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# SAXS and DSC study of co-crystallisation of low molecular-weight PEO fractions in polymer blends

## Abstract

*This study is aimed at a better understanding of co-crystallisation phenomena in PEO/PEO and PEO/PEO-*b*-PPO-*b*-PEO blends in the course of crystallisation. Simultaneous real-time SAXS measurements and the DSC method were used for observing the development of the structure during isothermal melt-crystallisation and during linear cooling and subsequent heating.*

*PEO/PEO blends. Binary mixtures of PEO (3000) and PEO (4000) were studied. During all temperature treatments, co-crystals are always formed. Under certain conditions a small amount recrystallises to another lamellar system. The thickness of the co-crystal lamellae depends on the composition of blends and crystallisation temperature, and increases with growing concentration of the higher- $M_w$  component (PEO 4000). During heating, on approaching the melting points of the components, all blends recrystallise giving a single, more stable co-crystal structure.*

*PEO/PEO-*b*-PPO-*b*-PEO blends. During isothermal melt-crystallisation, two different lamellar systems, LP1 (with thicker lamellae) and LP2, are simultaneously formed in the neat copolymer and in blends with predominating copolymer content. This tendency gradually vanishes with the decreasing copolymer content. In blends with a majority of neat PEO, a single lamellar system is developed. In all blends, co-crystal systems are formed during crystallisation.*

**Key words:** PEO/PEO blends, PEO/PEO-*b*-PPO-*b*-PEO blends, SAXS, DSC, crystallisation, co-crystals

## 1. Introduction

Co-crystallisation phenomena in polymer blends consisting of homopolymers have been studied in the last decade. Extensive studies have been devoted to different types of polyethylene blends and their models [1-11]. It has been shown that the extent of co-crystallisation strongly depends on melting points, crystallisation rates, molecular weights and their distribution, and on branching of the components.

Binary mixtures of high- (100 000) and low- (3500–20 000) molecular-weight PEO were studied by Cheng [12-14] to characterise the growth rates and phase behaviour of the blends. At low undercoolings, the components were found to co-crystallise, and at higher undercoolings, to phase-separate. Molecular segregation in the blends occurs before the temperature reaches the equilibrium melting point of the low molecular-weight component. A time-resolved SAXS and DSC study of the crystallisation of PEO270000/PEO5000 blends showed [15] that at low crystallisation temperatures the components co-crystallise depending on composition. In blends with high contents of the low molecular-weight polymer, the co-crystals are thin, and vice versa. At higher temperatures, the components form defective co-crys-

tals which dynamically split into the components. Blends of two low molecular-weight PEO (1300/4000) crystallise separately within a broad range of crystallisation temperatures, and co-crystallise after quick quenching [16,17].

Intensive studies in recent years have been devoted to an important family of polymer blends, namely block copolymer/homopolymer mixtures, where the homopolymer is identical with one block of the copolymer. The predominant part of these studies was devoted to blends with amorphous homopolymer admixture. However, very little is known about the structure behaviour of the crystalline/crystalline blends, and co-crystallisation studies are still lacking. The purpose of the present paper was to investigate the conditions for co-crystalline structure formation in blends made of two narrow low molecular-weight PEO polymers and blends of these polymers with a symmetrical tri-block copolymer PEO-*b*-PPO-*b*-PEO using time-resolved SAXS and DSC methods.

## 2. Experimental

### Materials

■ Hydroxy-terminated low molecular-weight PEOs ( $M_w = 3000$ ,  $T_m = 62^\circ\text{C}$ ;  $M_w = 4000$ ,  $T_m = 65.2^\circ\text{C}$ ) (P3, P4) supplied by Fluka AG.

■ Symmetric tri-block copolymer PEO-*b*-PPO-*b*-PEO (F), (Synperonic F68),  $T_m = 54.7^\circ\text{C}$ ; from Serva. The molecular weights of blocks are 3340, 1780, 3340. The PPO block is amorphous.

