Annealing in Low Density Polyethylene at Several Temperatures

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ABSTRACT: By using differential scanning calorimetry (DSC) techniques we show that three kinds of endotherms arise in low density polyethylene (LDPE) annealed between 45 °C and 115 °C. Of particular importance is the endotherm II, which reflects the melting of the crystallites generated at the annealing temperature by the partial melting/recrystallization mechanism. For this case, the analysis of both the changes in the melting enthalpy and in the peak temperatures leads to the conclusion that the crystallization at the annealing temperature is not essentially different from that taken place isothermally and with an overall amorphous initial state. Finally, we also find the interesting result that the crystallinity degree associates only to the endotherm II pass through a maximum when we vary the annealing temperature. [DOI 10.1295/polymj.36.679]

KEY WORDS Recrystallization / Annealing / LDPE / DSC /

The study of isothermal crystallization of polymers from an amorphous initial state is a subject broadly studied.^{1–3} For several polymers the analysis encompass a temperature range large enough to detect the so-called nucleation/reptation transition.⁴ As the temperature decreases from the melting condition, the lamellar growth rate, G , increases. After reaching a maximum, G starts to decrease, indicating then the transition from nucleation kinetic control to the reptation process.^{5–7}

For polyethylene in general and for low density polyethylene (LDPE) in particular the accessible temperature for an isothermic crystallization from an amorphous initial state is limited by the high crystallization rate of these polymers. Indeed, this high rate makes impossible to reach lower crystallization temperatures without some previous crystallization during the cooling. As a consequence, the isothermic studies are limited to the temperature ranges controlled by nucleation.^{8,9} Therefore, the values of different parameters (like the maximum lamellar growth rate) at their inversion temperatures are not obtained.

To access the low crystallization temperature region in polyethylenes two procedures can be followed. The first is through nonisothermal crystallization, obtained by quenching from the melt. The second is through positive temperature jump, the annealing.

There is a vast literature that uses different techniques to study annealing for semicrystalline polymers,^{10–12} but undoubtedly the main approach is DSC. For amorphous and crystalline phases rearrangements, the importance of annealing is that such experiments

can detect the partial melting followed by recrystallization^{13–15} as well as the phenomenon of isothermal thickening.^{1–16} The evident difference between the isothermal crystallization and the annealing experiment is the initial state of the processes. In the former case the system is almost totally amorphous at the beginning, whereas in the latter the crystallization starts from a semicrystalline condition.

The main purpose of the present work is to investigate if the existence of an initial crystalline fraction in LDPE originates specific features during the crystallization process different from those observed when the initial state is completely amorphous.

EXPERIMENTAL

Films of 100 μm of unfractionated LDPE ($M_n = 19.075$, polydispersity = 5.9) were obtained from thermopressing between two copper plates at 170 °C during 10 min, followed by quenching in water bath at 30 °C. The films were then placed (during 2 h) in a bidistilled water bath at several temperatures between 45 °C and 115 °C. After the thermal treatment, the sample was quickly transferred to another water bath, at 30 °C.

The thermal analysis was carried out in a DSC-Netzsch Geratebau GmbH equipment. All thermograms were obtained at a heating rate of 10 °C/min. The enthalpies under the endotherms were converted to degree of crystallinity through division by 69 cal/g, the polyethylene crystal perfect enthalpy.¹⁷

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Figure 1. Thermograms of LDPE. The annealing temperature is indicated.

RESULTS AND DISCUSSION

Figure 1 shows the heating thermogram for all annealed samples as well as for the unannealed one. This last exhibits the typical broad endotherm of quenched LDPE, which reflects the melting of the large lamellar thickness distribution, characteristic of quickly cooled LDPE.⁸ This endotherm will be called I. The thermograms of the annealed samples are different from the untreated case and they can be systematized considering the temperature region of the annealing.

