Interplay between amorphous and crystalline domains in semicrystalline polymers by simultaneous SAXS, WAXS and Dielectric Spectroscopy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.
(http://iopscience.iop.org/1757-899X/14/1/012011)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 161.111.22.173
The article was downloaded on 11/07/2013 at 11:03

Please note that terms and conditions apply.
Interplay between amorphous and crystalline domains in semicrystalline polymers by simultaneous SAXS, WAXS and Dielectric Spectroscopy

A. Sanz, Tiberio A. Ezquerra, A. Nogales
Instituto de Estructura de la Materia, CSIC. Serrano 121, Madrid 28006, Spain.
E-mail: emnogales@iem.cfmac.csic.es

Abstract. This work presents an experimental study on the interplay between structure and dynamics during isothermal cold crystallization of a copolymer based on poly(ethylene terephthalate) and poly(ethylene isophthalate) of poly(trimethylene terephthalate). Simultaneous X-ray scattering and dielectric spectroscopy measurements revealed that, during cold crystallization, crystalline lamellae tend form lamellar stacks during primary crystallization. A significant amount of rigid amorphous phase is formed during cold crystallization, and its location is assigned to the intralamellar stacks amorphous regions. The formation of the rigid amorphous phase during cold crystallization is less effective for the mobile amorphous phase, giving rise to the dielectric \( \alpha \) relaxation in the semicrystalline system is mainly located out of the stacks. The segmental dynamics of the amorphous phase is restricted by the growing crystals during secondary crystallization, but to a lesser extent than in the case of the homopolymer PET.

1. Introduction
When a glassy polymer is heated above its glass transition temperature (\( T_g \)), segmental mobility can enhance a large number of conformations in polymer chain segments. In some cases this conformation mobility may induce crystallinity, i.e., the formation of three-dimensional ordered crystallites, which are thermodynamically more stable. However, it is known that, in an assembly of random polymer chains which are coiled and mutually entangled, it is nearly impossible, for purely kinetic reasons, to reach a complete crystalline state [1]. Polymer systems thus always form structures which are partially crystalline. The structure of semicrystalline polymers exhibits a highly hierarchical structure, with different degrees of order depending on the studied length scales. Typical sizes of the crystalline unit of a semicrystalline polymer are in the order of several Angstroms (\( 10^{10} \) m). However, in the \( 10^8 \) m scale, in highly and intermediate crystalline polymers there is an alternation between crystalline regions (lamellar crystals) and amorphous regions (interlamellar amorphous regions). With a few exceptions, principally the case of highly crystalline polymers, this alternation does not extend to the whole volume of the sample.[2] The lamellae are packed into stacks which are separated by broad amorphous regions. The stacks can assemble themselves into superstructures, generally with spherical symmetry (spherulites) which can reach microns or even several millimeters. Therefore, an ideal two-phase model is not sufficient to understand the physical properties and processes occurring in semicrystalline polymers. Considering particularly the amorphous phase, one can understand that a

---

1 To whom any correspondence should be addressed.
hierarchical distribution of structures provokes strong heterogeneities in the amorphous phase depending on its crystalline environment.

Precise information about the changes occurring in a polymeric system during crystallization can be obtained by real time experimental setups.[3] High intensity synchrotron radiation provides the possibility of following the microstructure development by performing real time SAXS and WAXS [3]. The correlation between nanostructure and crystal development can be understood when both experiments are performed simultaneously.[4, 5] However, SAXS and WAXS, are based on x-ray diffraction and therefore they provide information about the structure of the ordered regions at different length scales. During nanostructure development, the remaining amorphous phase might experience some changes, from both, structural and dynamical points of view. Any change in the dynamics of the amorphous phase cannot be detected by the mentioned scattering techniques. Dielectric spectroscopy [6] experiments have shown that, upon crystallization, the dynamics of the amorphous phase is strongly affected by the progressive development of the crystalline phase [7-11]. Hence monitoring simultaneously, in real time, both, the microstructure development and the dynamic changes occurring in the amorphous phase, a more complete picture of the crystallization process could be obtained. So far, several reports on how the amorphous phase is restricted due to the development of crystals in homopolymers can be found in the literature [12-15]. Here we present an experimental work where the influence of a comonomer affects the interrelation between amorphous and crystalline phases in semicrystalline random copolymers of aromatic polyesters.

2. Experimental part

Copolymers of Poly(ethylene terephthalate dicarboxylate) (PET) and Poly(ethylene isophthalate) (PEI) were synthesized according to the well known two-stage polycondensation procedure. In order to obtain the two homopolymers and the copolymer family with different relative composition, several amounts of dimethyl terephthalate, dimethyl isophthalate, and ethylene glycol were used employing TisOBud4 as a catalyst [16]. The obtained copolymers are statistical, and in all cases the weight average molecular weight is around $M_w=50.000$ g/mol. The molar composition and the chain structure of the samples were determined by means of 1H–NMR spectroscopy [16]. After vacuum drying at 363 K for 24 h, the powders originated from the synthesis were melt pressed at 287ºC for 2 min and subsequently quenched to room temperature using water refrigerated metal blocks. In that way polymer films of about 250 µm were obtained.

