Morphology of Poly(ethylene naphthalene-2,6-dicarboxylate):

First Stages of Crystallization*

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ABSTRACT

The morphology of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) with a wide range of crystallinities has been determined by transmission electron microscopy. PEN thin films undergoing cold crystallization during annealing at temperatures above T_g have been investigated after selective chemical staining and cutting in an ultramicrotome. Crystallization appears in amorphous areas distributed in a non-crystallizable matrix by formation of lamellae inside these amorphous areas. For low annealing temperatures ($T_c \sim 145^\circ\text{C}$) the emerging morphology of PEN is seen prior to the occurrence of crystallinity in the X-ray diffraction pattern. With increasing time and temperature of crystallization the number and thickness of lamellae increase, in accordance with increasing crystallinity and crystalline thickness, as determined by X-ray investigations. Dendritic superstructures are also observed with a rough starting internal structure which becomes finer with increasing crystallization time.

* Volume dedicated to the memory of Prof. H.G. Zachmann

INTRODUCTION

Poly(ethylene naphthalene-2,6-dicarboxylate)-PEN- is attracting increasing attention and a larger scale commercialization is underway. PEN is very similar to poly(ethylene terephthalate) (PET) in its structure but contains naphthalene instead of benzene rings along the chain which produce stiffer molecular chains than those of PET [1,2]. Therefore, glassy PEN shows a higher glass transition temperature (120°C compared with 70°C) and enhanced mechanical properties such as tensile modulus, creep resistance and hardness and lowers shrinkage [3,4]. PEN can be crystallized in two different crystal modifications, the α and β form. In the α -form the chains lie parallel to the c-axis in a triclinic unit cell [5]. The β -form is also triclinic; however, in this modification every naphthalene ring is twisted by 180° within the cell [2]. At crystallization temperatures up to 200°C only the α -modification is formed. At temperatures higher than 200°C the β -modification can be also formed if the temperature is not far from the melting point. The kinetics of crystallization and melting behaviour of PEN have been studied by DSC and WAXS using synchrotron radiation [2]. The influence of the temperature and time of crystallization from the glassy state upon crystallinity and microhardness (H) has also been recently examined [6]. It could be shown that during primary crystallization microhardness increases linearly with the volume fraction of spherulites. In addition, H was shown to depend on the crystallization temperature and appeared to be a function of the thickness of the crystals. A detailed morphological description of PET after cold crystallization has been given previously [7]. However, knowledge about the development of the morphological units during crystallization in both PET and PEN is still missing.

In this paper the results of an investigation concerning the influence of isothermal cold crystallization on the morphology of the resulting crystallized PEN samples is presented. In order to describe the morphological parameters and their implications for the crystallization behaviour we have used the technique of transmission electron microscopy. As far as we know a complete electron microscopic study of semicrystalline PEN over the crystallization temperature range has not yet been reported. Special emphasis on the emerging morphology of PEN during the first stages of crystallization is made.

EXPERIMENTAL

Sample Preparation

Samples of PEN were synthesized from 2,6-dicarboxymethyl naphthalene and ethylene glycol using antimony trioxide and manganese acetate as catalysts [2]. The intrinsic viscosity in hexafluoroisopropyl alcohol was 0.5334. Amorphous films were obtained by melt pressing above the melting point ($T_m = 272^\circ\text{C}$) and quenching in ice-water. Samples were available in the form of 200 μm thick foils. Crystallization of the glassy materials was performed in a vacuum oven at temperatures in the range from 145 up to 220°C . Crystallization temperatures and crystallinity of the samples derived from WAXS are given in Table 1.

Electron Microscopic Investigations

From the PEN foils small pieces were prepared with a size of $0.1 \times 0.1 \text{ mm}^2$ at the tip, convenient to use in an ultramicrotome. To enhance the contrast between structural details, different chemical staining procedures were tested. The most successful procedure, giving a good contrast in the electron microscope without damaging the sample, is based on a combined application of a preactivation by chlorosulfonic acid (ClSO_3H) and formaldehyde (HCHO) followed by staining with OsO_4 . After chemical treatment the samples were embedded in araldite to enhance mechanical stability during cutting. Ultrathin sections with a thickness of about 70 nm were cut using a cryo-ultramicrotome MT 7/CR 21 from RMC. Electron microscopic investigations were performed in a 100 kV transmission electron microscope from JEOL.

RESULTS AND DISCUSSION

The data of Table 1 indicate that PEN is a low crystallinity material which even at the highest crystallization temperatures only reaches a degree of crystallinity below 30%.

From the results on chemical staining three different morphological regions can be distinguished on the electron micrographs (see the case of PEN crystallized at 155°C in Fig. 1):

- grey background **zones** without a structurization, forming a matrix
- dark stained areas
- bright areas inside the dark zones (see Fig 2).

Experience with chemical staining of semicrystalline polymers allows us to conclude that heavily stained areas have a lower density or a higher molecular disorder than weakly or non stained zones [8,9]. Therefore, we can distinguish a grey matrix with a medium density ρ_m , the dark zones containing amorphous material with a small density ρ_a , and the bright areas, appearing as crystalline material with a density ρ_c :

$$\rho_a < \rho_m < \rho_c \quad (1)$$

The appearance of crystallized lamellae in the dark amorphous zones can be better distinguished at larger magnification. Figure 2 illustrates the presence of lamellae for the PEN sample crystallized at 200°C for 0.5 hour. Within the grey matrix darker stained amorphous particles are distributed, containing white lines which are the crystalline lamellae.

