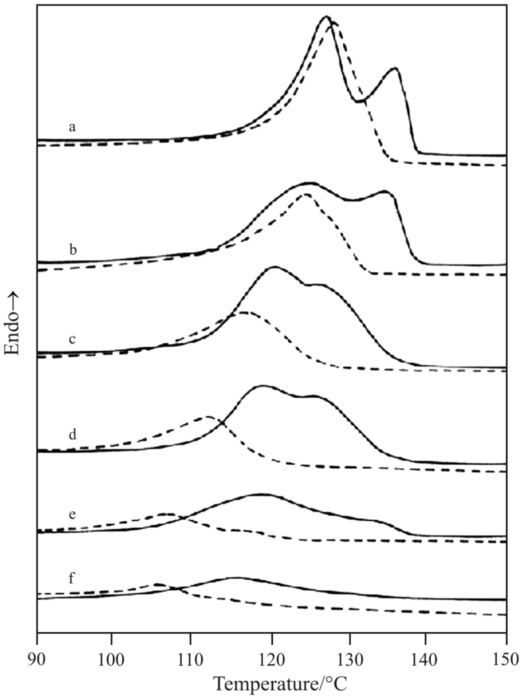

**Fig. 2** Normalized DSC curves for the first (—) and second (- - - ) heating scans of a – HMMPE and heterogeneously chlorinated HMMPE, containing b – 5.32% Cl, c – 10.36% Cl, d – 21.56% Cl, e – 37.00% Cl and f – 53.23% Cl; the heating rate is 5°C min$^{-1}$

It is well known, that the multiple endothermic peaks represent different populations of crystallizable sequences and thus crystallite size distribution [21, 27–29]. The presence of the bimodal endotherm in initial HMMPE suggests the corresponding type of crystallite size distribution. This type of distribution was preserved up to, approximately, 22% chlorine content in CHMMPE, and it was followed by stronger decrease of the higher temperature peak of the endotherms. According to Jokela *et al.* [30], the higher temperature peak for PE copolymers could be related to crystalline phase, formed by the existence of longer methylene group sequences. Therefore, it could be assumed that in as-prepared solid-phase CHMMPE of chlorine content, exceeding 22%, some averaging in the lengths of the crystallizable sequence units occurred, under the influence of chlorine atoms in the polymer chains.

When the chlorinated PE samples were recrystallized from the melt, the corresponding endotherms showed a single melting peak predominantly. This was probably due to promoted cocrystallization of structural sequences of various length. For CPE samples only, containing 10.14 and 22.16% Cl, endotherms with bimodal melting peaks at scanning rates, varying from 2 to 20°C $\text{min}^{-1}$ were recorded (Fig. 1, curves *c* and *d*). This could be explained by a model, that allows for the crystallizable sequences to be partioned into two fractions with different lengths [21, 27, 28]. Apparently, at chlorine content between 10 and 22%, which corresponds to 4–11 chlorine atoms per 100 carbon ones, some kind of fractionation takes place. The latter is facilitated by the sequences of crystallizable units with appropriate length formed previously. On the other hand, at chlorine content over 5%, the area of the endotherms and their peak temperatures of melting decreased continuously (Figs 1 and 2). Since the endotherms of the chlorinated PEs were compared at the same heating rate (5°C $\text{min}^{-1}$), their shape after recrystallization from melting state would depend mainly on the size and degree of perfection of the crystallites [31]. The latter were apparently diminished as the relative part of the non-crystallizable units such as chloromethylene and dichloromethylene groups increased.

The corrected values of the enthalpy of melting ($\Delta H_{\text{m(corr)}}$) for powdered and melt-crystallized chlorinated PEs are shown in Fig. 3. For the as-prepared powdered CPE and CHMMPE samples (curves 1 and 2, respectively), the values of parameter $\Delta H_{\text{m(corr)}}$, determined for the concentration range of 1 to 15% chlorine are from 2 to 6% higher, compared to $\Delta H_{\text{m}}$ of the initial polymers. An increase of $\Delta H_{\text{m(corr)}}$ up to chlorine content of, approximately, 25% was observed by Guzmán *et al.* in chlorinated PE single crystals at their first heating scan [18]. Other authors found, that $\Delta H_{\text{m(corr)}}$ values remained nearly constant until reaching chlorine content of ca. 20% in chlorinated PE single crystals [14, 32] or in suspension-chlorinated PEs [9, 14]. The constant values of $\Delta H_{\text{m(corr)}}$ or their slight increase for as-prepared chlorinated samples were explained by preferential attack, occurring in the non-crystallizable regions [14, 18].