In the samples treated between 45 °C and 55 °C the general shape of the endotherm I is still seen, however, one can also identify a new endothermic peak (hereafter II) inside the endotherm I, which begins immediately above the annealing temperature. For the annealing temperatures from 65 °C to 95 °C, endotherms I and II are present, but a new third endotherm (hereafter III) can be observed in a temperature region below T_a . Between 105 °C and 115 °C the endotherm below T_a is very pronounced but there is only one peak above T_a .

The crystalline fraction (which has melting temperature below or equal to that of the annealing) inside the overall distribution of the quenched polymer melts during the heating from room temperature to T_a and then isothermally at T_a . This new amorphous material recrystallizes at T_a towards the stabler lamellae, becoming thicker than the original material before melting. The whole process is known as partial melting–recrystallization.^{13–15} It is important to note this mechanism does not generate new types and sizes of crystals not present in the original distribution. It only increases the fraction of a given range of lamellar thickness values. The final result is the creation of a different distribution of lamellar thickness within the overall distribution. The less stable crystal fraction of the distribution of the recrystallized material melts

immediately above the annealing temperature. Therefore the endotherm II is due to the melting of the recrystallized material.

At and above the annealing temperature of 65 °C the melted fraction crystallizes completely, doing it during the cooling between T_a and room temperature. This non-isothermal crystallized material has the melting represented by the endotherm III. From such description one can conclude that the endotherm situated above the endotherm II reflects the melting of the fraction of the crystals present in the original distribution which has melting temperature above that of the annealing. For $T_a = 105$ °C the recrystallized crystals have their lamellar thickness values in the same range than that of unmelted material. Therefore, only one endotherm appears above 105 °C. At 115 °C all crystals of the original distribution melt and the sharp endotherm centred at 117.2 °C reflects the melting of the crystals generated at T_a .

The mean lamellar thickness of the fraction II crystals can be determined by the well known Gibbs–Thomson equation¹⁷

$$C_2 = \frac{2\sigma_e}{\Delta h_f} \left(\frac{T_m^0}{T_m^0 - T_{m2}} \right). \quad (1)$$

Here, T_m^0 is the equilibrium melting point, Δh_f is the perfect crystal heat of fusion by unit of volume and σ_e is the specific fold surface free energy. The constants values are 141.2 °C, 4.11 kJ/mol CH₂ and 0.0918 J/m² for T_m^0 , Δh_f and σ_e , respectively.¹⁷

The melting temperature of both, peak I and peak II, and the mean lamellar thickness of the fraction II crystals are shown in Figure 2a and b, respectively. The constancy of the T_{m1} with the annealing temperature shows that the crystal fraction unmelted at the annealing temperature exhibits some structural rearrangement, such as thickening, to improve its thermal stability. For ethylene–hexene copolymer in a similar experiment, it has been also found¹⁸ the independence of the T_{m1} on the annealing temperature at a low temperature range, but for higher temperatures an increasing in T_{m1} has been observed. Poly(ether ether) ketone isothermally crystallized shows a double endotherm behaviour, with the most important of the two also presenting the melting temperature initially independent and then increasing with the crystallization temperature.¹ These two examples may indicate that the improvement of the thermal stability of the fraction I crystals needs a temperature above 105 °C, nevertheless at the same time below 115 °C because at this temperature the fraction I crystals does not survive.

Regarding the temperature T_{m2} and its corresponding values of C_2 , it is important to note that the endotherm II is unequivocally present for T_a varying from

Figure 2. (a) Lamellar thickness of the crystals of the endotherm II; and (b) T_{m1} and T_{m2} of the endotherms I and II as a function of the annealing temperature. The dashed line corresponds to $T_m = T_a$.

45 °C to 95 °C, as can be seen in Figure 1. Hence, the temperature of the maximum of the only endotherm present for $T_a = 105^\circ\text{C}$ can be only superficially associated to T_{m2} . In fact, the Figure 2 leads to the conclusion that for $T_a = 105^\circ\text{C}$ the values of T_{m2} and C_2 are slightly shifted in relation to the curve obtained from the data for T_a between 45 °C and 95 °C.

