

Crystallization and Viscosity Behavior

Dynamic SAXS and WAXS Investigations on Melt Crystallized Linear Low Density Polyethylene Using Synchrotron Radiation: Crystallization and Melting Behaviour

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Summary

The crystallization and melting behaviour of linear low density polyethylenes, with propene and 1-octene as comonomers, has been studied by differential scanning calorimetry and dynamic SAXS and WAXS, using synchrotron light, under identical conditions as in the DSC. Preliminary analysis of the experimental data makes clear that the combination of these techniques is a powerful tool in the understanding of crystallization and melting phenomena as observed in DSC-traces. A molecular segregation process has been detected resulting in the crystallization of part of the material below the isothermal crystallization temperature T_c . The influence of T_c and the comonomer concentration on this segregation has been explored.

Introduction

Linear low density polyethylenes (LLDPE) are novel types of polyethylenes with superior performances compared to high and low density polyethylenes. They are copolymers of ethylene and alpha-olefins, such as propene, 1-butene, 1-hexene and 1-octene. The chain microstructure of LLDPE, which is determined by the type, concentration and distribution of the comonomer, as well as the molecular weight and molecular weight distribution, has an important influence on the resulting amorphous-crystalline superstructure. Thermal treatments also affect the morphological structure of the semi-crystalline copolymer.

In the present paper, we report preliminary results of a study, using differential scanning calorimetry and synchrotron radiation - time resolved diffraction, of the influence of the type and concentration of the comonomer and of the crystallization temperature on the resulting morphology. Synchrotron radiation was mainly used as an explorative method for the study of the molecular segregation phenomena, crystallization and melting in LLDPE.

Experimental

Differential scanning calorimeter (DSC) scans were performed on a Perkin-Elmer DSC-2C. The degree of branching of the various LLDPE samples was determined by ¹³C-NMR spectroscopy (NMR Bruker WM250 Cryospec, PW=60°, RD=10s), according to the ¹³C chemical shifts established by J. Randall(1). Wide-angle (WAXS) and small-angle (SAXS) X-ray diffraction patterns were recorded on the double focusing mirror-monochromator camera (X13) of the EMBL Outstation at the storage ring DORIS (2,3) using a linear position

sensitive detector (PSD) (4). The latter was centered on the relevant parts of the pattern as determined from a preliminary survey of the two dimensional pattern with a vidicon system (5). The distance between sample and detector in the SAXS experiments (approximately 2.5 m) resulted in a resolution of 0.17 mradians/channel. In the WAXS experiments the corresponding resolution was 2.6 mrad/channel. The samples were heated in an improved version of the programmable oven designed by Elsner (6). This device allows linear heating up to a constant temperature and rapid cooling as determined by the analogue program. During the SAXS experiments, the samples were heated at a constant rate of 5°C/min to follow the evolution of the long spacing under identical heating conditions as used for the DSC scans. The background scattering of the apparatus was measured and subtracted from the scattering curves of the samples. The correspondence between the channels of the PSD and the values of the scattering angle were established from the position of the primary beam detected through a transparent beam stop, and of the sixth order reflection of a sample of dry bovine cornea (11 nm).

Each spectrum was normalized for the variable incident beam intensity; allowance was made for sample absorption, and the Lorentz correction was applied on the SAXS-data.(7) For data collection and processing, a program package provided by EMBL was used (8). The wavelength of the monochromatic radiation was $\lambda = 0.145$ nm.

Results and discussion

A. Molecular segregation

In order to study the influence of the crystallization temperature on the molecular segregation processes in LLDPE, it is necessary to give a well defined thermal treatment to the specimen.

A 1-octene LLDPE sample (containing 10.3 branches per 1000 carbon atoms in the backbone) was heated up to 150°C in a nitrogen atmosphere and kept for 20 minutes at this temperature to eradicate the thermal history of the sample. Subsequently, the sample was isothermally crystallized at $T_c = 120^\circ\text{C}$ for 1000 minutes and finally cooled to room temperature. From inspection in the optical microscope, it was observed that these conditions correspond to space-filling, impinging spherulithes within the sample. A DSC scan was recorded between 65°C and 140°C at a heating rate of 5°C/min. The thermogram (Fig.1) exhibits a very broad endotherm (I) at temperatures below the isothermal crystallization temperature (120°C), and a second endotherm (II) above T_c with a peak maximum at 129°C.

