

# Lamellar structure in melt crystallized low density polyethylene

## I. Controlled study of the chlorosulfonation technique

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**Abstract:** The investigation of representative details in the lamellar microstructure of LDPE observed after controlled chlorosulfonation using both EM and SAXD is reported. For this purpose melt crystallized PE with two branch contents ( $\epsilon = 0.28$  and 2.53 branches per  $10^2\text{CH}_2$ ) has been prepared using Kanig's technique over a range of temperatures and treatment times. During the first treatment hours the selective incorporation of electron-dense atoms at the lamellar surface produces a macroscopic weight increase, swelling of the sample and a concurrent decrease of the SAXS intensity. The main result, however, is that the thickness of the lamellar structure does not vary with treatment time. After long chlorosulfonation times a saturation of electron-dense atoms within the surface layer and a reduction in the lateral dimensions of the lamellae take place. Optimum conditions for revealing the representative morphology are such as to lead to a weight increase of 50% for PE with  $\epsilon = 0.28$  of branches and only to an increase of 10% for material of branch content represented by an  $\epsilon$  value of 2.53.

**Key words:** Lamellar structure, low density polyethylene, chlorosulfonation, small angle X-ray diffraction, electronmicroscopy.

## Introduction

The lamellar structure of high density polyethylene (PE) represents the main morphological feature of the polymer crystallized from the melt. Raman spectroscopy, small angle X-ray diffraction (SAXD), electron-microscopy (EM), density or differential scanning calorimetry (DSC) data lend indeed support to the view of stacks of crystalline lamellae alternating with 10–20% disordered material [1]. When chain defects, however, (branches, saturations, etc.) are introduced along the polymer chains a more complex picture emerges. This is so because of the preferential rejection from the lattice of chain segments containing defects [2, 3]. The lack of longitudinal acoustic modes (LAM) in branched PE ( $\epsilon > 1\%$ ) [4] and the multiplicity of DSC peaks [5] reduce the techniques available for the evaluation of the lamellar thickness in LDPE to EM or SAXD and even in this case only when a particular model is adopted. The successful

results obtained with the application of etching techniques [6–7] (chlorosulfonation, permanganic etching) as a means of a better understanding of the lamellar structure of PE offers a new route for the study of the LDPE microstructure (lateral size, distribution of crystal thicknesses, grain boundaries, lamellar stacking regularity and segregation of non crystallizable material). While previous investigations [8, 9] have tackled the problem of the lamellar structure of LDPE using chlorosulfonation a kinetic study of the treatment relating to the microstructure is still missing. The objective of the first part of this series is the systematic investigation of the kinetics of chlorosulfonation in order to establish the optimum conditions for the study of the original lamellar morphology while avoiding any modification of the original structure during treatment. Specifically we report in this paper the comparative examination of some of the typical structural details (lamellar thickness and interlamellar spacing) as obtained when chlorosulfonated LDPE is observed using EM and SAXD. For this purpose two samples with different branching contents were prepared by using Kanig's chlorosulfonation technique [10] and employing various temperatures and treat-

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ment times. This work forms part of a large study which will include a wider range of branching concentrations and different etching techniques (perman-ganic treatment, etc.).

## Experimental part

The PE's used were, Hostalen GC, a slightly branched PE ( $\epsilon = 0.28$  branches per  $10^2\text{CH}_2$ ) with  $M_w = 50,000$  and Lupolen KR1032 a typical LDPE ( $\epsilon = 2.53$  branches per  $10^2\text{CH}_2$ ) with  $M_w = 53,000$ . Samples were prepared for the X-ray diffraction study in the form of  $250\ \mu\text{m}$  thick films by quenching the squashed melt at  $160\ ^\circ\text{C}$  to  $15\ ^\circ\text{C}$ . The resulting crystallinities as measured by density were of 73% and 45% for the former and the latter samples respectively. Thicker samples ( $\sim 700\ \mu\text{m}$ ) were also crystallized in compression moulded form for EM studies under identical conditions. All samples were treated at 20, 45 and  $60\ ^\circ\text{C}$  by means of Kanig's  $\text{ClHSO}_3$  technique using a concentration of  $0.08\ \text{g/ml}$  at various times till macroscopic deterioration was visually observed. After each treatment the samples were washed in water till a neutral pH was reached. The resulting materials were subsequently vacuumdried at room temperature to constant weight. SAXD patterns were recorded onto films using a point collimation  $\text{CuK}\alpha$  source operating at 7 Kw. For transmission electron-microscopy (TEM) studies sections of approximately  $80\ \text{nm}$  were cut at room temperature using a diamond knife. The polymer with chlorine and sulphonic groups attached to the lamellar surfaces becomes easier to section and its image contrast is relatively stable to the electron beam of the EM. The sections were subsequently stained with uranyl acetate for periods of  $\sim 45\ \text{min}$ . Care was taken to obtain the very first sections of each sample. The sections were finally collected onto a carbon coated grid. Samples were observed under the EM using very low beam intensities to minimize the shrinkage effect.