Blends of P3/P4, F/P3, F/P4 with 80, 50 and 20 wt.% of the first component were prepared by dissolution in chloroform and subsequent drying at  $30^\circ\text{C}$  for 2 days and then in a vacuum oven at  $40^\circ\text{C}$  for one week. The samples were placed in a sample holder and used for SAXS experiments. Structure development was studied first during isothermal melt crystallisation at 35, 40 and  $45^\circ\text{C}$ , and further during controlled linear cooling of the melt from  $80^\circ\text{C}$  to  $30^\circ\text{C}$  and subsequent heating to the melt. A new sample was used for each experiment.

It has been shown [18-21] that low molecular-weight PEO ( $M_w = 2000$ -10 000) crystallise either fully extended (EC) or integrally folded (IF) when incorporated in crystalline lamellae. This fact was supported by the discontinuous change in lamellar thickness with varying crystallisation conditions. On the basis of time-resolved SAXS and DSC measurements, it has been reported that non-integrally folded-chain (NIF) crystals can also be found in low-molecular-weight PEO fractions [22-27]. At the beginning of

crystallisation, these crystals grew rapidly as the first, transient state, and later on they recrystallise to either IF or EC crystals through an isothermal thinning or thickening processes, respectively.

Chain lengths and the corresponding lamellar thicknesses of studied samples are summarised in Table 1.

### Small-Angle X-ray Scattering

The time-resolved SAXS measurements were performed on the Austrian SAXS beamline at the ELETTRA synchrotron in Trieste, Italy. X-ray radiation of  $\lambda = 0.15$  nm (8 keV) was detected with a linear position-sensitive detector. A 1.6-mm thick sample in a special holder was melted at 80°C for 20 min. in an oven, and then quickly inserted into the sample cell placed in the X-rays' path. In the melt-crystallisation experiment, the cell was kept at constant temperatures. After inserting the sample, the corresponding crystallisation temperature was reached within 60 s. In the ramp experiments, the cell was first kept at 80°C, then it was linearly cooled at a rate of 1.5°C/min. and subsequently heated at a rate of 1°C/min. Measurements on the synchrotron consisted of 256 (or 512) frames each 10 s (or 5 s) long. The scattering data were corrected for the detector efficiency (using the Fe standard), and then the Lorentz correction was applied ( $I_L = I_{meas} q^2$ ,  $q = (4\pi/\lambda) \sin\theta$ , where  $\lambda$  is the X-ray wavelength and  $2\theta$  is the scattering angle). In the case of the synchrotron data, no desmearing was performed due to the high degree of collimation. Peak positions were employed to obtain long periods according to Bragg's law,  $L = 2\pi/q$ .

### DSC

Calorimetric measurements were done by a Perkin-Elmer Pyris 1 calorimeter. The temperature and power scales were calibrated with indium as standard. The temperature regime of measurement was the same as for the time-resolved SAXS experiments.

## 3. Results and discussion

### 3.1. P3/P4 blends

#### Isothermal melt-crystallisation

Figure 1a shows real-time changes in SAXS patterns of the 2/8 blend during isothermal crystallisation at 35°C. The development of lamellar thicknesses in blends are summarised in Table 2. The series of SAXS peaks corresponds to the lamellar structure with a lamellar thickness of 15 nm. The lamellar system does not change during crystallisation. A single lamellar system (lamellar thickness

14.8 nm) was also obtained for a crystallisation temperature of 40°C.