Table 1 : Fractions of the total integrated area in the interval $65^\circ\text{C} < T < 140^\circ\text{C}$, under endotherm (I) and endotherm (II), in fig. 1, as a function of the crystallization time for 1-octene LLDPE (10.3 branches/1000 C atoms)

Crystallization time (min)	Segregated fraction (area I)	Crystallized fraction at $T_c = 120^\circ\text{C}$ (area II)
1000	55.5 %	45.0 %
4800	54.2 %	45.8 %
10000	52.2 %	47.8 %

Table 2 : Influence of the crystallization temperature on the amount of segregated material for 1-octene LLDPE (10.3 branches/1000 C atoms).

Crystallization temp. (°C)	Segregated fraction (area I)	Crystallized fraction (area II)
105	18.7 %	81.3 %
120	55.0 %	45.0 %

Table 3 : Propene concentration, degree of branching of different specimens as determined by ^{13}C -NMR, and molecular segregation

Sample No	Propene concentration (%)	Number of Branches per 1000 C in the backbone	Relative area under endotherm I
1	0.9	3.0	0.5 %
2	5.2	17.7	33.8 %
3	8.3	28.4	45.4 %

There is clearly a fraction of the polymer which does not crystallize at the crystallization temperature ($T_c=120^\circ\text{C}$). This fraction is probably rejected into the amorphous zones between the crystalline lamellae and crystallized at temperatures below $T_c=120^\circ\text{C}$. During the heating run, the melting of these crystals results in the broad endotherm (I) below T_c . The amount of rejected polymer is appreciable : the ratio of the area under the low temperature endotherm (I) to the total area under the DSC curve is 55 %. Inspection of Table 1 shows that this segregated material does not crystallize even after very long crystallization times. The crystallization temperature has a drastic influence on the amount of segregated material. This is illustrated in Table 2 by the fractions of the area under endotherm I and II for two different crystallization temperatures: 105°C and 120°C , respectively. Similar observations are obtained by using LLDPE's with propene as comonomer.

In order to study the influence of the comonomer concentration, three samples with the same melt index ($\text{MI} = 1\text{g}/10\text{min}$), but with different propene contents were considered and the NMR results are given in table 3. DSC scans for each specimen, recorded under the same experimental conditions as described above, are given in figure 2. The segregated fraction as a function of number of branches per 1000 C atoms in the backbone, as given in table 3, clearly illustrates the influence of the comonomer content on the amount of segregated polymer.

B. Dynamic structural changes using synchrotron radiation

The high brightness of storage rings allows to monitor the morphological changes during melting or crystallization by evaluating the changes in time-resolved WAXS and SAXS patterns. All samples were heated up to 150°C for 20 minutes, and subsequently isothermally crystallized at $T_c=105^\circ\text{C}$. WAXS and SAXS spectra were recorded separately on samples mounted in an oven allowing to perform similar heat treatments as during the DSC experiments. To record the WAXS spectra, the temperature program shown in figure 4 was used.

1. Starting from room temperature, the isothermally crystallized sample was heated quickly to the original crystallization temperature, $T_c=105^\circ\text{C}$, and kept at this temperature for 4 minutes.
2. In the next step the specimen was heated at a constant heating rate of $10^\circ\text{C}/\text{min}$ to 150°C and remained for 275 s at this temperature.
3. Finally, the sample was cooled quickly to the original crystallization temperature $T_c=105^\circ\text{C}$.

Each run consisted of 256 times 5s frames recorded in the range of scattering angles $14^\circ < 2\theta < 28^\circ$. The evolution of the WAXS patterns as a function of time (or temperature) is illustrated in Figure 3, for a sample of 1-octene LLDPE with 10.3 branches per 1000 C atoms. For reasons of clarity only every fourth pattern during the experiment is shown. The

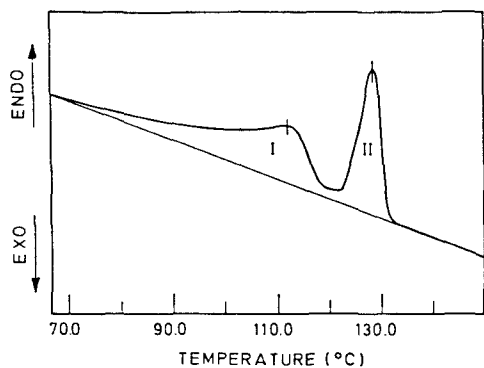


Fig.1 DSC scan for a 1-octene LLDPE specimen, $T_c = 120^\circ\text{C}$, heating rate = $5^\circ\text{C}/\text{min}$.