## Results and discussion

### Weight increase

Figures 1a and 1b illustrate the relative weight increase,  $\Delta P$ , (%) as a function of exposure time,  $t$ , to the acid for the two investigated samples. Characteristic of the curve for the sample with  $\epsilon = 0.28$  is a clear increase in weight for about 100 h the slope being steepest for the sample treated at  $60\ ^\circ\text{C}$ . The leveling off in the weight increase curves after 100 h suggests that the amorphous surface layer ( $\sim 65\ \text{\AA}$  thick), more accessible to the acid reaction than the crystal core, has been filled up with attached electron dense atoms. The weight increase for the samples treated at the two higher temperatures (45,  $60\ ^\circ\text{C}$ ) is the same after prolonged treatment times. As expected, at a given temperature, the weight increase becomes steeper for the sample with a larger number of defects ( $\epsilon = 2.53$ ) (fig. 1b) having a substantially thicker amorphous layer ( $\sim 95\ \text{\AA}$ ). Here, for instance, the final leveling off occurs only after  $\sim 20\ \text{h}$  for the sample treated at  $45\ ^\circ\text{C}$ . On the other hand while for the PE with  $\epsilon = 0.28$  the attack is negligible at any given time at

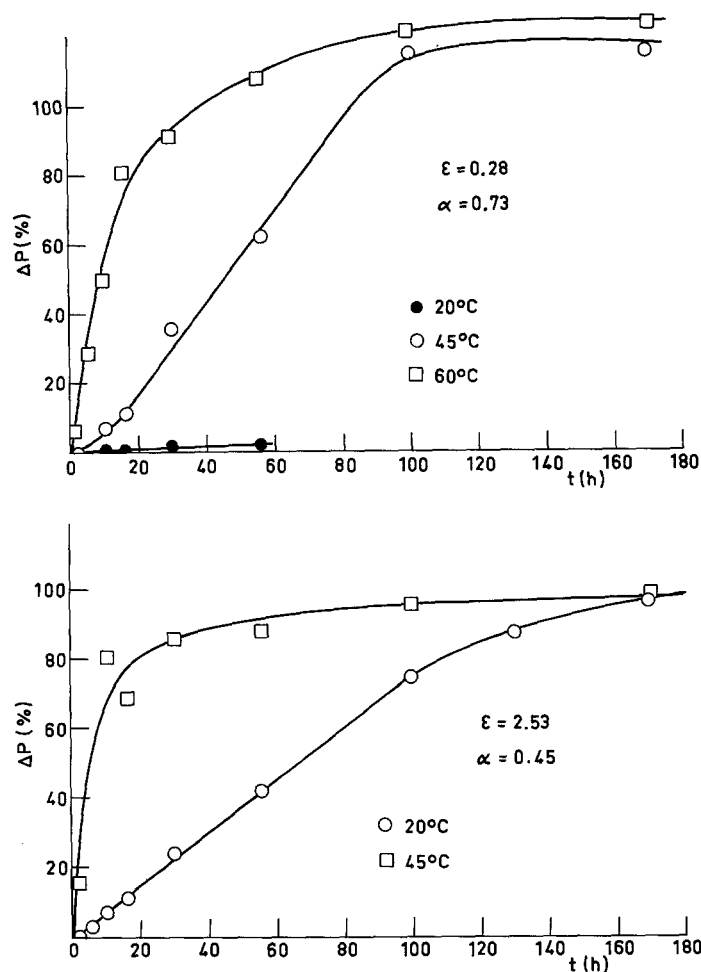


Fig. 1. Weight increase in percent of original weight as a function of treatment time with Chlorosulfonic acid for melt crystallized polyethylene having two different branch concentrations

room temperature, for the sample with  $\epsilon = 2.53$  the influence of the attack on the weight increase is already notable after short treatment times ca. 10 hours. If one assumes that the groups fixed at the chain after reaction are predominantly  $\text{HSO}_3$  [10] one can estimate, from the weight increase at the saturation point, the concentration of these groups to be of  $\sim 12\text{--}14$  groups per 100 carbon atoms within the amorphous layer. Comparison of both sets of curves in figures 1a and 1b shows a higher saturation level for the sample with  $\epsilon = 0.28$ . This difference could be attributed to a partial digestion and consequent weight-loss of low molecular weight material for PE with  $\epsilon = 2.53$  after long treatment times.