The changes in the parameter $\Delta H_{\text{m(corr)}}$ for the solid-state chlorinated PE and HMMPE up to chlorine content of 15% can be better understood if the amorphous phase of these polymers is regarded as consisting of two distinguished fractions: an ordered fraction and really amorphous one [33, 34]. The ordered amorphous fraction is located within the intermediate phase, where, according to Cheng *et al.* [35], the C–C bonds are in *trans* conformation predominantly, as in the crystallites but possess higher mobility compared to the crystalline state. As a result of the initial chlorination of the really amorphous and intermediate phases of high-density PE and HMMPE, some stresses caused by the bulky chlorine atoms occur in the polymer chains. According to Schneider [36], the release of the macromolecules from the induced stresses can be implemented by the corresponding conformational changes, which depend on the intramolecular cooperativity and the flexibility of the interconnected monomer units. Chlorine content up to 10–15% corresponds to one chlorine atom per 22–14 carbon ones. In such a case, the elasticity of the carbon-carbon bonds is still high, since the CHCl units in structures such as $\text{CHCl(CH}_2)_n\text{CHCl}$ restrict slightly the internal rotation of the intermediate $\text{CH}_2$ groups, provided that $n \geq 9$ [37]. This suggests the possibility of implementation of *gauche–trans* and the respective *trans–gauche* transitions for the longer sequences of $\text{CH}_2$ groups. It was established previously, that in the solid-state chlorinated high-density PE and HMMPE, containing up to 10–15% chlorine, formation of isolated CHCl groups of a $\text{S}_{\text{HH}}\text{TT}$ conformational mode occurred predominantly [38]. This conformation is related to a hydrogen atom, located in *trans* position with respect to the chlorine atom on both sides of the secondary C–Cl bond. It could be assumed, that the relatively high content of these groups is due not only to the chlorination of the existing *trans*-$\text{CH}_2$ groups in the intermediate phase but, also, to the chlorination of *trans*-$\text{CH}_2$ groups, emerging from *gauche–trans* transitions. These transitions are facilitated by higher-energy conformation, being transformed into the lower-energy one. The stretched structures thus formed can be arranged

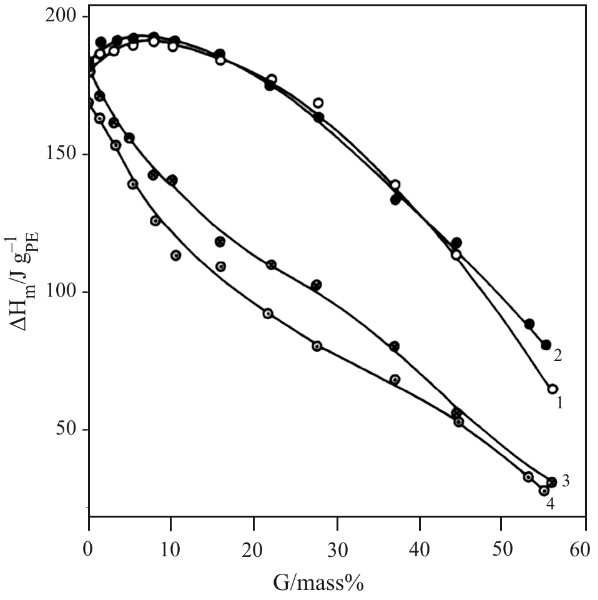

**Fig. 3** Enthalpy of melting ($\Delta H_{\text{m}}$) *vs.* chlorine content (G) for: as-prepared powdered 1 – CPE and 2 – CHMMPE samples: melt-crystallized 3 – CPE and 4 – CHMMPE samples; the heating rate is 5°C $\text{min}^{-1}$