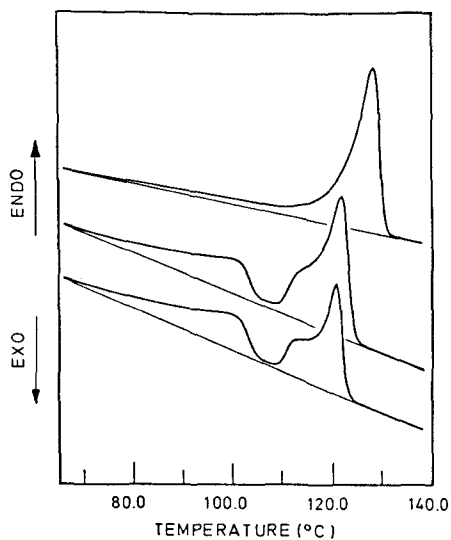


Fig.2 DSC thermograms for 1-propene LLDPE specimens with different propene contents

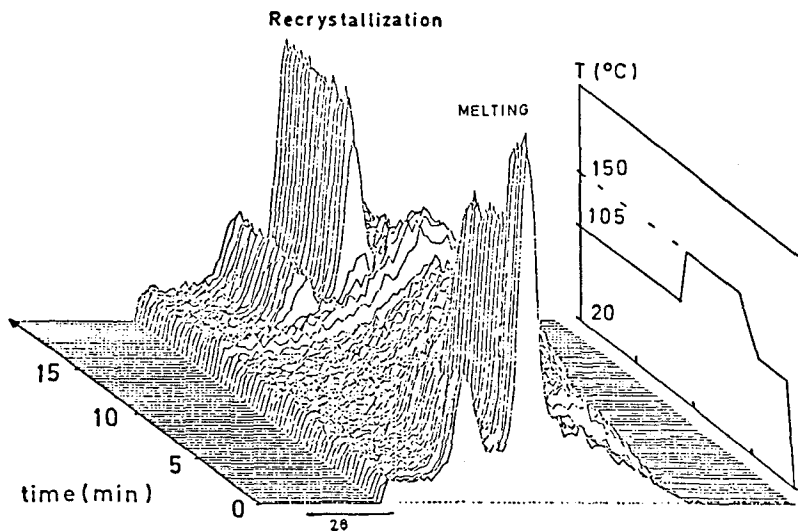


Fig.3 WAXS diffraction spectra during thermal treatments. Only every fourth pattern in the run is shown.

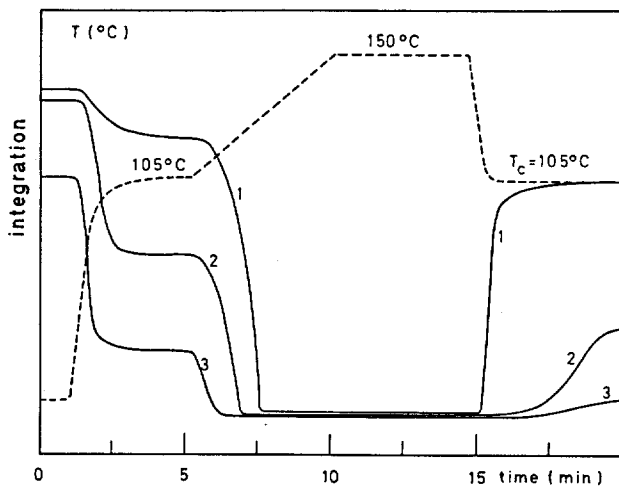


Fig.4 Integrated intensity under the (110) reflection for different propene LLDPE specimens as a function of thermal treatments.

