DENSITY FLUCTUATIONS AS PRECURSORS OF CRYSTALLIZATION IN POLYAMIDE 6,6 USING TIME-RESOLVED X-RAY SCATTERING TECHNIQUES

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ABSTRACT

The present study attempts to throw light in the mechanisms leading to primary nucleation in polymer crystallization. Previous studies in this field are not conclusive. Aiming to investigate the induction period prior to crystallization, time-resolved simultaneous small and wide angle X-ray scattering (SAXS and WAXS) measurements have been made in situ for Polyamide 6,6 while it was crystallized from the melt. For this polymer it is confirmed, that at a very low supercooling ($\Delta T \simeq 28^\circ\text{C}$) during the induction period, a well resolved SAXS pattern appears. The time evolution of this scattering pattern can be described by the kinetics of spinodal decomposition as previously reported for the glass crystallization in PEKK and TPI. According to this analysis, a value for the most probable scattering vector q of density fluctuations at around 0.43 nm^{-1} is found. It corresponds to a characteristic wavelength of 14.7 nm of long range density fluctuations growing with time.

KEYWORDS: Electron density fluctuations, simultaneous small-angle X-ray scattering and wide-angle X-ray scattering, melt crystallization, polyamide.

INTRODUCTION

The clarification of the structure formation mechanism during the embryonic period of polymer crystallization is a field of increasing interest with respect to, both, basic and applied research. One of the attractive features is the interdisciplinary character of the field. On the one hand, crystalline polymers are widely employed as industrial materials for general use, and the development of high performance parts from these polymers is a demand from the industrial side. On the other hand, polymer processing is closely related to the crystallization mechanism that can be modelled successfully with nucleation and growth theories. However, many questions relating to the early stages of crystallization still remain unanswered.

In a phase transformation such as crystallization, the two basic processes are the initiation or nucleation process by which a new phase is initiated within the parent phase, and the subsequent growth of the new phase at the expense of the preceding one [1,2]. Initiation and growth are concurrent processes that have been extensively analyzed. The former may occur homogeneously, by statistical fluctuations in the parent phase, or by formation of nuclei catalyzed by heterogeneities or impurities present in the melt. Strobl [3] describes the initial step of crystallization as the creation of a mesomorphic layer which spontaneously thickens up to a critical value where it solidifies through a cooperative structural transition. For most flexible polymers crystallization from the melt takes place well below T_m . Thus, a high supercooling is required for crystallization. The reason for this behaviour is related to the high interfacial free energy associated to the basal planes of the laminar crystallites and the difficulty in extracting ordered sequences of sufficient length from the disordered melt. In case of polymer glasses, crystallization takes place in the temperature window between the glass transition temperature, T_g , and

T_m (cold crystallization) [2].

However, in polymers, nucleation followed by growth is not the only mechanism inducing the building-up of a micro-phase separated system consisting of an amorphous and a crystalline phase. Amorphous polymers, for example, may exhibit crystallization processes governed by the spinodal decomposition (SD) mechanism [4,5]. Due to the fact that the formation of a nucleus implies the appearance of surfaces, the nucleation step requires an induction time where no crystals are present. We understand by induction period, as the time from the beginning of the experiment until the first WAXS crystalline peaks show up. In the induction period, pre-crystallization processes may be present tending to promote the development of conformational order followed by the parallel arrangement of chain segments creating a density fluctuation across the system. It is worth mentioning that a recent study on modelling of polymer crystallization from solution has given rise to some controversy [6]. Welch and Muthukumar show that crystallization at the very early stages is formed by nucleation and growth although the computed scattering intensity can be fitted to a SD description.