**Table 1** Melting characteristics of high-density PE, HMMPE and their chlorinated products of various chlorine content

| Sample | First melting | | | | Second melting | | | |
|---|---|---|---|---|---|---|---|---|
| | $T_m^r$/°C | $\Delta T_m^r$/°C | ν | | $T_m^r$/°C | $\Delta T_m^r$/°C | ν | |
| | | | N($CH_2$) | Å | | | N($CH_2$) | Å |
| PE | 125.0 | 5.9 | 109 | 139 | 126.6 | 4.8 | 135 | 172 |
| CPE 5.08% Cl | 119.5 | 11.0 | 57 | 72 | 121.0 | 9.1 | 69 | 88 |
| CPE 22.16% Cl | 115.9 | 13.6 | 45 | 57 | 110.2 | 12.1 | 49 | 63 |
| CPE 56.09% Cl | 111.8 | 19.2 | 31 | 40 | 104.7 | 18.6 | 31 | 40 |
| HMMPE | 125.2<br>134.0 | 14.9 | 43<br>45 | 55<br>57 | 125.0 | 9.1 | 71 | 90 |
| CHMMPE 5.32% Cl | 122.7<br>132.1 | 22.6 | 28<br>30 | 36<br>38 | 121.9 | 16.2 | 39 | 50 |
| CHMMPE 21.56% Cl | 115.5<br>123.3 | 23.9 | 26<br>27 | 33<br>34 | 110.0 | 18.5 | 32 | 41 |
| CHMMPE 53.23% Cl | 112.7 | 25.0 | 24 | 31 | 104.5 | 18.9 | 31 | 39 |

as structural domains with more restricted motions [32]. The formation of more compact structures within the interlamellar regions gives rise to higher $\Delta H_{m(corr)}$ values for the as-prepared chlorinated PEs containing from 1 to 15% Cl. The observed trend corresponds to the statement, that the structural changes in the amorphous phase could influence both the enthalpy and heat capacity values of the semicrystalline polymers [21, 39].

Significant decrease of $\Delta H_{m(corr)}$ for the as-prepared CPE and CHMMPE (Fig. 3, curves 1 and 2, respectively) was observed for samples of chlorine content from 15 to 56%. The decrease in the enthalpy of melting is principally associated with disturbance in the order of the polymer crystals, which leads to appearance of a large number of considerably smaller and disordered crystals [21, 27, 40]. The solid-state chlorination of PE below its peak temperature of melting $T_m$ obviously takes place, according to a mechanism similar to that for chlorination in suspension. The latter involved disruption of the crystals, directed from the edges inward, rather than from the surfaces [9]. The penetration of the reactant into the depth of the crystallites was facilitated by both the distortion of crystalline lattice under the influence of the bulky chlorine atoms [15] and the segmental mobility of PE chains, since the reaction was conducted at temperatures higher than the glass-transition one. The change in the parameter of the intrachain cooperativity of melting ν could serve as an evidence for the influence of the degree of chlorination on the size of the crystallites in the solid-state chlorinated PEs (Table 1). Since the values of this parameter corresponded with first approximation to the crystalline lamellar thickness [20, 21], they should not be accepted as absolute ones; rather, they should be considered as comparative values only. The increase in the degree of chlorination led to a gradual decrease in the number of crystallizable $CH_2$ groups (N($CH_2$)) and the length of the corresponding sequences for powdered CPE samples, whereas, for CHMMPE samples, they remained almost unchanged (Table 1). For melt-crystallized CHMMPE samples, the $CH_2$ sequences were longer than for the as-prepared ones. This is probably caused by the inclusion of a part of the non-chlorinated $CH_2$ groups from the interfacial layers into the ordered regions of the polymer in the course of its crystallization from the melt.