The SAXS data of 5/5 blend for both crystallisation temperatures shows that at the beginning of crystallisation a single lamellar system is developed. The thicknesses of lamellae are 14.3 nm and 15 nm for crystallisation at 35 and 40°C respectively. After about 40 s, a very small fraction of lamellae recrystallises to the thinner lamellae of 10.4 nm. The thicknesses of lamellae in both systems do not change during thermal treatment. This structure behaviour is more pronounced in blends with 80% of P3. This is demonstrated in Fig. 1b, which shows real-time Lorentz-corrected SAXS data for the blend crystallised at 35°C. When starting isothermal crystallisation, a single lamellar system is formed. This system partly recrystallises after about 90 s to a different system of lamellar stacks with thinner lamellae. Neither of the lamellar systems change during further crystallisation. The thicknesses of the starting lamellae are 13.7 and 14.2 nm, and those of the recrystallised lamellae are 10.7 and 10.5 nm for crystallisation at 35 and 40°C respectively.

The co-crystalline lamellar systems are formed during isothermal melt-crystallisations in all blends, as the lamellae developed at the beginning of crystallisation consist of the chains of both P3 and P4 components. The co-crystals developed in the 2/8 blends do not change during crystallisation. In the 5/5 and 8/2 blends, the starting co-crystal structure partly recrystallises through isothermal thinning into a new lamellar system. The starting lamellae consist of NIF chains of both components. The thicknesses of recrystallised lamellae correspond to the 1F lamellae of P3. As these lamellae are formed in blends with high contents of P3, it is probable that they consist of P3 only. The thickness of starting lamellae increases with the increase in content of P4.

Figure 2a shows the thermograms of isothermal crystallisation of the P3/P4 blends. One can see that the character of crystallisation is similar to the SAXS results. When the crystallisation temperature is reached, the formation of lamellae begins very quickly. Around 120 s, we can see in the thermogram of the 8/2

Table 1. Thicknesses of stable lamellae of used polymers

Polymer		EC, nm	1F, nm	2F, nm
P3		19	10	no
P4		25	12	8
F	PEO block	21	11	no
	PPO block <sup>1</sup>	7	-	-

<sup>1</sup>chain length

Table 2. Development of lamellar thicknesses in P3/P4 blends during thermal treatments.

Composition	2/8	5/5		8/2	
		Isothermal crystallisation			
	L, nm	L <sub>1</sub> , nm	L <sub>2</sub> , nm	L <sub>1</sub> , nm	L <sub>2</sub> , nm
35 °C	15.0	14.3	10.5	13.7	10.7
40 °C	14.8	15.0	-	14.2	10.5
	L, nm	Cooling and Heating		L, nm	
		L, nm			
T <sub>start</sub>	17.1	16.6		20.4 ← 15.2 → 10.4	
T <sub>cool</sub>	16.0	16.0		20.4 ← 15.0 → 10.6	
T <sub>heat</sub>	18.9	22.4		21.2	
T → T <sub>m</sub>	20.6	23.3		22.9	

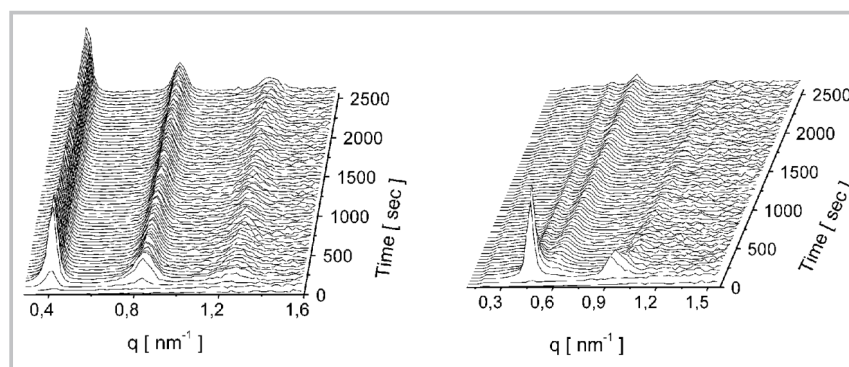


Figure 1. Time-resolved Lorentz-corrected SAXS data of P3/P4 blend (a) 2/8 and (b) 8/2 during crystallisation at 35°C.

blend two shallow exothermal minima, probably due to recrystallisation, as observed by SAXS.