Simultaneous wide and small angle X-ray scattering (WAXS and SAXS respectively) experiments performed, in recent years, in isotropic glasses during the induction time of crystallization, have revealed the existence of an excess of scattering at low angles. The latter has been interpreted as a signature of ordering phenomena acting as precursors for the crystallization process [7,8]. The finding, that a scattering peak appeared in the SAXS pattern before crystallization from the glass, was observed for the first time in PET by Kaji and co-workers [7–9]. SAXS studies on the glass crystallization of other semi-rigid polymers: PEEK [10], PEN [11] and PBT [12], have supported as well the occurrence of electron density fluctuations as pre-

cursors of crystallization. Lately, the occurrence of electron density fluctuations broadened to include very rigid glassy polymers [13] and melt crystallization of flexible polymers [14].

The objective of this study is to extend the above investigations aiming to examine the possible evidence of density fluctuation as precursors of melt crystallization in Polyamide 6,6 using time resolved X-ray scattering techniques. A further point of interest in this work is that so far there are few reports on the fundamental aspects of the crystallization behaviour of polyamides [15].

EXPERIMENTAL

Polyamides are known to absorb water from the surroundings in a substantial proportion which, in the case of Polyamide 6,6, can reach a value as high as 9% by weight. The absorbed water penetrates the amorphous phase and its presence has a plasticizing effect that facilitates chain mobility. In order to avoid the latter effect, dry samples were prepared for our experiments. Polyamide 6,6 (Ultramid A5 from BASF) was received in the form of pellets. The material has a melting point of 265°C and $T_g = 50^\circ\text{C}$. 200 μm thick films were prepared by compression moulding at 285°C. Small ribbons (1mm wide) were cut and then inserted into glass capillaries. The capillaries were dried at 70°C for 24 hours and then closed. Simultaneous WAXS and SAXS experiments were performed using a double-focusing camera in the Soft Condensed Matter Research Beamline-A2 at HASYLAB, attached to a source of synchrotron radiation at the storage ring DORIS (DESY, Hamburg). A constant wavelength of 0.15 nm (~ 8 keV) was used. X-ray intensity data were collected in time intervals of 30 seconds, using linear position sensitive detectors and corrected for fluctuations in intensity of the primary beam and detector response. Position calibration was performed using standards of PET and rat-tail tendon for WAXS and SAXS respectively. The initial X-ray scattering pattern was subtracted from all

the rest of diagrams during isothermal treatment, to observe the appearance of the excess of scattering. Analysis of the experimental curves was accomplished by means of a computer fitting program, starting from the better resolved SAXS and WAXS curves at longer times and proceeding backwards towards the first stages of crystallization.

RESULTS AND DISCUSSION

Fig. 1 shows the variation of the SAXS invariant Q and of the degree of crystallinity w_c from WAXS as a function of crystallization time for various temperatures. For the low T_c temperatures Q -values different from zero and the appearance of crystallinity are seen from the very early stages of the experiment. Concerning the time resolution for these rapid crystallization processes, in the present experimental setup it is not possible to establish any difference in the appearance of both signals. For instance, during isothermal crystallization of the dry polyamide at 235°C ($T \simeq 30^\circ\text{C}$) both SAXS and WAXS appear simultaneously after about 8 min from the start of the experiment. However, at a smaller supercooling $T = 237^\circ\text{C}$ ($\Delta T \simeq 28^\circ\text{C}$) a slower crystallization process is achieved and one sees a clear time interval ($\Delta t \sim 100$ min) after the SAXS signal emerges, before the first WAXS peaks appear.

Fig.2 illustrates more in detail that the SAXS signal appears much earlier than the first traces of WAXS intensity. For this purpose, the first pattern from both SAXS and WAXS data was subtracted from the following ones. The resulting excess intensity is represented in Fig. 2 as a function of the wave vector q ($q = 2\pi s$ and $s = 2\sin\Theta/\lambda$) and the scattering angle 2Θ respectively. For the sake of clarity, the same Savitzky–Golay smoothing procedure was applied to the displayed curves. It can be observed that already after 50 min of crystallization time, there is a clear difference in the SAXS scattering from the initial pattern. However, the first WAXS