The $\Delta H_{m(corr)}$ values for melt-crystallized samples decreased from 8.6% (CPE-1.27% Cl) to 52.3% (CPE-56.09% Cl), and, respectively, from 7.4% (CHMMPE-1.26% Cl) to 66.0% (CHMMPE-55.21% Cl), compared to the values of the original powdered polymers (Fig. 3, curves 3 and 4). At the same chlorine contents, $\Delta H_{m(corr)}$ values of CHMMPE were lower than those of CPE. Three concentration ranges could be located on curves 3 and 4, for which $\Delta H_{m(corr)}$ values were consecutively decreased as follows: from 1 to 15% Cl, $\Delta H_{m(corr)}$ values changed by 59–65 J $g^{-1}$ PE; from 15 to 37% Cl the corresponding change was 39–41 J $g^{-1}$ PE; and from 37 to 56% Cl the change amounted to 41–49 J $g^{-1}$ PE. According to a number of authors, the depression in the enthalpy of melting of chlorinated PEs after melt recrystallization is consistent with the inclusion of defects within the crystalline lattice, thereby lowering the crystallinity [4, 5, 9, 10, 14]. The steeper reduction of $\Delta H_{m(corr)}$ for the first section of the curves corresponded to the fact that, within this concentration interval, single CHCl groups were predominantly formed in the chlorinated PE chains. This was previously established by employing $^{13}$C-NMR spectroscopy [22]. The joint cocrystallization of CHCl groups with $CH_2$ groups not only leads to lowering the $\Delta H_m$ values but, also, to an increase of crystallite dimensions towards the [110] and [020] crystallographic directions [41]. Chlorine content over 15% resulted in an increased concentration of the vicinal CHCl groups; for samples of more than 30% Cl, the presence of $CCl_2$ groups was also registered [22]. Regardless the fact, that the vicinal CHCl units could cause more significant crystallographic defects than the single ones [5], the $\Delta H_{m(corr)}$ depression in the second and the third section was smaller than that in the first one. This is probably associated with the hampered inclusion of the bulkier comonomer units such as vicinal CHCl–CHCl and isolated $CCl_2$ groups into the PE crystalline lattice. However, their presence in the proximity of crystalline surfaces could cause significant distortion of crystals [10, 15], which also results in $\Delta H_{m(corr)}$ depression.

The change in the peak temperatures of melting ($T_m$), depending on both the scanning rates and degree of chlorination was given on Figs 4 and 5. By an extrapolation towards zero scan rate, the real values of $T_m$, and, also, $T_i$, $T_f$ and their difference $\Delta T_m^r$ were determined (Table 1). Since the dependence of $T_m$ on the scanning rates was linear, it could be assumed, that the processes of recrystallization and reorganization in the metastable lamellas for the initial and chlorinated polymers are strongly restricted. Moreover, the difference between $T_m$ of the samples at $\beta$= 20°C $min^{-1}$ and $\beta$=2°C $min^{-1}$ was within the limits of 1.6 to 5°C, which pointed to slight overheating of the crystals during their melting [20, 21]. As seen from Fig. 4, $T_m$ of the melt-crystallized samples was less sensitive towards the differences in scanning rates, compared to the $T_m$ of the powdered samples. Similar change in the slope of lines was also observed for melt-crystallized CHMMPE samples. If assuming, that the heat conduction of the powdered and recrystallized samples of the same chlorine content would be the same at the corresponding scanning rate, the reason for the lesser influence of the heating rates onto the $T_m$ values of the second melting probably lies in the lower heterogeneity of the samples geometry after the melt recrystallization [42]. The structural heterogeneity of the samples, however, increased with the degree of chlorination, which was proved by the continuous increase in the $\Delta T_m^r$ values (Table 1). Since $\Delta T_m^r$ reflects the real difference between $T_f^r$ and $T_i^r$, the change in its values does not depend on the scanning rate. The parameter $\Delta T_m^r$ is mainly associated with the lamellas distribution in accordance with their thickness and perfection [21, 27] as well as the effect of the intrachain cooperativity of melting [21] and the boundary premelting of the crystals [27]. With the CPE samples, $\Delta T_m^r$ values were, approximately, the same for powdered and melt-crystallized samples at the same chlorine content. However, the observed difference in the $\Delta T_m^r$ values for powdered and melt-crystallized CHMMPE samples could be related to the change in the parameter of the intrachain cooperativity of melting ν. It can be seen from