Furthermore, the content of white lamellae inside the dark areas increases with crystallization temperature. Fig. 3 illustrates the concentration increase of crystallized (white) areas with an increase in crystallization temperature from 145°C to 165°C. With increasing temperature the samples show an increasing tendency in the maximum thickness of the lamellae. Table 1 also gives the variation of lamella thickness, D , as determined directly on electron micrographs. Crystallization only takes place in the dark stained amorphous parts within the grey matrix. Therefore, during the first stages of precrystallization a phase separation must occur between a non-crystallizable matrix part and a disperse, distributed amorphous but crystallizable, part. A rough estimation of this crystallizable part on the micrographs yields a volume content of 20-30%, which in principle correlates to the final degree of crystallinity reached (see Table 1). These crystallizable zones ought to be related to the regions where the ordering process just before crystallization, for stiff chain polymers (PET, PEKK) takes place [10,11].

As superlamellar morphological details dendrites with lengths of a few μm appear. An example is shown in Fig. 4 for the sample crystallized at 165°C after 40 min.

We have examined the influence of the crystallization time t_c on the emerging morphology of PEN isothermally crystallized, using the temperature of 165°C as an example. After the first 10 min of crystallization the first morphological units as a precursor of a dendritic superstructure can be observed (Fig. 5a). The incipient dendritic structure develops with longer times (Fig. 5b), and after 40 min the superstructure is already characteristic of that for the crystallized samples (Fig. 5c). With increasing crystallization time more crystalline lamellae appear inside the dark

areas. Therefore, the dark areas become smaller and their dendritic superstructure changes from a coarse to a finer morphology - Fig. 5. These changes are schematically depicted in the sketch of Fig. 6.

It is noteworthy that for lower temperatures, $T_c = 145^\circ\text{C}$ after 2h of crystallization, a dendritic morphology with an emerging lamellar like structure is also observed (Fig. 3). Most interesting is the fact that this emerging morphology at low temperature is not connected with the presence of crystallinity in the X-ray diffraction pattern. However, it contributes to a conspicuous hardening of the material as reported in a previous study [6]. Only after very long crystallization times (17 h) was the appearance of 1.9 - 3.3 nm thick lamellae within the dark contrasted amorphous regions first evident (See table 1). PEN crystallized at higher temperatures (165, 200, 220°C) exhibits at high magnifications a branched lamellar structure, but bundles of lamellae with radial orientation also emerge (fig.4). It is known that the stacking of a few lamellae in polyethylene [8,12] is sufficient to give rise to the observed diffraction maxima at low scattering angles.

It is to be noted that the morphology of crystallized PEN differs considerably from that of commercial PET [13]. PET may show spherulitic regions, but usually there are irregularly arranged lamellae. In addition, the PET lamellae are thicker ($\bar{D} \sim 7.5$ nm) and longer (100-200 nm) than those of PEN (length: ~ 50 nm).

In table 1 also the X-ray long period L and the calculated crystalline thickness l_c ($l_c = L \cdot x_c$) are given. It is noteworthy that values for the thickness D of the lamellae measured from the electron micrographs (also given in Table 2), increase with the temperature as well as with the time of crystallization and are in agreement with the average lamellar thickness values estimated from SAXS. The increase in lamellar thickness obtained at higher crystallization temperature leads to the increase of microhardness which has been evidenced previously [6].

CONCLUSIONS

In conclusion, during the induction period prior to crystallization the morphology of PEN as studied by electron microscopy suggests the following stages:

- 1) A phase separation into crystallizable and non-crystallizable regions -incipient dendritic superstructure- (for short times).

- 2) A further phase separation within the crystallizable regions into crystalline lamellae and non crystalline zones (intermediate times).
- 3) An increase of number and size of the crystalline lamellae (for longer times and or higher crystallization temperature).

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FIGURE CAPTIONS

Fig. 1: Overview of different morphological details in PEN crystallized from the glass at $T_c = 155^\circ\text{C}$ for $t_c = 2\text{ h}$: selectively stained ultrathin section under TEM.

Fig. 2: Lamellae inside dark stained amorphous areas ($T_c = 200^\circ\text{C}$; $t_c = 0.5\text{ h}$).

Fig. 3: Increase of lamellar content with increasing crystallization temperature [a) $145^\circ\text{C} - 2\text{ h}$, b) $165^\circ\text{C} - 2\text{ h}$].

Fig. 4: Well developed dendritic structure in the sample crystallized at 165°C for 40 min.

Fig. 5: Change from a coarse dendritic structure to a finer structure through formation of crystalline lamellae inside the amorphous areas with increasing crystallization time. Crystallization temperature: 165°C a) 10 min, b) 30 min, c) 40 min.

Fig. 6: Sketch showing the gradual changes within the amorphous areas with increasing crystallization time - cf. Fig. 5; a) phase separation between crystallizable (dark shaded areas) and noncrystallizable regions; b) development of crystalline zones in the dark areas; c) final dendritic morphology.

Table 1: PEN investigated samples: variation of lamellar thicknesses D (from electron micrographs), crystallinity x_c , long period L , and crystal thickness l_c (from X-ray measurements)(ref.6) as a function of temperature T_c and time t_c of crystallization from the glass.

T_c (°C)	t_c (h)	x_c	L [nm]	l_c [nm]	D [nm]
145	2	0.0	-	-	(2.8 - 4.7)
145	17	0.0	-	-	1.9 - 3.3
155	2	0.2	-	-	2.3 - 4.0
165	0.17	0.0	-	-	-
165	0.25	0.01	-	-	-
165	0.50	0.09	-	-	1.4 - 2.1
165	0.67	0.16	-	-	1.4 - 2.8
165	2.0	0.24	13.7	3.3	1.4 - 4.3
200	0.5	0.28	16.4	4.5	1.6 - 4.7
220	3.0	0.3	18.7	5.2	1.9 - 7.6

Fig 1

Fig 2

Fig 3

Fig 5.

Fig 6.