## SAXD and morphology

The SAXD pattern of the treated samples shows for the sample with  $\epsilon = 0.28$  two distinct maxima with a ratio  $L_1/L_2 \approx 2$  and for the PE with  $\epsilon = 2.53$  only one broader maximum. In both samples the long period  $L$  increases after the first hours of acid treatment, however, thereafter it remains nearly constant (table 1). The increase of  $L$  parallels the macroscopic swelling of the sample. Both effects are a result of the incorporation of the electron dense atoms at the lamellar surfaces. The sample thickening can be of the order of 20% after 56 h (60 °C). In addition, a progressive reduction in the diffracted intensity of the Bragg's peak, as a consequence of gradual penetration of  $\text{HSO}_3$  groups in the amorphous layer, is detected for both samples as a function of  $t$ . Figure 2 illustrates the position and intensity loss of the diffraction peak at different times for the sample with  $\epsilon = 0.28$  treated at 60 °C. For the sample with  $\epsilon = 2.53$  the maximum is not detected anymore after 16 h and only a continuous scattering remains instead. Figures 3 and 4 illustrates the typical features of the lamellar morphology as obtained with TEM throughout the treatment time for both samples. The images show an alternating sequence of dark and light lines where the dark regions correspond to the stained electron dense material. We attribute such images as being due to stacks of crystal lamellae where the white bands correspond to the crystal core, which remains unstained and the dark bands to the disordered or amorphous lamellar surface and interlamellar material. The gradual increasing penetration of electron dense atoms within the amorphous layers during the 1st 100 h accounts for the observed weight increase and concurrent SAXD intensity decrease. Regions of lower contrast contain lamellae in other orientations. The initial structure for the PE with  $\epsilon = 0.28$  is composed of a more regular stacking of lamellae which are thicker and ostensibly wider than for the highly branched material. These

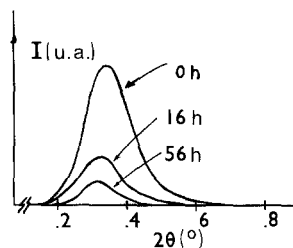


Fig. 2. Scattering intensity of the SAXD peak at different treatment times with Chlorosulfonic acid for PE with  $\epsilon = 0.28$  branches per  $10^2$  carbon atoms

two different stacking structures are consistent with the differences observed in the SAXD patterns. However, the main result from the inspection of figures 3 and 4 is that the lamellar thickness of the white bands, hence crystalline portions of the lamella, remains absolutely unaltered during the treatment time. Here it is noteworthy that Kanig [11] pointed out previously the constancy of the lamellar thickness for linear PE at chlorosulfonation times up to 16 h. It is further interesting to remark that after sufficiently long treatment times (100 h, 45 °C for PE with  $\epsilon = 0.28$  and 24 h, 20 °C, for PE with  $\epsilon = 2.53$ ) the acid attack produces a destruction of lamellae with a resulting decrease in lateral length. These long treatment times causing such a catastrophic effect correspond to weight increases of about 100%. The destruction of thinner lamellae causing a lateral reduction in PE with a higher branching content, thus, occurs at notably shorter times and lower temperatures than for linear PE. In addition, the irregular location of the amorphous component for this more defective material provokes the presence of a continuous SAXS after sufficient incorporation of electron dense atoms masking, finally, the diffraction maximum. The above results indicate that when a certain proportion of chain defects is incorporated into the backbone structure of the polymer the conditions of chlorosulfonation have to be sensibly modified in temperature and treatment time if one wishes to have a reasonably representative morphology of the original sample.

In conclusion, the thickness of the crystal core portion of the lamellar structure of LDPE treated with chlorosulfonic acid does not vary throughout the range of times investigated till its final destruction. The lateral dimensions of the lamellae are, however, notably reduced after long treatment times. The adequate temperature and time of treatment for TEM corresponds to a weight increase of  $\sim 50\%$  for  $\epsilon \sim 0.28$  and only of  $\sim 10\%$  for  $\epsilon = 2.53$ .