### Cooling and heating

Changes to the Lorentz-corrected SAXS curves of P3/P4 2/8 blend during cooling and heating are shown in Fig. 3a. During continuous cooling, the molten blend crystallises in a single co-crystal lamellar system. The thickness of lamellae starts at 17.1 nm for 2/8 blend and 16.6 nm for 5/5 blend, and then slowly decreases during crystallisation to 16.0 nm (2/8) and 16.0 nm (5/5) at 30°C (Table 2). The molten 8/2 blend crystallises at the

beginning of cooling to a single system with a lamellar thickness of 15.2 nm (Fig. 3b). After 130 s of cooling, the lamellar system partly recrystallises into stacks of thinner (10.4 nm) and to a small extent also to thicker lamellae (20.4 nm). Further cooling does not change these structures.

During heating, on approaching the melting points of the components, the structures of 2/8 and 5/5 blends recrystallise in the bulk to a single lamellar system with thicknesses of 18.9 and 22.4 nm for 2/8 and 5/5 blends respectively. Their thicknesses increase with the increase in temperature, and reach values of 20.6 nm and 23.3 nm immediately before melting. Three lamellar systems developed in 8/2 blend also recrystallise near  $T_m$  to a single lamellar system with a lamellar thickness of 21.2 nm. This means that a new more stable co-crystal system is formed in all blends before melting. The DSC results in Fig. 2b show a two-stage course of crystallisation and melting of P3/P4 8/2 blends, and agree very well with the SAXS results.

All molten blends crystallise during cooling into a single system of co-crystalline lamellae, which consist of NIF chains of both components, similar to the case of isothermal crystallisation. The periodicity of this initial and dominant lamellar system grows with the increasing content of P4. In the blend with the highest content of P3, a part of the starting co-crystalline lamellar stacks recrystallise to the lamellae with thicknesses similar to the 1F and EC structures of P3. These lamellae probably consist of P3 chains only. These structures recrystallise during heating in all three blends to a single lamellar system with slightly thicker lamellae than the thickness of EC lamellae of P3. A new and more stable co-crystal system is formed before melting. The thickness of these lamellae is given by co-crystallisation of EC chains of P3 with longer molecules of P4.

Single co-crystalline lamellae, or this system partly recrystallised to one or two different lamellar systems, are formed in the blends during both crystallisation treatments. The polymer chains of P3 and P4 show a high ability to co-crystallise in a common crystalline lattice. The thickness of co-crystal lamellae depends on the composition of blends. The partial recrystallisation of co-crystals to 1F and EC structures in the 5/5 and 8/2 blends during crystallisation, probably consisting only of P3 chains, is caused by a higher content of the P3 component, which has a lower melting temperature and higher chain mobility. Besides the P3 content, the higher temperature also facilitates this recrystallisation.

### 3.2. F/P3 and F/P4 blends

#### Isothermal melt-crystallisation

Blends of block copolymer F with P3 and P4 were studied during isothermal melt-crystallisation. Two different lamellar systems, LP1 (with thicker lamellae) and LP2, are simultaneously formed in neat copolymer and in the blends with 80 and 50% of copolymer during this thermal treatment. Figure 4 demonstrates this fact on time-resolved development of SAXS patterns during isothermal melt crystallisation at 35°C for the case of the F/P3 8/2 blend. Similar results were obtained for crystallisation temperatures of 40 and 45°C, for 5/5 blends, and also for blends with P4. In the blend with 80% of P3, only one lamellar system is formed. In blend with P4 besides predominant lamellar structure, a very small part of the second lamellar system is developed. A small part of F/P4 blends crystallises in EC of P4 structure, which probably consists of neat P4. Figure 5 shows a thermogram of the melting of neat copolymer F and blends F/P3 after isothermal crystallisation at 40°C. The two melting peaks for copolymer F and F/P3 8/2 blend and the one peak for 2/8 blend agree well with the SAXS results.