crystalline peak which corresponds to the (100) reflection of the pseudohexagonal α_2 phase of Polyamide 6,6 at temperatures above the Brill transition [16], is only appreciable after 125 min. Fig. 3 shows the time evolution of $\log I(t)/I(0)$ of the normalized SAXS integrated intensity in the range $0.24 < q < 1.1 \text{ nm}^{-1}$. For the highest T_c value, an increase of intensity during the induction period is observed. For times $t > 130$ min the start of crystallization is denoted by a larger increase of $I(t)$ concurrent to the appearance of the Bragg's peaks (signalized with an arrow).

During the induction period $I(t)$ increases exponentially with time at different q values, as shown in Fig. 4 for the sample treated at $T_c = 237^\circ\text{C}$. According to the formalism of Cahn and Hilliard [17], from the intercept in the plot $R(q)/q^2$ vs q^2 with the abscissa, a value $q_c = 0.364 \text{ nm}^{-1}$ is estimated, from which the most probable wave vector of fluctuation is derived $q_m = 0.427 \text{ nm}^{-1}$ (see Fig. 5). This value corresponds to a long-range order structure of about 14.7 nm, that is not far away from the sizes of long-range order structures derived from spinodal decomposition data during crystallization of rigid polymers from the glass and from the melt. Further experimental data aiming to obtain new values of the density fluctuations of different polymers with varying chain rigidity and at different degrees of supercooling would be desirable in order to establish possible relationships to other fundamental thermodynamical variables.

The analysis of the SAXS scattering maximum permits to calculate the long period according to Bragg's law. Figure 6 shows the variation of the long period values as a function of time at $T_c = 237^\circ\text{C}$. During the induction time, in spite of the large experimental errors, it is seen that the long period tends to remain constant. This result is also in accordance with the SD model [18]. Once primary crystallization starts ($t > 130$ min), the peak position tends to shift with time to

higher values of q . The final average long period for Polyamide 6,6 at 237°C is 15.5 nm. For the other temperatures investigated (235°C, 230°C and 225°C) the final long periods are 14.0, 13.6 and 12.1 nm respectively.

CONCLUSIONS

In conclusion, the use of simultaneous real time WAXS/SAXS techniques permits to analyze the molecular ordering process prior to crystal growth in case of a flexible polymer. For the investigated Polyamide 6,6 cooled from the melt, under a low degree of supercooling, the SAXS signal appears to occur before WAXS, i.e. evidence for long-range fluctuations, with sizes similar to those found in glassy rigid polymers, is obtained. The data presented suggest that the spinodal temperature should be higher than about 230°C. For lower crystallization temperatures (higher supercooling), the present experimental setup does not permit to separate the appearance of both SAXS and WAXS signals for Polyamide 6,6.

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Figure 1: Normalized invariant Q from SAXS (top) and relative crystallinity w_c from WAXS (bottom) for Polyamide 6,6 during isothermal crystallization at various temperatures.

Figure 2: Simultaneous SAXS (a) and WAXS (b) intensity data as a function of time during isothermal treatment of dry Polyamide 6,6 at a degree of supercooling $\Delta T = 28^\circ\text{C}$ from the melt. Increasing intensity curves correspond to crystallization times of 0, 50, 75, 100, 125, 150, 175 and 200 min.

Figure 3: Variation of the integral intensity, $\log [I(t)/I(0)]$ in the range $0.24 < q < 1.1$ nm^{-1} as a function of time for various temperatures. Downward arrow denotes the onset of crystallization for $T_c = 237^\circ\text{C}$.

Figure 4: Plot of $\log I$ as a function of time for $T_c = 237^\circ\text{C}$, for different q values.

Figure 5: Plot of $R(q)/q^2$ as a function of q^2 at $T_c = 237^\circ\text{C}$.

Figure 6: Time variation of the long period L derived from Bragg's law at $T_c = 237^\circ\text{C}$.