Changes in the amorphous and crystalline phases of the system were studied by simultaneous SAXS, WAXS and dielectric spectroscopy experiments. They were performed in the soft condensed matter research beamline A2 at HASYLAB (DESY, Hamburg), using an experimental setup (SWD setup) developed specifically for this purpose [17]. The wavelength used in the X-ray scattering study was 1.5 Å. The collected data were corrected for background and primary beam intensity fluctuations during the experiment. The dielectric study in the case of the SWD setup was performed using a Novocontrol system integrating a SR830 lock in amplifier with a dielectric interface. A circular film of the copolymer (3 cm diameter) was sandwiched between two electrodes and introduced in an on purpose designed cell described elsewhere [17]. Simultaneous wide and small angle X-ray scattering was recorded for 90 s with 90 s wait time between frames. Each dielectric spectrum, obtained simultaneously with the X-ray experiments, took 180 s to collect.

3. Data analysis

Wide angle X ray scattering. The crystallinity of the final pattern was obtained as the ratio of the decomposed crystalline peaks over the total diffracted area. By this method, the diffraction pattern of the crystalline phase at any moment of the crystallization process was considered fixed in shape, and only its intensity was varied. The contribution of the amorphous halo was taken from the initial pattern (crystallization time $t_c=0$). Therefore, at any time, the diffraction pattern was considered to be a linear combination of the crystalline contribution ($A_c$) and the amorphous one ($A_a$). The crystallinity was obtained by:
Dielectric spectroscopy: The description of the dielectric relaxation in terms of the Havriliak–Negami empirical equation [18] for the dielectric permittivity has been widely used for polymeric materials. This formalism gives the following expression for the imaginary part of the complex dielectric permittivity:

\[
\varepsilon'' = \text{Im} \left( \frac{\Delta \varepsilon}{1 + (i \omega \tau_{HN})^b} \right)
\]

where \( \omega \) is the angular frequency (\( \omega = 2\pi F \), being \( F \) the frequency), \( \Delta \varepsilon \) is the dielectric strength of the relaxation, \( \tau_{HN} \) is the most probable value of the relaxation time distribution function and \( b \) and \( c \) are shape parameters related to the symmetric and asymmetric broadening [18, 19] respectively.

4. Results and discussion

Figure 1 shows the comparison between the structural parameters of a crystallization at \( T_c = 105^\circ C \) of PET (ET100) and the copolymer ET80. When a 20% of EI units is incorporated to the polymer chain, the crystallization process becomes slower due to the chemical heterogeneity of the copolymer. At the end of the crystallization process, the amount of crystalline fraction in PET reaches 30% whereas, under the same conditions the sample ET80 only reaches 18%. SAXS measurements indicate the formation of lamellar crystals ordered into lamellar stacks. The average distance between lamella, given by \( L_b \), is about 1 or 2 nm higher for the copolymer ET80 comparing to that of PET.

Figure 2 shows, dielectric spectra and wide and small angle X-ray scattering diagrams obtained simultaneously for three selected moments of the crystallization process of ET80 from the glassy state at 105°C. The initial state of the sample is amorphous, as revealed by the absence of Bragg peaks in the WAXD diagram and of any intensity in the SAXS diagram. As the sample is crystallizing, a clear
decrease of the dielectric relaxation intensity is observed. This fact is accompanied with the emerging Bragg peaks superimposed to the amorphous halo and the development of a maximum in the SAXS intensity, located around 0.1 nm\(^{-1}\). The Bragg peaks in the copolymer ET80 are located in the q positions that correspond to the triclinic unit cell of PET. That means that the EI units in the copolymer are not incorporated in the crystalline structure of this material. This fact has been recently reported for PEI-co-PET systems with a molar content of EI units among 5 and 10 %. [20].

![SWD experiment](image)

**Figure 2.** SWD experiment. Left, dielectric experiment for given crystallization times. Centre, WAXD and right SAXS at the same times. On the left, different lines indicate different contributions in the dielectric spectra. On the centre, different continuous lines indicate different Bragg peaks.
Regarding the dielectric spectra, as crystallization proceeds, the intensity of the initial $\alpha$ relaxation decreases at the expenses of a new slower process, labelled as $\alpha'$ relaxation. This new process have been already observed for the PET homopolymer [13] and is due to the dynamic restriction of the amorphous phase due to the growing of secondary crystals. Both, the dielectric spectra and the WAXD curves have been analyzed at different crystallization times. In this way it is possible to obtain the time evolution of structural and dynamic parameters simultaneously. In that way, it is possible to correlate dynamic parameters with the degree of crystallinity obtained from the WAXD patterns.

Figure 1 shows the variation of the degree of crystallinity and the long period (calculated from the Bragg law) as a function of crystallization time for the copolymer ET80 at 105ºC. The crystallinity exhibits a sigmoidal shape, which is often obtained in cold crystallization of polymer systems[15]. The final value of the long period $L_b$ is about 8.5 nm.