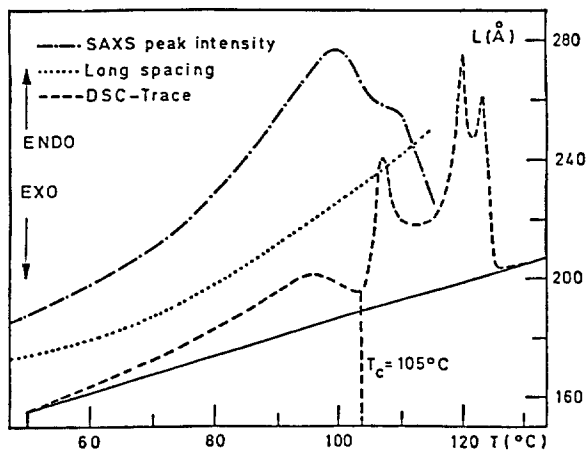


Fig.5 The DSC thermogram and the temperature dependence of the long spacing and the peak height obtained from SAXS patterns of a 1-octene LLDPE specimen with 15.5 branches/1000 C atoms.

melting of the segregated material, total melting and recrystallization are clearly demonstrated.

For the samples containing propene as comonomer referred to in Table 3, the area under the 110 reflection was integrated for each pattern to monitor changes in crystallinity on a relative scale; the time course of this integral is shown in Figure 4 for the different samples. Values of the integral between 20°C and 105°C, and between 105°C and 150°C are clearly correlated with the relative areas I and II+III in the DSC thermograms in Figure 2.

It should be noticed from figure 4 that the kinetics of recrystallization which is very fast, can easily be monitored continuously in contrast to the classical approaches as for example by dilatometry or optical microscopy. This is another unique possibility of synchrotron radiation only paralleled by SALS (9).

A specimen of 1-octene LLDPE with 15.5 branches per 1000 carbon atoms in the backbone and isothermally crystallized at 105°C was used for SAXS experiments. The long spacing was obtained by application of Bragg's law to the maximum of the Lorentz corrected scattering curve. Figure 5 illustrates the DSC thermogram recorded at a heating rate of 5°C/min. Superimposed on it are the variations of the long spacing and the peak height of the SAXS diffraction maximum as a function of the temperature. Besides the endotherm due to the melting of crystals of the segregated material, 3 melting endotherms are observed. The origin of the highest melting peak is as yet not understood and will be the subject of further study.

During heating a continuous increase of the long spacing is observed up to $\pm 118^\circ\text{C}$, where it is no longer possible to observe a distinct maximum. The increase in long spacing between 50°C and 105°C can be explained by melting of the less stable crystals of the segregated material between the lamellae of the spherulitic structures formed at $T_c=105^\circ\text{C}$. As soon as the sample passes the second endotherm, melting of the structure formed at $T_c=105^\circ\text{C}$ occurs. (This is apparent from the onset of a decrease in the peak intensity of the SAXS maximum which coincides with the beginning of endotherm II). It is noteworthy that there is at the same time a further increase in long spacing, which is cut off by a lack of resolution of the instrument. The changes of the SAXS maximum are roughly proportional to changes in Q , the mean square of the electron density fluctuations :

$$Q = \int_0^\infty I(s)s^2 ds$$

which for semi-crystalline systems is related to the degree of crystallinity ϕ_c by :

$$Q = \phi_c (1 - \phi_c) (\rho_c - \rho_a)^2$$

In this formula ρ_c and ρ_a stand for the electron densities of the crystalline and amorphous phases respectively.

The initial crystallinity of the present sample is 33,4% and by heating up to 105°C this crystallinity drops to 25,6 % which, at constant $\Delta\rho$, should result in a decrease of the invariant. However an increase is observed as a consequence of the melting of the segregated material between the crystalline lamellae and the thermal expansion of the residual amorphous phase (10). Similar results have been obtained by Koberstein and Russell (11).

The present results give no definite answer regarding the origin of endotherms III and IV. It seems probable that these endotherms reflect the melting of the most stable lamellar crystals as a result of considerable reorganisation during the DSC-scan; these reorganized crystals however can no longer be considered as present in a stacklike structure. The present experimental results do as yet not allow to determine at which temperature the transition between a "dilute" lamellar stack and randomly oriented lamellar crystals occurs.

Conclusions

LLDPE's with propene or octene as comonomer exhibit strong segregation phenomena on isothermal crystallization as manifested by the observation of an endotherm (I) in the DSC-traces below the isothermal crystallization temperature. Synchrotron radiation is a new and promising tool to relate DSC-observations with changes in morphological parameters as obtained from dynamic diffraction experiments.

Changes in crystallinity observed at small angles (long spacing, invariant) as well as at wide angles (degree of crystallinity) allow a partial understanding of the different melting endotherms observed in the DSC. In contrast to optical microscopy or dilatometric measurements, the very rapid crystallization kinetics of LLDPE's can easily be followed.

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