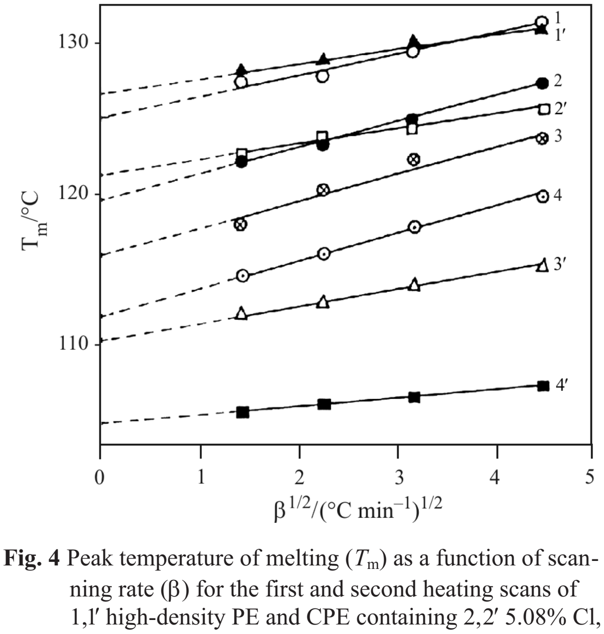

**Fig. 4** Peak temperature of melting ($T_m$) as a function of scanning rate ($\beta$) for the first and second heating scans of 1,1′ high-density PE and CPE containing 2,2′ 5.08% Cl, 3,3′ 22.16% Cl and 4,4′ 56.09% Cl

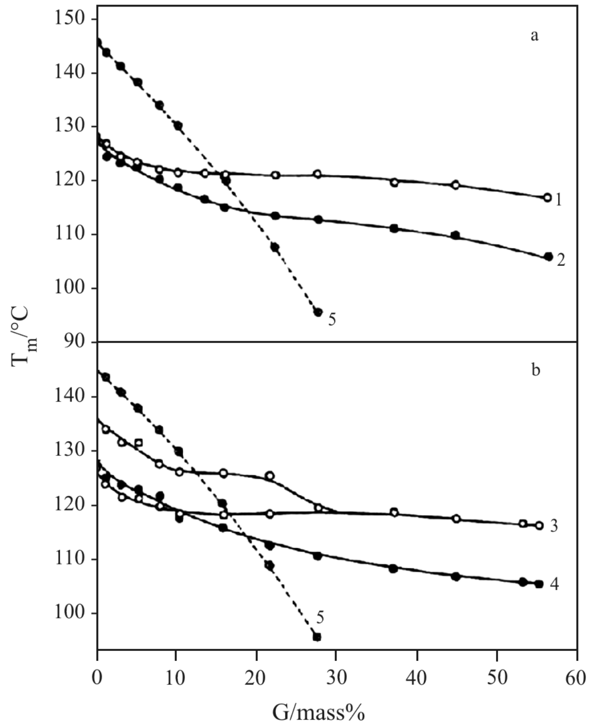

**Fig. 5** Peak temperature of melting ($T_m$) *vs.* chlorine content (G) for: as-prepared powdered 1 – CPE and 3 – CHMMPE samples; melt-crystallized 2 – CPE and 4 – CHMMPE samples; 5 – random ethylene copolymers according to Flory's equation; the heating rate is 5°C $min^{-1}$

**Table 2** Values of the overall melting entropy ($\Delta S_u$), conformational entropy ($\Delta S_c$) and the parameter of thermodynamical stiffness of macromolecules ($\sigma$) for high-density PE, HMMPE and their chlorinated products of various chlorine content

| Sample | First melting | | | Second melting | | |
|---|---|---|---|---|---|---|
| | $\Delta S_u$ /J K$^{-1}$ mol$^{-1}$ | $\Delta S_c$ /J K$^{-1}$ mol$^{-1}$ | $\sigma$ | $\Delta S_u$ /J K$^{-1}$ mol$^{-1}$ | $\Delta S_c$ /J K$^{-1}$ mol$^{-1}$ | $\sigma$ |
| PE | 6.42 | 4.81 | 2.33 | 6.46 | 4.84 | 2.32 |
| CPE 5.08% Cl | 6.54 | 4.91 | 2.30 | 5.33 | 4.00 | 2.68 |
| CPE 22.16% Cl | 6.56 | 4.92 | 2.29 | 3.56 | 2.67 | 3.92 |
| CPE 56.09% Cl | 2.69 | 2.02 | 5.88 | 1.23 | 0.92 | – |
| HMMPE | 6.16 | 4.62 | 2.40 | 5.76 | 4.32 | 2.53 |
| CHMMPE 5.32% Cl | 6.46 | 4.84 | 2.32 | 5.12 | 3.84 | 2.77 |
| CHMMPE 21.56% Cl | 6.32 | 4.74 | 2.36 | 3.48 | 2.61 | 4.03 |
| CHMMPE 53.23% Cl | 3.14 | 2.35 | 4.60 | 1.26 | 0.94 | – |

Table 1, that at higher values of this parameter, the phase transition occurred within narrower temperature range.