Figure 3 shows the variation of the dielectric parameters obtained through the Havriliak-Negami formalism, for the initial $\alpha$ relaxation and for the constrained $\alpha'$ relaxation, as a function of crystallinity.

![Figure 3](image_url)

Figure 3. Dependence of $\Delta \varepsilon$ (a), the average relaxation time of the two observed processes (b), $\Delta \varepsilon_{\alpha + \alpha'}$ (c) and the shape parameters obtained through the H-N eq. in the SWD experiment during crystallization of ET80 at 105ºC.

$\Delta \varepsilon_{\alpha}$ decreases as $X_c$ increases. However, $\alpha'$ starts developing when $X_c$ reaches about 5%. As observed also in figure 3a, $\Delta \varepsilon_{\alpha'}$ reaches its maximum value for $X_c = 15\%$ and after it starts decreases as $\Delta \varepsilon_{\alpha}$ does.

In figure 3c the decrease of $\Delta \varepsilon_{\alpha + \alpha'}$ with $X_c$ is observed. This dependence is nearly linear although with a slope different than 1. Once the experiment finishes, with a 20% of crystallinity, there is still a 60% of mobile fraction, according with the dielectric strength. That means that there is about
a 20% of material that is not relaxing in the available frequency window of the experiment, but on the other hand, is not crystalline. This means that a 20% of rigid amorphous phase has been formed during the crystallization process. Figure 3b shows the average relaxation times $\tau$ of the $\alpha$ and $\alpha'$ relaxations. Both average relaxation times start increasing as crystallinity reaches 15%. Before that, they remain constant. Finally in figure 3d, the variation of the shape parameters $b$ and $c$ with crystallinity is shown. $b$ decreases, indicating a broadening of the relaxation process, while $c$ starts to increase, indicating that the relaxation times distribution is becoming symmetric. Around $X_c=15\%$, there is a stronger variation of the shape parameters of the $\alpha$ relaxation. Due to the lower crystallinity in the copolymer than in PET, and because of the isophthalic units do not participate in the crystalline structure, the interlamellar amorphous regions are thicker in the copolymer than in the PET case, while the lamellar crystals retain the same thickness [20, 21].

The crystallization dynamics of the copolymer ET80 as compared with that of PET, is much slower in the former case. During the initial stages of the crystallization, the dielectric spectrum in the $\alpha$ relaxation region for the ET80 copolymer can be described by a single relaxation. However, as crystallization goes on, the $\alpha$ relaxation becomes broader and it is necessary to include a new process, the $\alpha'$ relaxation, as in the case of PET. The original $\alpha$ relaxation shifts with time towards lower frequencies, but it does so to a lesser extent than in the case of the homopolymer. This fact indicates that the segmental dynamics responsible for the $\alpha$ relaxation in the ET80 system is less affected by the lamellar crystals appearing during crystallization. In addition, the remaining amorphous phase is enriched by non crystallisable units of EI, which are more flexible than the ET units, favouring a lower restriction of the segmental dynamics.

The new process $\alpha'$ is also slowed down as crystallization occurs. But when ones compare the evolution of this new process during crystallization in the ET80 copolymer with that of PET it is revealed that the $\alpha'$ relaxation is less developed in the copolymer at the end of the crystallization process. Assuming the origin of this $\alpha'$ relaxation proposed for PET [13], it is reasonable to expect that this fact is due to a strong impediment of the secondary crystallization in the copolymer due to the enrichment of the remaining amorphous regions with non crystallisable sequences of EI units. This fact is also supported by the fact that the long period of the copolymer remains constant during crystallization, indicating that there is no s the insertion of new lamellae in between existing ones.

5. Conclusions

In summary, our results support the idea that for copolymers based on PET and PEI crystal lamellar stacks are separated by broad amorphous regions. The amorphous phase within the stacks is highly restricted. In the copolymer system, secondary crystallization is highly inhibited because of the enrichment of the amorphous phase with EI non crystallisable sequences. Therefore, at the end of the crystallization process, just a small contribution to the segmental dynamics comes from restricted amorphous phase, which is in strong contrast with what happen in the homopolymer.

Acknowledgments

We thank Dr. N. Lotti for handing over us the samples. The authors thank the financial support from the MICINN (grant MAT2009-07789 and FPU AP2005-1063,) Spain. The experiments performed at A2 in HASYLAB (DESY.Hamburg) were supported by the European Community (Contract RI3-CT-2004-506008 (IA-SFS) ). We also thank Dr. S.S. Funari for assistance during measurements at A2 beamline in HASYLAB. A.S. also acknowledges the Higher Council for Scientific Research (CSIC) for the JAE-doc tenure.

References


[8] Ezquerra T A, Baltà-Calleja F J and Zachmann H G 1994 Real time dielectric relaxation of poly(ethylene terephthalate) during crystallization from the glassy state Polymer 35 2600-6