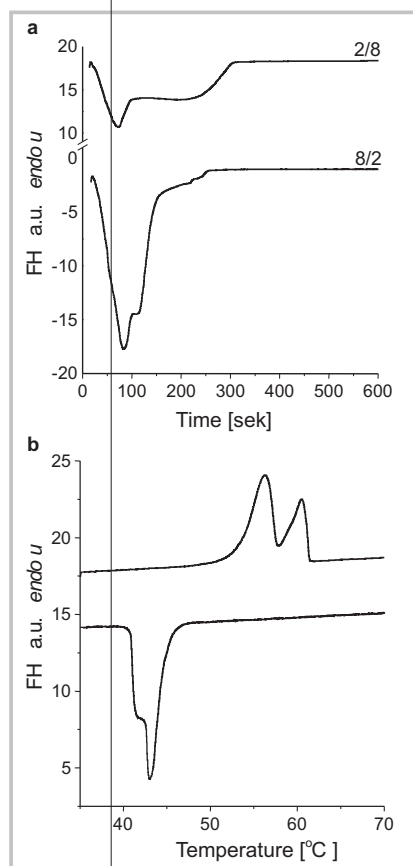


Figure 2. DSC thermograms of isothermal crystallisation of P3/P4 blends at 41 °C (a) and of 8/2 blend during crystallisation and melting (b); (HF- Heat Flow).

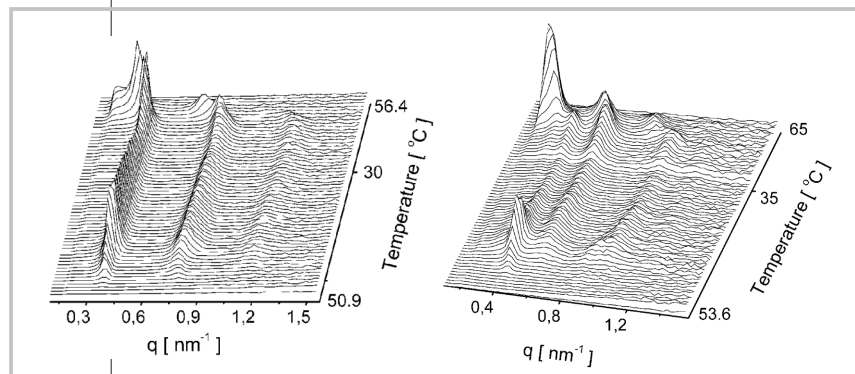


Figure 3. Changes of Lorentz-corrected SAXS curves of P3/P4 blend (a) 2/8 and (b) 8/2 during cooling and heating.

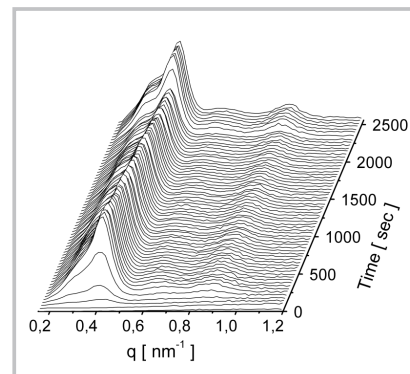


Figure 4. Time-resolved Lorentz-corrected SAXS data of F/P3 blend 8/2 during crystallisation at 35°C.

The thickness of lamellae does not change during crystallisation in the majority of the blends. In F/P4 2/8 and 5/5 blends, however, a slight increase in the thickness of LP2 lamellae with the crystallisation time is observed. The not too well developed structure, after a temperature jump from melt to the crystallisation temperature, improves during thermal treatment. The relatively broad SAXS reflections in neat copolymer F and in blends, in comparison with the situation in P3/P4 blends, mean that the lamellar structure of these blends is not well developed. The presence of the copolymer partly restrains the crystallisation process.