For annealing at 115 °C the only peak above this temperature is related to the melt of the crystallites, originated from the totally melted sample, as already pointed out above. This is an initial condition of crystallization different from those related to generation of the fraction II crystals because in this last case the process started from a configuration characterized by the coexistence of both crystalline and amorphous phases. Therefore, the nature of the higher temperature endotherm found for the annealing temperature of 115 °C is somehow different from the endotherm II. Despite these observations, we plot the maximum temperature of the higher temperature endotherm for $T_a = 115^\circ\text{C}$ as well as their lamellar thickness values together with T_{m2} and C_2 in Figure 2. Below it will become clear the convenience of including the data of $T_a = 115^\circ\text{C}$ with the data for lower temperatures.

It is a very well known fact that if a general isothermal crystallization takes place from a totally amorphous initial state, then there is a linear increasing of the melting temperature T_m of the crystallized material with respect to the increasing of the crystallization

temperature T_c .^{17,19} Furthermore, this dependence allows one to obtain the equilibrium melting point T_m^0 of the polymer from the interception between the experimental straight line and the theoretical curve $T_m = T_c$.^{17,19} This procedure was used for our data (within the range 45 °C to 95 °C) assuming T_{m2} as T_m and T_a as T_c . The resulting T_m^0 was 139.2 °C as can be seen in Figure 2. Several annealed ethylene polymer systems also show a linear plot of the melting temperature of the crystal fraction generated at the annealing temperature against the annealing temperature as, for instance, high density polyethylene (HDPE)²⁰ and ethylene-hexene copolymer.¹⁸ Important to mention that in neither these examples the present kind of data is used to estimate T_m^0 . For HDPE the temperature difference between the annealing range and the zone inside which it is possible to start crystallization from a totally amorphous condition (*i.e.*, in a high temperature range) prevents the determination of T_m^0 from the annealing data.²⁰ It also has been reported²¹ that the melting temperature of a crystalline fraction of poly(ether ether ketone) starts to increase after the crystallization of another fraction corresponding to larger crystallites. The melting temperature of the latter cannot be used to determine the equilibrium melting point, since the growth of the small crystallites does not take place freely because the spatial confinement imposed by the bigger ones. In spite of this, the values of T_m^0 we obtain here are very close with those obtained from studies of crystallizations¹⁷ where the initial states are totally amorphous. It suggests that the crystallization process, taking place at T_a and in the presence of larger crystals (previously formed), is not essentially different from the one that starts with a random coil initial condition.

For $T_a = 115^\circ\text{C}$, we see in Figure 2 that the corresponding T_{m2} and C_2 values are well fitted from the curve comprising T_a between 45 °C and 95 °C. However, the reason for a separate analysis for the data at $T_a = 115^\circ\text{C}$ is due to the way it is generated, *i.e.*, through a crystallization process from an amorphous initial state.

Similarly to the observed linearity between T_{m2} and T_a , resulting in a very good value of T_m^0 , also the adjust of T_{m2} and C_2 for $T_a = 115^\circ\text{C}$ (by using the curves where the crystallization occurs for an initial state characterized by the presence of a crystalline phase) is in agreement with the idea of a crystallization taking place during the annealing without suffering influence of the crystals already formed at the beginning of the process.

The lamellar thickness seems to be a good parameter to evaluate the influence of the initial state condition on the subsequent crystallization process. As pointed out by Hsine *et al.*²² from SAXS analysis

for HDPE, the lamellar thickness value is very sensible to the melt macroconformations at the beginning of the process. Although these studies have been limited to a completely non-crystalline initial state, it can be easily extrapolated to the condition where a crystal phase is already formed. This is so because such crystal phase does not influence the amorphous arrangements as, for instance, those originated from mobility restrictions of the chain ends of the crystal blocks.