The experimental values of the peak temperature of melting for as-prepared powdered and melt-crystallized chlorinated PEs are presented in Fig. 5. The low- and high-temperature peaks of the first heating scan are shown for CHMMPE samples (Fig. 5b, curve 3). For all chlorinated samples, $T_m$ decreased at the highest rate within the concentration range of 1 to 10% Cl as follows: for powdered samples the rates are 0.66°C/mass% Cl (CPE) and 0.84–0.93°C/mass% Cl (CHMMPE), respectively; for melt-crystallized samples they are as follows – 0.84°C/mass% Cl for CPE and 0.74°C/mass% Cl for CHMMPE. For the interval from 10–15 to 35% Cl, $T_m$ of the powdered samples were, approximately, constant; and from 35 to 56% Cl the corresponding values decreased at the rate of 0.13–0.17°C/mass% Cl (Fig. 5, curves 1 and 3). The melt-crystallized CPE and CHMMPE samples melted at lower temperatures than the powdered ones. The rate of $T_m$ diminution of these samples was 0.22–0.23°C/mass% Cl in the interval of 15–56% Cl (Fig. 5, curves 2 and 4).

The depression of $T_m$ for powdered and melt-crystallized chlorinated PEs within the interval from 1 to 10% Cl was probably affected by various factors. On one hand, $T_m$ depression of the powdered samples could be associated with an increase of the interfacial free energy as established previously for the chlorination of PE single crystals [14, 18]. On the other hand, taking into account that the main reason for the depression of $T_m$ is the presence of defects in the crystallites [27], it could be assumed that, at lower degrees of chlorination, the defects appear on their boundary surfaces predominantly. According to Bikson *et al.* [15], the bulky chlorine atoms closely located to the crystalline surface cause non-destructive distortion of crystallites. This, however, leads to slight increase of both the overall ($\Delta S_u$) and conformational ($\Delta S_c$) entropy of the as-prepared CPE and CHMMPE, containing up to 22% Cl (Table 2), which is analogous to the observed enthropy increase of primarily chlorinated and brominated PE single crystals [32, 43]. Regardless the gradual decrease in the length of the crystallizable methylene sequences for the concentration range of 22 to 56% chlorine (Table 1), $T_m$ values remained almost constant or slightly decreased (Fig. 5, curves 1–4). It is well known, that the parameter $T_m$ depends not only on the size but, also, on the degree of perfection of crystallites [27]. Apparently, for the solid-phase chlorination process, the perfection of crystallites is not significantly affected. Negligible change in $T_m$, on the other hand, could be also ascribed to the enhanced intrinsic chain stiffness caused by the induced dipole-dipole interactions in the chlorinated PE structural sequences. This is proved by the change in the values of the parameter of thermodynamical stiffness of the macromolecules $\sigma$. For powdered CPE and CHMMPE, this parameter was nearly constant up to ca. 22% Cl, following which, it increased markedly and for 53–56% Cl reached the values of 4.5–6 (Table 2; Fig. 6, curves 1 and 2).

The difference between $T_m$ of powdered and melt-crystallized samples increased continuously at chlorine content over 10% (Fig. 5). However, the rate of $T_m$ depression for the melt-crystallized samples was higher again for the first section of curves (1–15% Cl), compared to the second one (15–56% Cl). The depression of $T_m$ in the first concentration interval was consistent with the depression of the enthalpy of melting in the same interval. Based on this, it is believed that the defects in the crystalline structure of CPE and CHMMPE caused by inclusion of isolated CHCl groups result in higher $T_m$ depression than the defects caused by the existence of vicinal CHCl groups. This corresponds to the statement that the trend towards cocrystallization of CHCl groups with $CH_2$ ones increases as the substitution in the chlorinated polymers becomes more random [9, 27]. Moreover, after the first heating cycle, the chlorinated structures are located more uniformly within the bulk of the melt, which results in increased intermolecular interactions. This was evidenced by the essential increase of the σ parameter (Fig. 6, curves 3 and 4), which correlated with the continuous decrease of the $\Delta S_u$ and $\Delta S_c$ values (Table 2). Therefore, more slightly pronounced $T_m$ depression, particularly, at higher degrees of chlorination is suggested.