Table 1. Long period (nm)

Hostalen GC ( $\epsilon = 0.28\%$ )			Lupolen KR 1032 ( $\epsilon = 2.53\%$ )		
$t$ (h)	T °C		$t$ (h)	T °C	
	20	60		20	60
0	24.4	24.4	0	17.0	17.0
6	25.0	27.5	1	18.0	22.5
16	26.0	27.5	16	19.6	continuous
50	26.0	27.5	56	19.6	scattering

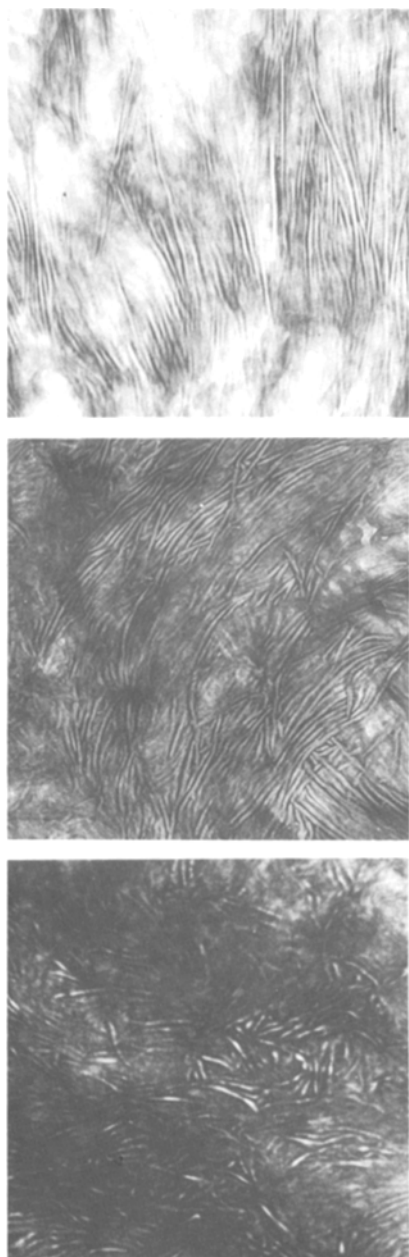


Fig. 3. Electron micrographs showing representative lamellar stacks within the interior after different treatment times with chlorosulfonic acid stained with uranyl acetate. For PE with  $\varepsilon = 0.28$ ; Treatment temp: 45 °C; Top: 10 h; middle: 50 h; bottom: 100 h ( $\times 70,000$ )

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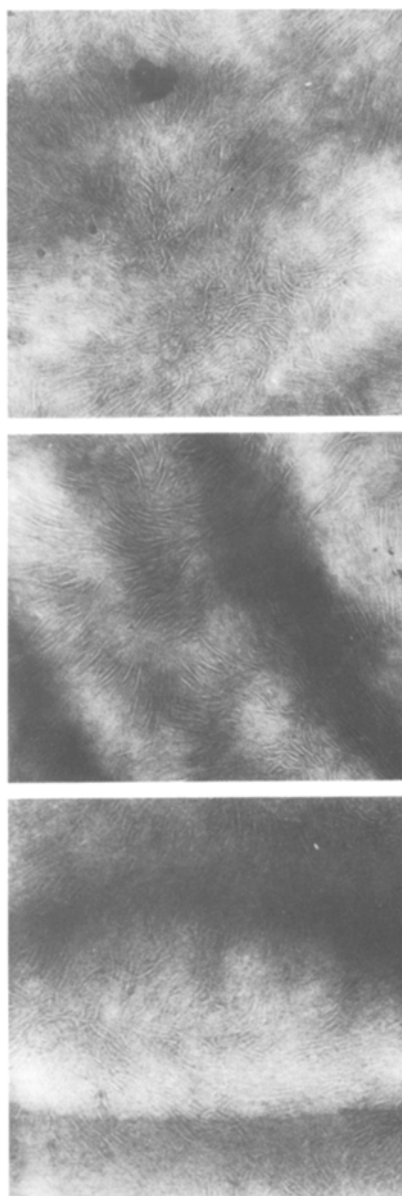


Fig. 4. Electron micrographs illustrating details of the lamellar structure of PE with  $\varepsilon = 2.53$  after selected treatment times with chlorosulfonic acid stained with uranyl acetate. Treatment temperature: 20 °C ( $\times 70,000$ ). Top: 10 h; middle: 15 h; bottom: 25 h

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