The discussed independence of the crystallization path with respect to the pre-existence of crystals during the annealing may be a consequence of two interconnected causes. The first is the low crystallinity degree (around 0.4 for any T_a , as estimated by melting enthalpy) and the consequent broad amorphous region where the crystallization takes place not close to a lamellar crystal condition. The second aspect is related to both, the branched and the unfractionated nature of LDPE samples used here. On the quenching from the melt, the first molecules that crystallize are just the less branched ones, which are the most crystallizable. The branched segments as well as the molecules near to them do not crystallize even at lower temperature values, excepting the small fraction of molecules with very short chain branching.²³ Hence, this segregated material can form a type of cloud around the crystals. For decreasing temperatures, continuously the more branched chains start to crystallize. As a consequence, the crystals are thinner than the ones formed at higher temperatures and so their amorphous clouds are more prominent. This whole sequence of crystallization activation of higher branched chains, generating thinner crystals and larger amorphous clouds, ends up just at quenching temperature. The very branched chains that are not incorporated into a given cloud around the crystals form a general amorphous region, thus not belonging to any crystal fraction.

At a particular annealing temperature the melting of small, less stable crystals, generates a crystallizable amorphous material, which is spatially separated from the remaining crystals by its amorphous clouds, by its own amorphous region and by a part of the general amorphous region.

From all the previous aspects discussed about LDPE quenching crystallization followed by annealing, we see that the recrystallization takes place through a path almost independent of the pre-existent crystals. This is so because such crystals cannot either to act as heterogeneous nuclei or to limit the growth of the new crystallized material by confining it.²²

Marand *et al.*,²⁴ working with ethylene/1-octene copolymers, found no independence between successive crystallizations in a continuous cooling from the melt. They propose two crystallization mechanisms, with the second being influenced by the crystals origi-

nated in the first. The first fraction to crystallize on cooling is constituted by lamellar crystals, originated from the longest ethylene sequences of the copolymer. The second fraction has morphology of fringed-micellar crystals or chain clusters, coming from shorter ethylene sequences. This result is in agreement with Flory's equilibrium theory,²⁵ which states that at a given temperature T , only the fraction of ethylene sequences of length larger than some critical length can participate in the crystallization process. When the crystallization temperature decreases, the critical length decreases too. However, in our experiments the fraction that crystallize independently of the previously existent crystals does it isothermally (at T_a) and therefore does not have any continuously crystallization of shorter ethylene sequences, which is the case in cooling experiments.

Figure 3 shows the crystallinity associated only to the enthalpy under the endotherm 2, $(1 - \lambda)_2$, as a function of annealing temperature. The transition from its ascending behaviour from the descending one must be a consequence of the well known transition from the zone of reptation kinetic control at low temperatures to the zone of nucleation kinetic control at higher temperatures.⁴ Thus, the results of the Figure 3 also agree with the idea of a crystallization process during annealing not different from that of isothermal crystallization with an overall amorphous initial state. This reptation/nucleation transition is detected in several polymers through the behaviour of the lamellar growth rate that pass through a maximum with the increasing of crystallization temperature.⁵⁻⁷ For polyethylenes in general and for LDPE in particular, this kind of behaviour is not usual because the high crys-

Figure 3. Degree of crystallinity of the crystals associated to the endotherm II as a function of annealing temperature.

tallization rates makes difficult isothermic experiments at lower temperatures, since some polymer fraction crystallizes on the cooling process.⁸ As a consequence, the isothermic studies are limited to the region nucleation controlled and therefore the maximum lamellar growth rate or even the values of other parameters at their own inversion temperature are not obtained. In this way, the plots shown in Figure 3 are important because they make possible to know the inversion point of the degree of crystallinity.

CONCLUSIONS

Analysis through differential scanning calorimetry (DSC) makes possible to detect three types of endotherms in low density polyethylene (LDPE) annealed between 45 °C and 115 °C. The first endotherm reflects the melting of the crystallites present before the annealing procedure (so not previously influenced by the thermal treatment). The second reflects the melting of the crystals generated at the annealing temperature through a partial melting recrystallization mechanism. Finally, the third is related to the melting of the crystallites generated during the cooling from annealing to the room temperature. The crystallization at the annealing temperature is not influenced by the crystals already existents. Therefore, it is not different from isothermal crystallizations of states initially completely amorphous. The degree of crystallinity related only to the endotherm II pass through a maximum as a function of the annealing temperature.

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