The experimental values of $T_m$ were compared to the estimated ones, according to Flory's equation for linear irregular copolymers (Fig. 5, curve 5). The $T_m$ values of chlorinated PEs were lower than the theoretically predicted ones up to approximately 15–20% Cl, which could be attributed to the random nature of chlorine substitution in the chlorinated PE chains. However, for the region of higher chlorine content (20–56%), the experimental $T_m$ values were higher than the theoretically predicted ones. This corresponds to well pronounced block-like structure of the chlorinated methylene sequences. The observed trend is similar to the previously established one for PE, chlorinated in suspension [11] as well as chlorinated PE single crystals [18]. In fact, the cross-point of the Flory's curve with the experimental melting curves corresponded to the changes in the microstructure of solid-state chlorinated PE chains found by employing $^{13}$C-NMR and IR analyses. These microstructural changes can be summarized as follows: formation of individual CHCl groups to approximately 10–15% Cl and continuous increase of the molar fraction of vicinal CHCl groups in the chlorinated PE blocks at higher concentrations of chlorine [22, 38].

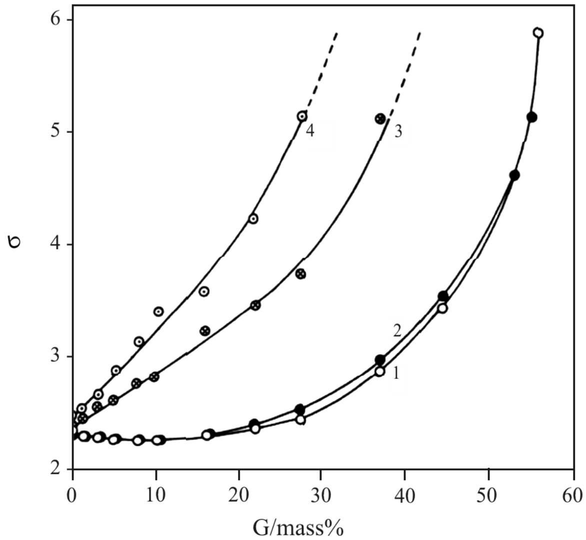

**Fig. 6** The parameter of thermodynamical stiffness of the macromolecules (σ) *vs.* chlorine content (G) for: as-prepared powdered 1 – CPE and 2 – CHMMPE samples; melt-crystallized 3 – CPE and 4 – CHMMPE samples

## Conclusions

The melting behavior of the heterogeneously chlorinated polyethylene samples of various molar mass is studied by using DSC analysis. A number of thermal and thermodynamic characteristics of the chlorinated products are determined and their changes with respect to the chlorine content in samples are described. Some increase in the enthalpy of melting ($\Delta H_m$) of the powdered chlorinated polyethylenes as the chlorine content becomes higher is found within the concentration interval of 1 to 15%. This can be associated with changes in the structure of interlamellar regions, taking place during the chlorination of polyethylene samples. The $\Delta H_m$ values of the melt-crystallized samples decrease continuously with the increase in the degree of chlorination. This suggests an inclusion of defects of the comonomer units into the crystalline lattice of PE. The crystalline structure of the recrystallized CHMMPE possesses more defects than that of CPE which is confirmed by the differences in the $\Delta H_m$ values of the corresponding chlorinated PEs, containing up to 40% chlorine.

On the other hand, defects caused by the inclusion of single chloromethylene groups result in higher depression of the peak temperature of melting ($T_m$) than those, induced by the vicinal chloromethylene groups in the polymer chain. Moreover, the more slightly pronounced depression of $T_m$ at higher degrees of chlorination (20–56% Cl) corresponds to increased values of the thermodynamical stiffness (σ) of the macromolecules. For recrystallized samples of CHMMPE, the values of the latter parameter are higher than those of CPE with the same chlorine content. It could be assumed that this is due to the existence of less pronounced block-like structure of solid-state CHMMPE and to the possibility of more homogeneous distribution of its chlorinated structural sequences in the melt during the first heating run.

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