The crystallisation temperature influences the development of lamellar systems in blends as the crystallisation rate decreases with increasing  $T_C$ . With

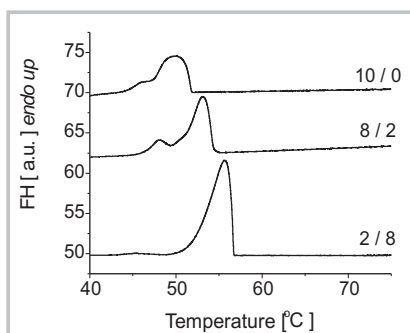


Figure 5. Melting of copolymer F and F/P3 blends after isothermal crystallisation at 40°C; (HF- Heat Flow).

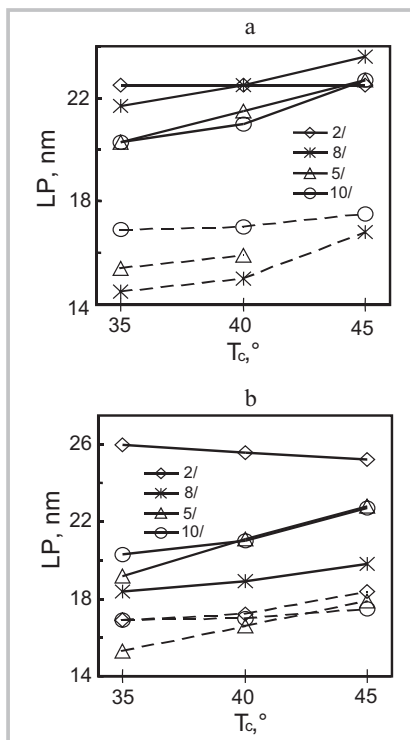


Figure 6. Changes in lamellar thickness LP1 (—) and LP2 (---) systems in (a) F/P3 and (b) F/P4 blends with crystallisation temperature

growing  $T_C$ , the thickness of lamellae in both lamellar systems (Fig. 6) and also that of the content of lamellar system LP1 increase. While in the blends with P3, the lamellar thickness of LP1 system is greater than in neat copolymer; in blends with P4 it is smaller. The reason for this effect is probably the higher mobility of P3 chains, which are shorter than the P4 chains and can therefore easily crystallise as extended. In the case of LP2 systems, lamellar thickness is in both kinds of blends smaller than in the neat copolymer (Fig. 6).

The development of lamellar thickness LP1 and LP2 in (a) F/P3 and (b) F/P4 blends with crystallisation temperature are summarised in Fig. 6. The similarity of the LP1 and LP2 structures in the neat copolymer with those observed in the blends suggest that co-crystal systems are formed during crystallisation in all blends. Blends of P3 with P4 with the highest contents of P3 show P3's high ability to form two different lamellar structures during crystallisation. In contrast, copolymer F, with a high tendency to crystallise in two lamellar systems, blended with 80% of P3, surprisingly forms a single co-crystalline lamellar system. Blends with P4 show a similar tendency.

The LP1 lamellae in blends with P3 consist of extended chains of P3 and extended chains of copolymer PEO tails. The LP1 co-crystal structures developed in blends with P4 are probably formed by NIF chains of P4 and NIF and EC chains of PEO in copolymer. The LP2 lamellar systems are, in both kinds of blends, co-crystals consisting of 1F and NIF chains of both components. The PPO component of the copolymer forms an amorphous phase with chain ends and folds of PEO.

## 4. Conclusions

Both kinds of blends P/P and F/P form co-crystalline structures during crystallisation.

Lamellae in polymer/polymer blends crystallise in better ordered structures than in polymer/block copolymer blends.

Single co-crystalline lamellar structures are developed in P4/P3 blends and polymer/block copolymer P3/F 8/2.

The development of lamellar structures depends on the composition of blends, and is strongly influenced by the predominant component. Besides co-crystalline lamellar systems, the EC lamellae of the predominant component are observed.

During heating, blends recrystallise on approaching the melting points of the components, giving a single, more stable co-crystal structure.

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